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Azithromycin removal using pine bark, oak ash and mussel shell

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ABSTRACT

Adsorption is considered an interesting option for removing antibiotics from the environment because of its simple design, low cost, and potential efficiency. In this work we evaluated three by-products (pine bark, oak ash, and mussel shell) as bio-adsorbents for the antibiotic azithromycin (AZM). Furthermore, they were added at doses of 48 t ha^{-1} to four different soils, then comparing AZM removal for soils with and without bio-adsorbents. Batch-type experiments were used, adding AZM concentrations between 2.5 and 600 μmol L^{-1} to the different bio-adsorbents and soil + bio-adsorbent mixtures. Regarding the bio-adsorbents, oak ash showed the best adsorption scores (9600 μmol kg^{-1}, meaning >80% retention), followed by pine bark (8280 μmol kg^{-1}, 69%) and mussel shell (between 3000 and 6000 μmol kg^{-1}, 25–50% retention). Adsorption data were adjusted to different models (Linear, Freundlich and Langmuir), showing that just mussel shell presented an acceptable fitting to the Freundlich equation, while pine bark and oak ash did not present a good adjustment to any of the three models. Regarding desorption, the values were always below the detection limit, indicating a rather irreversible adsorption of AZM onto these three by-products. Furthermore, the results showed that when the lowest concentrations of AZM were added to the not amended soils they adsorbed 100% of the antibiotic, whereas when the highest concentrations of AZM were spread, the adsorption decreased to 55%. However, when any of the three bio-adsorbents was added to the soils, AZM adsorption reached 100% for all the antibiotic concentrations used. Desorption was null in all cases for both soils with and without bio-adsorbents. These results, corresponding to an investigation carried out for the first time for the antibiotic AZM, can be seen as relevant in the search of low-cost alternative treatments to face environmental pollution caused by this emerging contaminant.

1. Introduction

Emerging contaminants (including substances such as pharmaceuticals, perfluorinated compounds, fire retardants, and many others) are causing an increasing concern as regards environmental and human health (Kumar et al., 2023; Núñez-Delgado et al., 2023; Puri et al., 2023; Ramírez-Malule et al., 2020; Wells et al., 2010).

In the last twenty years, pharmaceutical products have been found as micro contaminants in soils and waters, due to the improvement of the capacity to detected them by using advanced chemical analysis (Boxall, 2004; Carvalho and Santos, 2016; Puri et al., 2023). Within this group, antibiotics stand out (Fick et al., 2009; Cela-Dablanca et al., 2024; Conde-Cid et al., 2020; Rodríguez-López et al., 2022; Santás-Miguel et al., 2023). For example, in Beijing (China), in soils fertilized for greenhouse vegetable production different antibiotics were detected, within a wide range when expressed in μg kg^{-1} (Li et al., 2015; Wei et al., 2019).

The excessive use of antibiotics causes their environmental accumulation and may induce a negative impact in human health and degrade the environment (Cherian et al., 2023; Verlicchi and Zambello, 2015), since these compounds can reduce the microbial populations in soils and waters, delaying or blocking contaminant bioremediation, and being toxic to microorganisms (Rodríguez-González et al., 2023; Selvam et al., 2012). Furthermore, antibiotics in the environment are related to a significant increase of resistant genes (ARGs) and resistant bacteria (ARB) (Han et al., 2016; Hu et al., 2016; Koch et al., 2021; Li et al., 2023; Zhu et al., 2017). Several studies have indicated that, in soils, there is a correlation between residual antibiotic levels and ARGs (Awad et al., 2015; Lu et al., 2023; Ma et al., 2020; Tang et al., 2015; Zhang et al., 2023), although it is not always clear (Sun et al., 2022). This problem

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got worse recently with the appearance of COVID-19, which produced an increase in the antibiotic consumption to treat and prevent this disease (Núñez-Delgado et al., 2022; Race et al., 2020; Rawson et al., 2020).

Among antibiotics, AZM was used as a therapy for the treatment of SARS-CoV-2 pneumonia given its antiviral and immunomodulatory activity with well-known safety profile (Parnham et al., 2014; Gautret et al., 2020). In addition, it is considered as one of the relevant broad-spectrum therapeutic molecules (Firth and Prathapan, 2020), and overall is indicated for respiratory, urogenital, dermal and other bacterial infections, and exerts immunomodulatory effects in chronic inflammatory disorders (Parnham et al., 2014).

ARGs spreading in soils is mainly related to agricultural practices, such as intensive livestock farming (Forsberg et al., 2012; Gao et al., 2023). On the other hand, antibiotics of human consumption, which are excreted by feces and urine, enter the environment through effluents and sludge from wastewater treatment plants (WWTPs) (Carlesi-Jara et al., 2007; Hazra et al., 2022). Thereby, Hernández et al. (2019) detected the presence of eight different antibiotics in treated wastewater, with higher concentrations of two quinolones, ciprofloxacin and norfloxacin (at 0.89 and 0.75 μg L^{-1} respectively), and three macrolides, AZM and clarithromycin (with concentrations averaging 0.4 μg L^{-1}), and erythromycin (at 0.003 μg L^{-1}).

The presence of antibiotics like AZM and ciprofloxacin, transferred by biosolids, can introduce ARG transcriptional activities and mobilize genetic elements in biosolids and soils previously amended, in environmentally relevant concentrations (Sidhu et al., 2021). For this reason, there is a great concern regarding the entry of antibiotics into the environment through irrigation with reclaimed water or through the spreading of manure and sewage sludge used as fertilizers (Christou et al., 2017; Jia et al., 2023; Martínez, 2009; Sultana et al., 2023). The interest for the use of sewage sludge as fertilizer is owing to its characteristics such as elevated nutrient content, optimum properties to restore overexploited agricultural soils, and capacity to improve the organic matter content and water retention on sandy or eroded soils (Clarke and Smith, 2011; Inglezakis et al., 2014; Seleiman et al., 2020). Most WWTPs are expected to run well for organic matter and some macro-elements, such as C, N and P, but these treatment plants are not performant enough to effectively remove microcontaminants, like antibiotics (de Kreuk et al., 2010; Novo et al., 2013; Obaideen et al., 2022; Pal et al., 2015; Pronk et al., 2015). Therefore, WWTPs are one of the main sources of antibiotics that enter the environment (Gulkowska et al., 2008; Osińska et al., 2020). For example, in a WWTP in Beijing 22 different antibiotics were detected (eight quinolones, nine sulfonamides and five macrolides) with concentrations between 365 and 4916 ng L^{-1} (Li et al., 2013). Rodriguez-Mozaz et al. (2020) studied the presence of 53 antibiotics in WWTPs in seven different European countries and detected 17 antibiotics, among which ciprofloxacin, AZM, clarithromycin and trimethoprim stood out. Despite this, in Europe there is no legislation to regulate antibiotics concentration released into the environment from WWTPs (Carvalho and Santos, 2016; Marutescu et al., 2023). The 2008/105/EC Directive includes a list with 33 priority substances or groups of substances and their respective environmental quality standards, and in 2015 three antibiotics of the macrolides group (AZM, clarithromycin and erythromycin) were added (Barbosa et al., 2016). The UE included these three antibiotics in the list "Watch list of contaminants of emerging concern" of contaminants that can be controlled according to the Decision 2015/495 (European Union, 2015).

The maximum acceptable concentration for AZM, according to the Directive 2008/105/EC, is 90 mg L^{-1}. This antibiotic presents a low elimination rate from wastewater when using conventional treatments (Barbosa et al., 2016). In recent years, several studies have found the presence of AZM in wastewater effluents under conventional treatment. Specifically, Mirzaei et al. (2019) observed that the elimination of the macrolides AZM and erythromycin was not successful in a WWTP in Teheran (Iran). In previous studies, azithromycin was detected in influents of three WWTP and the antibiotic concentrations were 145 ng L^{-1}, 110 ng L^{-1} and 896 ng L^{-1} (Mirzaei et al., 2022). Furthermore, in previous decades, Mowery and Loganathan (2007) detected AZM in all the WWTPs analyzed in their research in Kentucky (USA), in concentrations up to 23.4 ng L^{-1}. On the other hand, this antibiotic was detected in treated wastewater recycled for agricultural use (Panthi et al., 2019). This demonstrates the convenience of developing new alternative treatments in order to achieve the complete (or much higher) removal of AZM and minimize the adverse effects caused by the presence of this antibiotic in wastewater and environmental compartments (Cano et al., 2020).

There are several techniques to remove or degrade antibiotics, such us hydrolysis, photodegradation, oxidization and biodegradation (Yang et al., 2021). Specifically, adsorption has been widely used for the removal of a variety of pollutants (Ahmed et al., 2021; Peña-Rodríguez et al., 2013), including antibiotics and ARGs, obtaining promising results (Fathy et al., 2017; Pan, 2020), because of its simple design and performance, low cost, and high efficiency removing antibiotics and not generating toxic subproducts (Ahmadi et al., 2017). The study of adsorption methods allows to analyze the retention/mobility of antibiotics in soils and their possible transport to groundwater (lixiviation), superficial water (run-off) and crops (plant uptake) (Pikkemaat et al., 2016; Toakoak-Asho and Cho, 2016). The adsorption process not only can determine the bioavailability of these compounds (Botero-Coy et al., 2018), but also would influence degradation reactions (Xiang et al., 2019). This technique has several advantages over other techniques used to remove antibiotics, so it would be interesting introduce an integrated system into existing treatment plants for a complete remediation (Mangla et al., 2022). The efficiency of this process depends on the type of adsorbent, adsorbate properties and the waste stream composition (Acevedo-García et al., 2020; Aksu and Tunç, 2005). There are multiple studies that analyze the use of adsorbents to remove antibiotics, including clay compounds and biochar to remove tetracycline (Premarathna et al., 2019); magnetic ion exchange resins to remove sulfamethoxazole, tetracycline and amoxicillin (Wang et al., 2017); magnetic imprinted polymers for the selective removal of erythromycin (Ou et al., 2015) or powdered zeolites to remove AZM, ofloxacin and sulfamethoxazole (de Sousa et al., 2018). Paredes-Laverde et al. (2018) also studied the elimination of norfloxacin by using natural adsorbents such as rice husk and coffee. Furthermore, various vegetable residues turned out promising as natural adsorbents for the treatment of pollutants, including grapefruit peel (Zou et al., 2012), papaya seed (Pavan et al., 2014), consumed tea leaves (Hameed, 2009), peanut hull (Ali et al., 2016), shell of wheat and lentil (Aydin et al., 2008), and banana and mango peel (Bhatnagar et al., 2015).

With the previous background and constituting the first steps in a more complex project (Núñez-Delgado, 2024), the main objective of the current research is to assess the capacity of three different by-products to adsorb AZM and their influence in AZM adsorption on agricultural soils with different physicochemical properties. Two of these bio-adsorbents derive from the forestry industry (pine bark and oak ash) and the other one from the food industry (mussel shell). Promoting the recycling of by-products while favoring the retention/removal of antibiotics that have reached the environment as pollutants can be considered of relevance at the level of research and social implications.

2. Material and methods

2.1. Soils and bio-adsorbent materials

Four soils were selected for this study, three of them under corn crops (C soils) and the fourth one being a vineyard soil (V soil), all of them situated in Galicia (NW Spain). The main characteristics of these soils are detailed in Table 1. It could be highlighted that these soils show pH values between 5.01 and 6.04, organic matter contents in the range 3.06–4.59%, and cation exchange capacity scores between 5.94 and

Table 1
Values corresponding to the basic physicochemical properties determined in the soils used in this research. Average values (n = 3), with coefficients of variation always <5%.

Soil	pH H_20	OC	OM	N	Sand	clay	eCEC	Ca	Mg	Na	K	Al	Feo	Fepir	Alo	Alpir
		%					cmol$_c$ kg^{-1}						mg kg^{-1}			
C1	5.33	2.66	4.59	0.27	43.42	24.65	6.88	5.35	0.67	0.02	0.44	0.40	5745	3159	3401	2871
C2	5.65	2.58	4.44	0.25	43.57	22.43	7.48	6.18	0.77	0.00	0.28	0.24	5780	3315	3881	2717
C3	5.01	2.04	3.52	0.21	45.64	22.43	5.94	4.58	0.67	0.10	0.17	0.43	4545	2923	2896	1945
V	6.04	1.77	3.06	0.10	49.57	24.14	7.42	4.94	0.86	0.16	0.69	0.77	1790	1171	1556	1141

C: corn soils; V: vineyard soils. OC: organic carbon; OM: organic matter; N: nitrogen; eCEC: effective cation exchange capacity; Al_o, Fe_o: non-crystalline Al and Fe (extracted with ammonium oxalate); Al_{pir}, Fe_{pir}: Al and Fe extracted with sodium pyrophosphate.

7.48 cmol$_c$ kg^{-1}.

Three bio-adsorbents were used to carry out this work, with pine bark being provided by Geolia (Madrid, Spain), oak ash being from a combustion boiler in Lugo (Spain), and mussel shell provided by the factory of Abonomar S.L, Pontevedra (Spain). The main characteristics of these bio-adsorbents are detailed in Supplementary Material (Table S1). To highlight that pine bark presents an acid pH (3.99), while mussel shell and oak ash have alkaline pH values (9.39 and 11.31, respectively).

For specific experiments, these bio-adsorbents were added as amendments to the soils, in a dose of 48 t ha^{-1}. Table S2 (Supplementary Material) shows the pH values of the soils and the soil + bio-adsorbent mixtures.

2.2. Chemical reagents

AZM was provided by Sigma-Aldrich (Barcelona, Spain). The reagents used for HPLC measurements, potassium phosphate (purity ≥99.5%), and acetonitrile (purity ≥99.9%), were supplied by Fisher Scientific (Madrid, Spain). $CaCl_2$ (95% purity) was provided by Panreac (Barcelona, Spain).

All the solutions used were prepared with milliQ water (Millipore, Madrid, Spain).

2.3. Adsorption and desorption experiments

Batch-type experiments were carried out to study the adsorption/desorption of AZM on/from the different bio-adsorbents and mixtures soil + bio-adsorbent. For this purpose, solutions with different antibiotic concentrations were prepared (in the range 2.5–600 μmol L^{-1}), using 0.005 M $CaCl_2$ as background electrolyte. These solutions were added to 0.5 g of each bio-adsorbent sample and to 2 g of each mixture soil + bio-adsorbent sample. The suspensions were shaken in the dark during 48 h (time needed to reach the equilibrium, as determined in previous experiments), using a rotary shaker. Then, the suspensions were centrifuged for 15 min at 4000 rpm by means of an Eppendorf centrifuge 5810 R (Eppendorf, Germany) and filtered through 0.45 μm nylon syringe filters. Finally, the antibiotic concentrations in the equilibrium solution were determined by means of an HPLC-UV LPG 3400 SD equipment (Thermo-Fisher, USA), with additional details included in Supplementary Material. AZM adsorbed was determined as the difference between the concentrations in the added solutions and concentrations present in the equilibrium. Triplicate determinations were performed in all cases.

Desorption experiments were carried out adding 10 mL of 0.005 M $CaCl_2$ to the material derived from the adsorption phase, then applying the same procedure as for the adsorption process. Fig. S1 (Supplementary Material) shows example chromatograms corresponding to the quantification of AZM.

2.4. Data treatment

The adsorption experimental data were adjusted to the Freundlich (Eq. (1)), Langmuir (Eq. (2)) and Linear (Eq. (3)) models, as indicated in Conde-Cid et al. (2021), and Cela-Dablanca et al. (2022a).

For this, the following equations were used:

$$qe = K_F Ceq^n \quad \text{(Eq. 1)}$$

$$qe = \frac{q_m K_L Ceq}{1 + K_L Ceq} \quad \text{(Eq. 2)}$$

$$Kd = qe/Ceq \quad \text{(Eq. 3)}$$

where qe is the amount of antibiotic retained by the adsorbent material (calculated as the difference between the concentration added and that remaining in the equilibrium solution, referred to the amount of adsorbent used); Ceq is the antibiotic concentration present in the solution at equilibrium; K_F is the Freundlich parameter related to the adsorption capacity; n is a parameter of the Freundlich model associated with the degree of heterogeneity of the adsorption; K_L is the Langmuir adsorption constant; q_m is the maximum adsorption capacity according to the Langmuir model; and K_d is the partition coefficient in the Linear model.

The SPSS statistics software (version 21) was used to perform the adjustments, as well as any additional statistical treatment and calculations needed.

3. Results and discussion

3.1. AZM adsorption on the three bio-adsorbent materials

Fig. S2 (Supplementary Material) shows a rise in AZM adsorption (expressed in μmol kg^{-1}) when the concentration added increased, especially for oak ash and pine bark, while the behavior was rather erratic when expressed as percentage. In addition, when analyzing the AZM adsorption values (expressed in percentage) by the different bio-adsorbents, it was observed that oak ash was the material showing the highest adsorption, with values greater than 80% for all the concentrations added (except for the lowest, 50 μmol L^{-1}). In the case of pine bark, the maximum adsorption was 69%, while mussel shell adsorption decreased from 50% (reached for the lowest AZM concentration added) to 25% (for the highest AZM concentration applied). Similar results were obtained by Kabir et al. (2022) in a study where AZM adsorption (studied for different bio-adsorbents) significantly decreased when the highest concentration was added, probably due to the progressive saturation of the adsorption sites (Wu et al., 2020). Conde-Cid et al. (2019) studied the adsorption of three tetracyclines on the same three bio-adsorbents used in the current research, in a ternary system, obtaining the highest adsorption scores for oak ash and pine bark.

Before performing the current investigation focused on by-products, we have previously studied AZM adsorption onto Galician soils (Cela-Dablanca et al., 2022b), while other authors have shown results corresponding to AZM retention/removal onto other different soils (Bustos-López et al., 2023) or on sorbent materials different to those used in the current research (Ameen et al., 2023; Balarak et al., 2021; Upoma et al., 2022), all of them needed to provide different but complementary results helping to increase the overall knowledge of this specific matter. In fact, previous studies have shown the applicability of low-cost sorbent materials to remove antibiotics from environmental compartments (Anthony et al., 2021; Anuar et al., 2023; Cela-Dablanca et al., 2022a), thus encouraging further research in this field.

Regarding adsorption curves (Fig. 1), it is shown that, for the highest concentration of antibiotic added, oak ash was the bio-adsorbent that presented the highest adsorption, reaching 9300 μmol kg^{-1}, followed by pine bark that reached 8054 μmol kg^{-1}. However, mussel shell showed a much smaller adsorption, with maximum of 2035 μmol kg^{-1}. These values are much higher than the ones obtained for the same antibiotic in a previous study with different soils (Cela-Dablanca et al., 2022b). Similarly, other authors have described high adsorption results for this antibiotic in other materials such as biosolids (Sidhu et al., 2019), and a high affinity for soils has been reported (Vermillion Maeir and Tjeerdema, 2018).

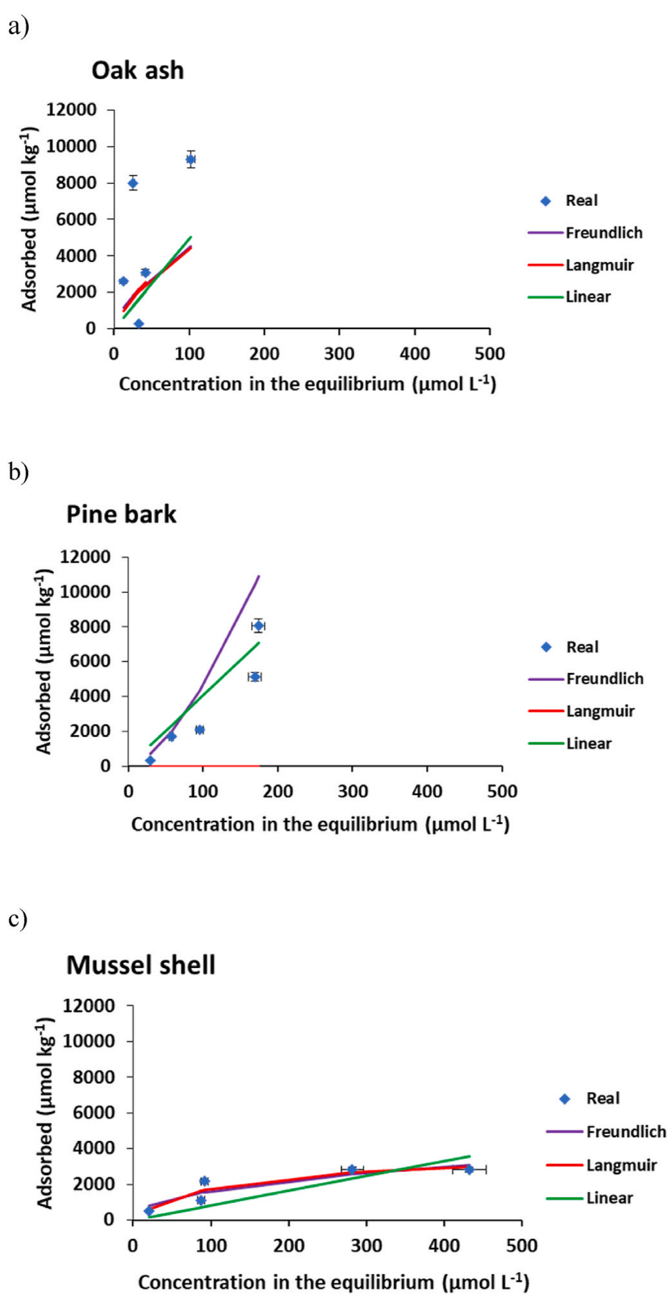

Fig. 1. Real and estimated adsorption curves for AZM corresponding to each of the three bio-adsorbents [a), b), and c)]. Average values (n = 3) with coefficients of variation always lower than 5%.

The results showed that the two bio-adsorbents having alkaline pH (oak ash and mussel shell) had adsorption capacities clearly different between them. Furthermore, comparing two of the bio-adsorbents having very different pH values, such as oak ash and pine bark, it was observed that both materials had high adsorption capacities. These facts suggest that the pH of these bio-adsorbents had not marked influence on AZM adsorption. However, in a previous work Cela-Dablanca et al. (2022b) found clearly increased AZM adsorption for the soils with higher pH within their study.

This controversial behavior may be related to the very different pH values characterizing the bio-adsorbents used in the current research. In fact, oak ash had a very alkaline pH (11.31), as well as non-crystalline Fe and Al concentrations much higher than the other two bio-adsorbents (Table S1; Supplementary Material), relevant due to being variable charge components negatively charged at these pH values. To note that Gravesen and Judy (2020) used multiple linear regression analyses showing relations between AZM adsorption and total Fe content, due to the propensity of AZM to react with Fe species. Furthermore, we must bear in mind that the pH value of the oak ash used in the current research (pH = 9.39) was higher than the pK_a of AZM (8.74) (Davoodi et al., 2019), therefore, at this pH AZM is deprotonated and negatively charged. Specifically, these authors reported that, due to that reason, AZM adsorption onto raw diatomite increased at pH > 9 and was highest at pH 11. Owing to this, the union between AZM and oak ash would take place by means of electrostatic interactions (Anastopoulos et al., 2020). However, mussel shell had fewer non-crystalline minerals and organic matter contents than oak ash and hence less negatively charges surface available for AZM adsorption. Related to that, Conde-Cid et al. (2019) also obtained higher adsorption for three tetracyclines (oxytetracycline, chlortetracycline and tetracycline) using oak ash than with mussel shell. On the contrary, pine bark pH was very acidic (3.99), although having a high organic matter content (>47%) (Table S1, Supplementary Material), and in these conditions there would be deprotonated carboxyl groups that acquire negative charge to adsorb this antibiotic. In this case, the union between AZM and the adsorbent would be by hydrogen bonds, since the acidic pH would generate an electrostatic repulsion between positive charges of the pine bark surface and the AZM cationic form (Zhao et al., 2016).

Data obtained from the AZM adsorption experiments were adjusted to the Freundlich, Langmuir and Linear models. As shown in Table S3 (Supplementary Material), for mussel shell real data adjusted well to the Freundlich model, while the fitting was clearly poorer for the Langmuir and Linear models. For pine bark, all three models were affected by high errors, invalidating the fittings. For oak ash, the best adjustment (although poor) corresponded to the Linear model. In a previous publication, Upoma et al. (2022) found the best fitting for the Freundlich model when studying AZM adsorption on graphene oxide.

In the current study, the values corresponding to the Freundlich *n* parameter were <1 (Table S3), indicating the presence of heterogeneous adsorption sites, where those being of high energy were first occupied (Foo and Hameed, 2010; Behnajady and Bimeghdar, 2014). As indicated above, for both oak ash and pine bark the fitting to the models was poorer or inexistent (Table S3). However, in previous research focused on a different antibiotic (amoxicillin), Cela-Dablanca et al. (2022a) found good fitting for the Freundlich and Linear models using the same three bio-adsorbents.

3.2. AZM desorption from the three bio-adsorbents

The results indicated that the three bio-adsorbents used adsorbed the AZM added in a highly irreversible way, as no antibiotic was detected in the equilibrium solution. Similar results were obtained in previous studies using soils (instead of bio-adsorbent materials) as adsorbent (Cela-Dablanca et al., 2022b), as well as for the antibiotic amoxicillin using the same bio-adsorbents (Cela-Dablanca et al., 2022a). However, the results were different for cefuroxime, where pine bark presented desorption percentages between 29.1% and 51.9% (Cela-Dablanca et al., 2021). Sidhu et al. (2019) also reported a high retention for this antibiotic on biosolids, with desorption no exceeding 1% in any case, while Vermillion Maier and Tjeerdema (2018) obtained a value of 9.2% for maximum desorption from soils. In addition, in the case of alluvial sediments Senta et al. (2021) described the recalcitrant character of AZM. Overall, it should be noted that the persistence of these emerging pollutants for long periods of time is considered as a factor able to favor the emergence of gene antibiotic resistance, for example in agricultural soils (Lau et al., 2020), especially when high doses are spread.

3.3. AZM adsorption on soils with and without bio-adsorbents

Fig. 2 shows the adsorption curves for each of the four soils used in this research, both without amendments and amended with each of the three bio-adsorbents at a dose of 48 t ha^{-1}.

The layouts clearly indicate that the amendments caused that all the AZM added was adsorbed in most cases, although it was very high even for not amended soils, especially when the lowest concentrations of the antibiotic were added.

The adsorption data corresponding to these experiments cannot be fitted to adsorption models due to the fact that no antibiotic remains in solution in most cases.

Considering the soils without amendment, AZM adsorption was 100% up to doses of 400 and 200 μmol L^{-1} added, for soils V and C3, respectively, while for the C1 and C2 soils, adsorption was 100% when the concentration added was 50 μmol L^{-1} or less. However, for the highest concentration added (600 μmol L^{-1}) adsorption oscillated between 50% and 85%, being the vineyard soil (V) the one showing the highest score. This could indicate a saturation of the adsorbent surfaces when the highest antibiotic concentration was added.

Fig. 3 shows AZM adsorption (expressed in μmol kg^{-1} and in percentage) onto the four agricultural soils with and without each of the three bio-adsorbents, as a function of increasing concentrations of the antibiotic added. The results indicate that adsorption increased in all cases after amending with the bio-adsorbents, and the difference was more marked for the highest concentrations of AZM added (400 and 600 μmol L^{-1}).

After the amendment, when any of the bio-adsorbents was added to the soils, AZM retention increased for all soils when the highest concentrations of the antibiotic were spread, reaching 100% adsorption in most cases (with the exception of the C3 soil mixed with mussel shell, where the maximum adsorption was limited to 87% when a concentration of 600 μmol L^{-1} of the antibiotic was added).

It must be noted that oak ash and mussel shell have a high pH value, increasing the pH of the soils amended with these materials (clearly in all cases, for oak ash, or slightly and not so clear, for mussel shell) (Table S2, Supplementary Material), raising the negative charge of the variable charge components (organic matter and non-crystalline substances), and therefore increasing the adsorption of the AZM molecules that are in cationic form over a wide range of pH (4–9) (Sidhu et al., 2019). These same authors found an increase in AZM adsorption when soils were amended with biosolids in comparison with soils without biosolids, due to the increase in pH caused by the addition of these materials (Sidhu et al., 2019). In addition, Davoodi et al. (2019) studied the capacity of raw and saponin-modified nano diatomite to absorb AZM from aqueous solutions, obtaining that adsorption was similar both at pH 5 and 7 (<60%), but when pH increased to 9 and 11 adsorption rose to 79% and 92%, respectively. However, in the case of raw nano diatomite, pH had no influence on adsorption. Upoma et al. (2022) studied the adsorption of AZM using wastes derived from graphene oxide and obtained a slight increase in adsorption at high pH values. At these pHs, adsorption can be explained due to the deprotonation taking place and generation of negative charge, which favor the electrostatic attraction between the negative charge of the adsorbents and the positively charged groups of AZM (Davoodi et al., 2019).

On the other hand, the amendment with pine bark (pH = 3.99) slightly decreased the pH of soils (Table S2, Supplementary Material), and also caused an increase in the organic matter content of the mixture. This bio-adsorbent can acquire negative charge in carboxyl groups in the range of pH 4.2–4.5, where AZM presents amino groups in protonated form (Vajdle et al., 2017). Thereby, in this case the adsorption

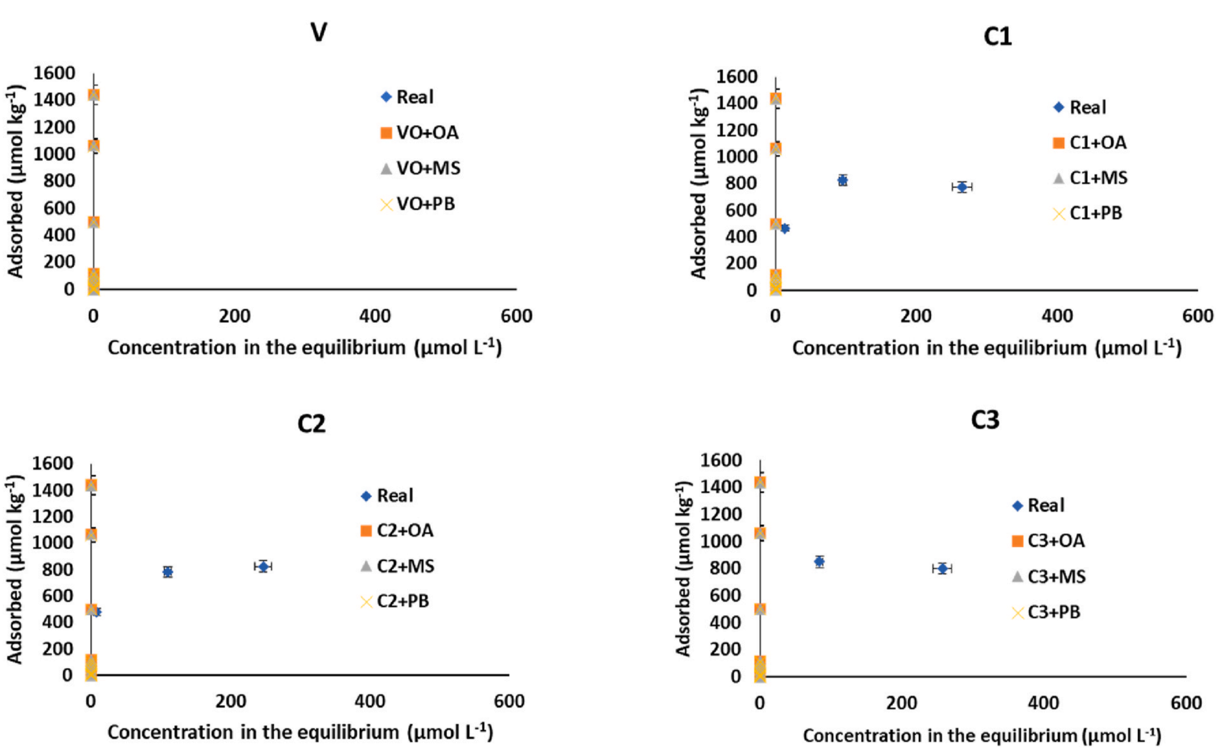

Fig. 2. AZM adsorption curves corresponding to four agricultural soils (V, C1, C2, and C3), with and without bio-adsorbents amendment. Real: unamended soil. V and VO: vineyard soil; C: corn soils; AO: oak ash; MS: mussel shell; PB: pine bark. Average values (n = 3) with coefficients of variation always lower than 5%.

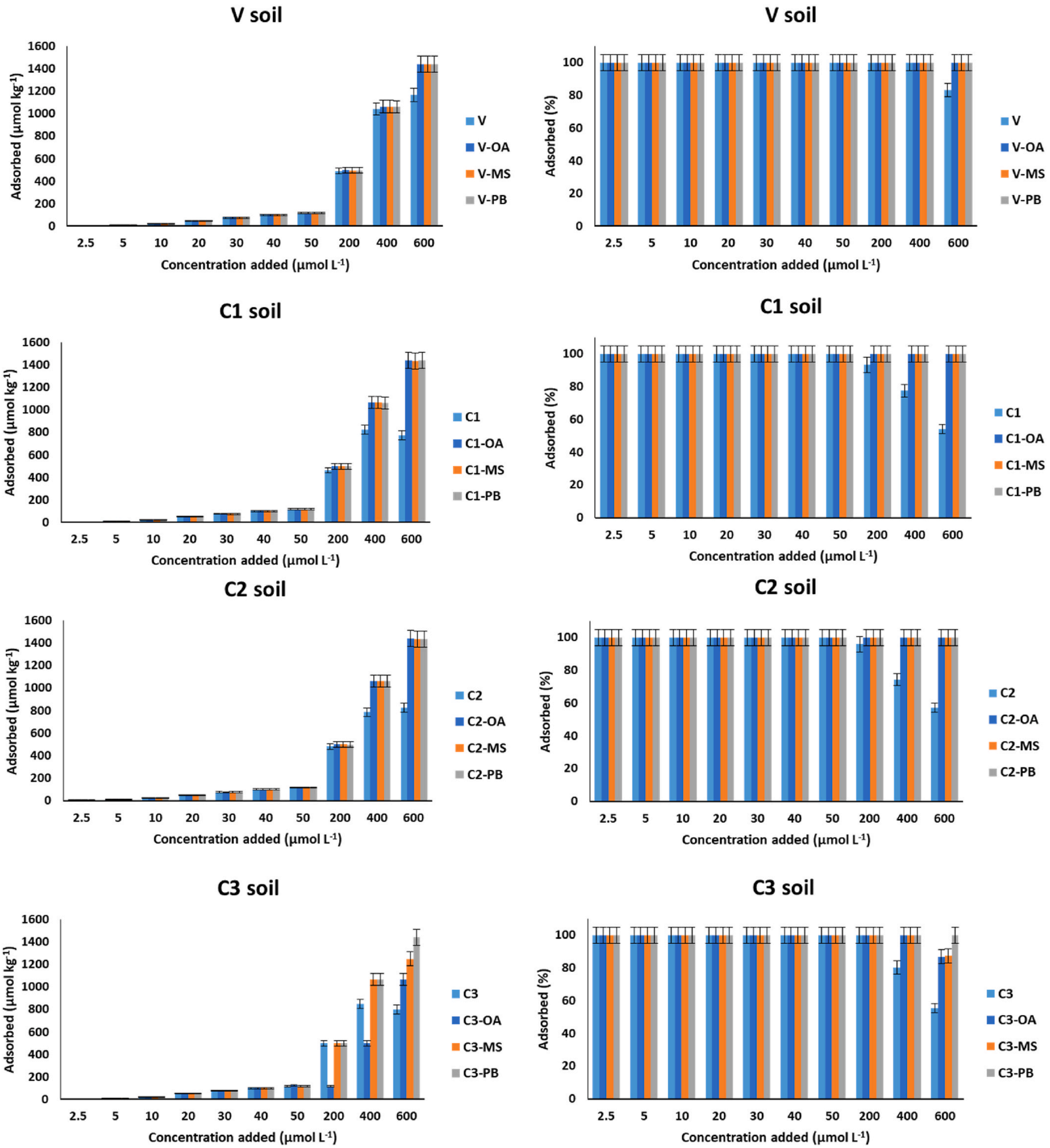

Fig. 3. AZM adsorption (expressed in µmol kg^{-1} and in percentage) for increasing concentrations of the antibiotic added to four agricultural soils, with and without bio-adsorbents amendment. V: vineyard soil; C: corn soils; OA: oak ash; MS: mussel shell; PB: pine bark. Average values (n = 3) with coefficients of variation always lower than 5%.

mechanism must be attributed to H-bonding and electrostatic interaction between the negative charges of the bio-adsorbent and the positive charges of AZM (de Sousa et al., 2018).

3.4. AZM desorption from soils with and without bio-adsorbents amendment

There was no AZM desorption from soils with or without bio-adsorbents amendment. These results are in line of those previously found for the three bio-adsorbents. In addition, Cela-Dablanca et al. (2022b) reported a strong retention of AZM in studies focused on soils not amended with bio-adsorbents. High AZM retention was also found for biosolids (Gravesen and Judy, 2020), for soils amended with biosolids (Sidhu et al., 2019), and for biochar (Mutera et al., 2019). Senta et al. (2021) reported a high AZM adsorption on sediments, while Vermillion Maier and Tjeerdema (2018) found desorption between 0.1

and 9% from riverbank soils. In a previous study carried out for the antibiotic amoxicillin using the same soil + bio-adsorbent mixtures as in the current research, desorption clearly decreased after the amendments (Cela-Dablanca et al., 2022c).

4. Conclusions

Among the three bio-adsorbents studied, oak ash was the one showing the highest adsorption capacity for the antibiotic AZM, being above the other sorbent with also alkaline pH (mussel shell). The third bio-adsorbent (pine bark) also showed high AZM adsorption capacity, in spite of having acidic pH, suggesting that the influence of pH in the adsorption of AZM on these materials was low. Regarding desorption, it was inexistent or very low, indicating that AZM presents a strong and rather irreversible adsorption onto the three bio-adsorbents. At the highest AZM concentrations added, the soils used were not able to retain 100% of the antibiotic they received, but the retention increased up to 100% when amending with any of the bio-adsorbents used (pine bark, oak ash or mussel shell). In addition, in the conditions tested there was no desorption, indicating a strong and rather irreversible retention of AZM after the amendments. These results show a rather low risk of AZM pollution for the soils studied and under most of the experimental conditions considered, although with potential hazards increasing as a function of the concentration of the antibiotic present in the environmental compartment being investigated. In these cases, the amendment with an appropriated bio-adsorbent (as the three included in this research) would be a good option to increase the overall adsorption capacity, preventing that this or similar emerging pollutants end up into other environmental compartments such as surface water and groundwater. In addition, it is relevant that the use of low-cost materials as effective bio-adsorbents promote recycling, sustainability, and the circular economy.

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CRediT authorship contribution statement

Raquel Cela-Dablanca: Writing – original draft, Visualization, Software, Investigation, Data curation. **Ana Barreiro:** Writing – original draft, Visualization, Software, Investigation, Data curation. **Lucía Rodríguez-López:** Visualization, Investigation. **Manuel Arias-Estévez:** Visualization, Validation, Supervision, Methodology, Conceptualization. **María Fernández-Sanjurjo:** Writing – original draft, Visualization, Validation, Supervision, Methodology, Conceptualization. **Esperanza Álvarez-Rodríguez:** Writing – original draft, Visualization, Validation, Supervision, Methodology, Data curation, Conceptualization. **Avelino Núñez-Delgado:** Writing – review & editing, Visualization, Validation, Supervision.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2024.119048.

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