



Potential of low-cost bio-adsorbents to retain amoxicillin in contaminated water

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ARTICLE INFO

Keywords:

Adsorbents
Antibiotics
By-products
Emerging pollutants
Soil pollution
Water pollution

ABSTRACT

Sewage sludge as agricultural amendment is the main route of human-medicine antibiotics to enter soils. When reaching environmental compartments, these compounds can cause significant risks to human and ecological health. Specifically, the antibiotic amoxicillin (AMX) is highly used in medicine, and the fact that more than 80% of the total ingested is excreted increases the chances of causing serious environmental and public health problems. As the use of low-cost bio-adsorbents could help to solve these issues, this research focuses on the retention of AMX onto four by-products of the forestry industry (eucalyptus leaf, pine bark, pine needles, and wood ash) and one from food industry (mussel shell). To carry out this study, batch-type tests were performed, where increasing concentrations of the antibiotic (0, 2.5, 5, 10, 20, 30, 40 and 50 $\mu\text{mol L}^{-1}$) were added to samples of 0.5 g of each bio-adsorbent. Eucalyptus leaf, pine needle and wood ash showed adsorption scores higher than 80%, while it was up to 39% and 48% for pine bark and mussel shell, respectively. For pine bark, wood ash and mussel shell, adsorption data showed good adjustment to the Freundlich and Linear models, while pine needles and eucalyptus leaf did not fit to any model. There was not desorption when the maximum concentration of AMX (50 $\mu\text{mol L}^{-1}$) was added. Overall, eucalyptus leaf, pine needles and wood ash can be considered good bio-adsorbents with high potential to retain AMX, which has significant implications regarding their eventual use to reduce risks of environmental pollution by this antibiotic.

1. Introduction

As antibiotics are highly used in the treatment and prevention of infectious diseases, both in humans and in animals, these compounds and related metabolites are often detected in waters, sediments, soils, and organisms (Radjenović et al., 2009; Rosal et al., 2010; Zhou et al., 2011). In general, its presence in the environment may cause harmful effects (Orozco-Hernández et al., 2019; Santás-Miguel et al., 2020; Shen et al., 2019).

Among these biocides, amoxicillin (AMX) is a broad spectrum β -lactam antibiotic, classified as one of the ten most commonly used drugs due to its high demand in livestock and human medicine treatments (Merlin et al., 2011). More than 80% of AMX is excreted through feces and urine after 2 h since ingestion, with subsequent presence in water and wastewater. In fact, most of the antibiotics that reach the

environment come from pharmaceutical industries, hospital effluents, and excretions from humans and farm animals (Sophia et al., 2016; Abazari et al., 2019). For instance, Henninger et al. (2001) found AMX concentrations between 28 and 82.7 $\mu\text{g L}^{-1}$ in wastewater from a hospital. In fact, the main route of human medicine antibiotics to enter the environment is through wastewater. After intake for therapeutic use, antibiotics are largely excreted as original compounds and partly as derived metabolites. After reaching Wastewater Treatment Plants (WWTP), antibiotics are subjected to different treatments, which are not always totally effective in the elimination of emerging pollutants (Krzeminski et al., 2019).

These treatments generate sludge, which is commonly used as amendments in agricultural plots, thus constituting a route of entry for antibiotics into the soil. Soil pollution by antibiotics has a negative impact (Li, 2014; Mackuřak et al., 2019), with an additional risk of

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<https://doi.org/10.1016/j.envres.2022.113621>

Received 10 January 2022; Received in revised form 24 May 2022; Accepted 3 June 2022

Available online 11 June 2022

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contamination of surface and ground water, as well as entering the food chain, which can take place through drinking water and food since many crops could absorb these pollutants from soil. In this regard, is noteworthy that the environmental risk assessment of antibiotics persistent in the environment is a challenge, which is accentuated due to their movement patterns through different compartments (Yi et al., 2019; Najafpoor et al., 2019).

Regarding the removal of this kind of emerging pollutants, one of the first steps to be considered are WWTPs treatments, as some of them include different antibiotic elimination techniques. The most popular methods are biological and chemical treatments. Specifically, electro-coagulation, photo- and electro-chemical catalytic degradation, and advanced oxidation methods have shown to be useful in the case of AMX present in wastewater (Flamur et al., 2015; Liu et al., 2015; Mohammad et al., 2015; Padilla-Robles et al., 2015); however, the cost of these methods is high. As an alternative, adsorption is considered one of the most effective techniques for removing antibiotics from effluents (Homem and Santos, 2011). This method is efficient, simple to design and operate, as well as inexpensive (Han et al., 2008).

In addition, once in the soil, adsorption/desorption processes are of main importance in conditioning the entry of antibiotic residues into surface- and groundwater, as well as into crops, largely controlling their passage to the food chain (Christou et al., 2017; Harrabi et al., 2018; Zhou et al., 2018). In addition, the behavior of AMX in the edaphic environment is highly conditioned by the pH of the medium, which affects the ionization of the compound and the surface charge of the soil colloids. AMX has amphoteric properties due to the existence in its structure of three functional groups: NH_2 , $-\text{COOH}$ and $-\text{OH}$ (Anastopoulos et al., 2020). The charge of the AMX molecule changes gradually as a function of pH, due to the pK_a of these functional groups. The carboxyl group has a $\text{pK}_{a1} = 2.68$, the amine group has a $\text{pK}_{a2} = 7.49$ and the phenolic hydroxyl group has a $\text{pK}_{a3} = 9.63$ (Homsirikamol et al., 2016). Therefore, in the pH range between 3 and 6, AMX is in its zwitterionic form, whereas at pH values below and above this range, the AMX molecule is mainly positively and negatively charged, respectively.

Currently, activated carbon has become one of the most common adsorbents (Liu et al., 2011), but its high cost of operation and regeneration represent disadvantages (Zazouli et al., 2013), creating a growing demand for other more economical adsorbents that do not require any additional costly pretreatment (Han et al., 2008). For example, Putra et al. (2009) used bentonite for the retention of AMX, achieving 88% efficiency in the elimination of this antibiotic. Also to be noted, the use of effective bio-adsorbents that are produced in abundance in the vicinity of the area where they are to be applied, would facilitate their supply and recycling, reducing costs. Specifically, in Galicia (NW Spain) there are abundant residues and by-products from the food industry, such as mussel shell, and from the forestry industry (such as pine bark, pine needles, eucalyptus leaves, and wood ash), which would be interesting candidates to study their capacity to adsorb AMX.

Considering this scenario, a first-time study was performed dealing with AMX adsorption and desorption on/from four by-products of the forestry industry (eucalyptus leaf, biomass combustion ash, pine bark and pine needles), and one by-product of the food industry (mussel shell). As all five are low-cost materials, their possible effective use in the retention of AMX present in the environment as pollutant would have a clear interest, both in terms of environmental protection, and promotion of recycling by-products within the precepts of the circular economy.

2. Materials and methods

2.1. Chemical reagents

AMX (with purity 95% or higher) was from Sigma-Aldrich (Barcelona, Spain). Acetonitrile and phosphoric acid (with purities of 99.9%

and 85%, respectively) were from Fisher (Madrid, Spain), while Panreac (Barcelona, Spain) provided CaCl_2 (with purity 95%). Millipore (Madrid, Spain) provided milliQ water used to prepare solutions needed to perform HPLC analyses.

2.2. Sorbent materials

The materials used as sorbents were: i) eucalyptus leaves sampled at forest exploitations situated in Lugo (Spain), pine bark provided by Geolia (Spain), pine needles sampled at forest exploitations situated in Lugo (Spain), and wood ash sampled at combustion boiler situated in Lugo (Spain), all four considered by-products from forestry industries; and ii) mussel shell (ground at <1 mm), from Abonomar S.L. (Pontevedra province, Spain), which is a by-product generated at food industries. As further details, it should be noted that eucalyptus leaves are from *Eucalyptus nitens*, pine bark and pine needles are from *Pinus pinaster*, and mussel shells are from *Mityllus galloprovincialis*. The age of the mussels varied and was not defined, derived from many different shells used in the cannery industry. The age of *Eucalyptus nitens* was 7 years, while it is not known for *Pinus pinaster*. All bio-adsorbents were ground until achieving particle size <1 mm and then were stored in the lab, at room temperature (around 20°C), until further analyses and use.

Supplementary Material includes the methodology used to characterize all five sorbent materials. In addition, complementary details have been previously published (Conde-Cid et al., 2019; Quintáns-Fondo et al., 2019).

2.3. Adsorption and desorption experiments

Batch experiments were performed to study the adsorption/desorption of AMX on/from all five bio-adsorbent materials. For this, 0.5 g of bio-adsorbent were weighed, and mixed with 10 mL of a solution with different concentrations of the antibiotic (2.5, 5, 10, 20, 30, 40, 50 $\mu\text{mol L}^{-1}$), also containing 0.005 M CaCl_2 as background electrolyte. The suspensions were shaken for 48 h in the dark using a rotary shaker (as 48 h was enough to reach equilibrium according to previous kinetic tests, data not shown). These suspensions were then centrifuged at 4000 rpm for 15 min. The resulting supernatants were filtered through 0.45 μm nylon syringe filters and the antibiotic concentration in the filtered liquids was determined by HPLC-UV with LPG 3400 SD equipment (Thermo-Fisher, USA).

More details regarding HPLC equipment and quantification are included in Supplementary Material, as well as selected chromatograms (Figure S1).

After adsorption, desorption was studied in those cases where the maximum AMX concentration ($50 \mu\text{mol L}^{-1}$) had been added, to evaluate the reversibility of the process. To do that, the material resulting from the adsorption process was added with a volume of 10 mL of 0.005 M CaCl_2 (with no antibiotic), then repeating the procedure performed for adsorption. Triplicate determinations were carried out in all cases.

2.4. Data treatment

Experimental adsorption data were adjusted to the Freundlich (Eq. (1)), Langmuir (Eq. (2)) and Linear (Eq. (3)) models (Ayawei et al., 2017).

$$q_e = K_F C_{eq}^n \quad (1)$$

$$q_e = \frac{q_m K_L C_{eq}}{1 + K_L C_{eq}} \quad (2)$$

$$Kd = q_e / C_{eq} (\text{Lkg}^{-1}) \quad (3)$$

In these equations q_e is the amount of AMX retained onto the sorbent, which was the concentration added minus that remaining in the equilibrium solution; C_{eq} is the AMX concentration in the solution at

Table 1

AMX adsorption, expressed in $\mu\text{mol kg}^{-1}$ and in percentage, for the five different sorbents, as a function of the concentration of antibiotic added (C_0 in $\mu\text{mol L}^{-1}$). -: no data. Average values ($n = 3$), with coefficients of variation always $< 5\%$. C_{eq} : concentration in the equilibrium; Ads: quantity adsorbed; -: no data.

	C_0 (μM)	C_{eq} (μM)	Ads ($\mu\text{mol kg}^{-1}$)	Ads (%)
Eucalyptus leaves	0	0	0	0
	2.46	0	49.12	100
	5.37	0	107.37	100
	10.93	0	206.22	100
	18.34	-	-	-
	29.13	0	560.19	100
	38.62	0	757.31	100
	52.07	12.42	762.56	76.15
Pine bark	0	0	0	0
	2.46	2.4	1.12	2.29
	5.37	5.2	3.37	3.14
	10.93	10.8	2.49	1.19
	18.34	14.58	75.18	20.49
	29.13	22.51	132.38	22.72
	38.62	23.66	299.20	38.73
	52.07	36.77	294.23	29.38
Pine needles	0	0	0	0
	2.46	0	48.16	100
	5.37	-	-	-
	10.93	0	214.30	100
	18.34	-	-	-
	29.13	0	582.60	100
	38.62	0	772.46	100
	52.07	0	1001.32	100
Wood ash	0	0	0	0
	2.46	0.31	41.99	81.19
	5.37	1.19	83.49	77.76
	10.93	1.98	178.90	81.84
	18.34	-	-	-
	29.13	4.67	470.40	83.97
	38.62	4.78	663.52	87.61
	52.07	5.36	934.21	89.71
Mussel shell	0	0	0	0
	2.46	1.52	18.35	38.10
	5.37	3.08	46.71	42.64
	10.93	7.33	70.55	32.92
	18.34	11.32	132.50	38.29
	29.13	16.66	226.69	42.80
	38.62	19.05	391.53	50.69
	52.07	27.00	501.46	48.15

equilibrium; K_F is a parameter representing the Freundlich's adsorption capacity; n is the Freundlich's parameter related to the degree of heterogeneity in adsorption; K_L is a parameter known as the Langmuir adsorption constant; q_m is the Langmuir's maximum adsorption capacity; and K_d is a parameter of the linear model known as partition coefficient. The fitting of adsorption data to the Freundlich, Langmuir, and Linear models was carried out by means of the SPSS 21 statistical package, also used to study statistical correlations involving adsorption results and parameters of the bio-adsorbents.

3. Results and discussion

3.1. Adsorption/desorption of AMX

Table 1 shows the adsorption values for the various bio-adsorbents, expressed in $\mu\text{mol kg}^{-1}$ and in percentage, depending on the concentration of antibiotic added. For the highest AMX concentration added, pine needles showed the highest adsorption value ($1001 \mu\text{mol kg}^{-1}$), followed by wood ash ($934 \mu\text{mol kg}^{-1}$), eucalyptus leaf ($762 \mu\text{mol kg}^{-1}$), mussel shell ($501 \mu\text{mol kg}^{-1}$), while pine bark presented the lowest adsorption capacity ($294 \mu\text{mol kg}^{-1}$).

Expressed as percentage, eucalyptus leaf, pine needles and wood ash showed high adsorption scores (higher than 76%), while pine bark and mussel shell displayed values that did not exceed 39% and 51%, respectively.

AMX adsorption data corresponding to the different bio-adsorbents were statistically analyzed. Firstly, a normality test was carried out, showing that all the bio-adsorbents (except pine bark) presented a normal distribution. Data for pine bark was log-transformed to get them normalized. Then, an ANOVA analysis (with Tukey test) was performed finding that there are no significant differences (at $p < 0.05$) among the various bio-adsorbents, considering all the concentrations together. However, when comparing data corresponding to the maximum concentration of antibiotic added ($50 \mu\text{mol L}^{-1}$), significant differences were found for the adsorption of the different bio-adsorbents, obtaining the following sequence: pine bark^a < mussel shell^b < eucalyptus leaves^c < wood ash^d < pine needles^e (different letters indicate significant differences for adsorption, at $p < 0.05$). Finally, the different concentrations of antibiotic added were compared, considering all the bio-adsorbents together. The result of this analysis showed that there are significant differences (at $p < 0.05$) among the various concentrations, resulting the following sequence (for concentrations expressed in $\mu\text{mol L}^{-1}$): $2.5^a < 5^a < 10^{ab} < 20^{abc} < 30^{abc} < 40^{bc} < 50^c$.

In Table S1 (Supplementary Material), it is shown that pine needles and eucalyptus leaves had an acid pH (3.68 and 4.88, respectively), while wood ash and mussel shell showed alkaline values (11.31 and 9.04, respectively).

It is important to bear in mind that amoxicillin has three different pK_a values, related to the carboxyl ($\text{pK}_{a1} = 2.68$), amino ($\text{pK}_{a2} = 7.49$) and phenolic ($\text{pK}_{a3} = 9.63$) functional groups (Homsirikamol et al., 2016). At $\text{pH} < 2.68$ the positive charge of the amino group predominates, whereas at pH values between 2.68 and 7.49 AMX behaves as a zwitterion with both deprotonated carboxyl groups and protonated amino groups, while at pH between 7.49 and 9.63 deprotonated carboxyl and amino groups predominate (with negative charge), and, finally, at $\text{pH} > 9.63$, phenolic groups are also deprotonated (Pezoti et al., 2016) and the molecule acquires a high negative charge.

The five bio-adsorbent materials used in this study have very different acid-base characteristics, favoring also different adsorption mechanisms. Wood ash has a very alkaline pH (11.31), and non-crystalline Fe and Al contents much higher than the other four bio-adsorbents (Table S1, Supplementary Material), all of them being variable charge components, which will have a high negative charge at that pH. At pH 11.31, AMX will have deprotonated amino, carboxyl and phenol groups, also acquiring a high negative charge. Therefore, AMX adsorption onto wood ash would be through a cationic bridge (such as Ca^{2+}) between the negatively charged part of the antibiotic and the surface of the bio-adsorbent, also negatively charged, forming ternary complexes (Gu et al., 2007), and this interaction would be favored by the high concentration of exchangeable Ca in the ash (Table S1, Supplementary Material). The adsorption mechanism would be similar in the case of mussel shell, where its lower adsorption values would be due to the lower amount of non-crystalline minerals and exchangeable Ca. In fact, the pH of mussel shell is not so alkaline (9.39), being lower than the pK_{a3} of AMX, causing that the negative charge density of the antibiotic is not so high under these conditions. Conde-Cid et al. (2019) also found high adsorption scores for three tetracycline antibiotics (oxytetracycline, chlortetracycline and tetracycline) onto wood ash, much higher than onto mussel shell.

In the other bio-adsorbents (pine needles, pine bark, and eucalyptus leaves) the pH is very acidic (3.68, 3.99 and 4.88, respectively), between the pK_{a1} and pK_{a2} values of AMX, causing that the molecules of the antibiotic behave as a zwitterion, with protonated amino groups and deprotonated carboxyl groups. The high adsorption of the antibiotic onto pine needles and eucalyptus leaves can be related to their high organic carbon content (50 and 53%, respectively) (Table S1, Supplementary Material), with a large number of carboxyl groups that can dissociate and present negative charge at $\text{pH} > 3$ (Edwards et al., 1996). At these pH values, AMX will have protonated amino groups that can bind through electrostatic interactions to the carboxyl groups of the bio-adsorbents of vegetal origin. The lower adsorption onto pine bark

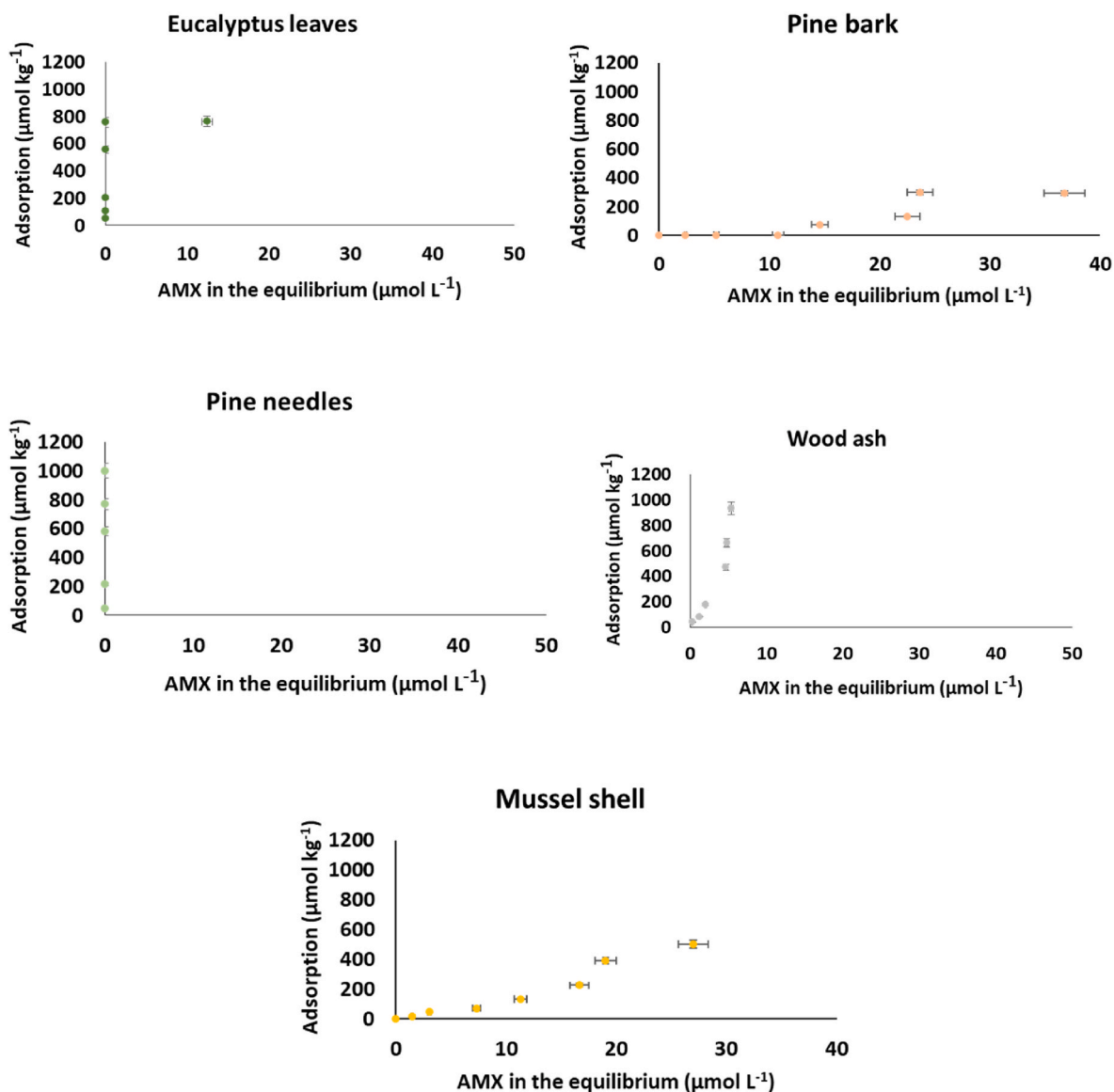


Fig. 1. AMX adsorption curves for the five bio-adsorbents. Average values ($n = 3$), with error bars showing that coefficients of variation were always $<5\%$.

Table 2

Fitting of the adsorption data to the Freundlich, Langmuir and Linear models. K_F ($L^n \mu\text{mol}^{1-n} \text{kg}^{-1}$); K_L ($L \mu\text{mol}^{-1}$); q_m ($\mu\text{mol kg}^{-1}$); K_d ($L \text{kg}^{-1}$); -: error values too high for fitting.

	Freundlich					Langmuir					Linear		
	K_F	Error	n	Error	R^2	K_L	Error	q_m	Error	R^2	K_d	Error	R^2
Eucalyptus leaves	-	-	-	-	-	-	-	-	-	-	-	-	-
Pine bark	-	-	1.37	0.43	0.822	-	-	-	-	-	7.92	1.13	0.789
Pine needles	-	-	-	-	-	-	-	-	-	-	-	-	-
Wood ash	100.88	77.59	1.21	0.49	0.816	-	-	-	-	-	139.61	16.15	0.812
Mussel shell	5.23	2.99	1.39	0.18	0.966	-	-	-	-	-	17.25	1.21	0.933

compared to pine needles and eucalyptus leaf is due to the different chemical composition of their organic compounds and also to the fact that the bark has a higher content in Fe and Al non-crystalline minerals, which would be positively charged at that pH.

In a previous research, Cela-Dablanca et al. (2021) studied the adsorption of the antibiotic cefuroxime onto the same bio-adsorbents used in this work, finding that pine bark and pine needles had the lowest adsorption capacities. However, Conde-Cid et al. (2021) found that pine bark performed as the best bio-adsorbent retaining three

sulfonamides (sulfadiazine, sulfamethazine and sulfachloropyridazine), while wood ash and mussel shell presented lower retention potential.

Fig. 1 shows AMX adsorption curves for the five bio-adsorbents, while Table 2 shows the fitting of the experimental data to the Freundlich, Langmuir, and Linear adsorption models.

The adjustment to the Freundlich model is valid just for mussel shell and wood ash (R^2 being 0.966 and 0.816, respectively), and partially valid for pine bark ($R^2 = 0.822$ for the n parameter), due to the high errors associated to the adjustment for the other adsorbents. The values

of the K_F parameter (related to the adsorption capacity) in the bio-adsorbents that fit the model range between 5.23 and 100.88 Lⁿ μmol¹⁻ⁿ kg⁻¹, for mussel shell and wood ash, respectively. The values of the n parameter (which are related to the reactivity and heterogeneity of the adsorption sites) range between 1.21 and 1.39. K_F is much higher for wood ash than for mussel shell, but it is much lower than that obtained in previous studies for the adsorption of tetracycline antibiotics onto these same adsorbents (Conde-Cid et al., 2019).

AMX adsorption fitted well the linear model for mussel shell, wood ash and pine bark (R^2 of 0.933, 0.812 and 0.789, respectively). The K_d values vary from 139.61 to 7.92 L kg⁻¹, following the sequence: wood ash >> mussel shell > pine bark. Therefore, according to these data, among the materials that fit the linear model, wood ash is the one that adsorbs AMX with the strongest interactions. The K_d values for wood ash and mussel shell are higher than those obtained in most of the soils evaluated in a previous study (Cela-Dablanca et al., 2021). However, these K_d values are lower than those reported by Cela-Dablanca et al. (2021) for the antibiotic cefuroxime in the same bio-adsorbents (mussel shell, wood ash and pine bark).

The high errors associated to the fitting of the experimental data to the Langmuir model make it invalid in this case (Table 2).

Regarding desorption, no release was detected when the maximum AMX concentration (50 μmol L⁻¹) was added, indicating that the adsorption process was not reversible. In fact, the desorption procedure showed no release taking place from any of the five bio-sorbent materials.

Overall, in the current study eucalyptus leaf, pine needle and wood ash performed as good bio-adsorbents for AMX, while pine bark and mussel shell would be less suitable to adsorb this antibiotic. These results are not coincident with those obtained for the antibiotic cefuroxime in a previous study (Cela-Dablanca et al., 2021), in which mussel shell gave good results, while pine needles and eucalyptus leaves could not be recommended for removing cefuroxime. However, in another previous study, Conde-Cid et al. (2019) found that pine bark was a good adsorbent for tetracycline antibiotics, since it had high adsorption and low desorption values, while mussel shell was not suitable for adsorbing these compounds.

4. Conclusions

Among the five bio-adsorbents here studied, eucalyptus leaf, pine needles, and wood ash showed high adsorption for the antibiotic AMX, with non-crystalline Al and Fe, exchange cations and organic carbon contents present in each bio-adsorbent being the parameters with the highest influence on the retention of this antibiotic. Regarding fitting to adsorption models, it was possible for pine bark, mussel shell and wood ash as regards the Linear and Freundlich equations. Referred to desorption, no release was detected when the highest concentration of the antibiotic was added. Therefore, except for pine bark and mussel shell, the remaining three materials would be good bio-adsorbents for AMX, with wood ash showing the best results. The overall results of this research encourage additional studies to elucidate in further detail key additional details on the use of these bio-adsorbents to protect environmental compartments from emerging pollutants such as AMX.

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.

Acknowledgements

This work was supported by the Spanish Ministry of Science, Innovation and Universities [grant numbers RTI 2018-099574-B-C21 and RTI 2018-099574-B-C22].

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envres.2022.113621>.

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