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THERMODYNAMIC MODELLING STUDIES ON BIOSORPTION OF REACTIVE AMOXICILLIN ANTIBIOTIC BY PITHOPHORA MACROALGAE IN AQUEOUS SOLUTION

Murad M. KHAMAYSEH[1], Rana KIDAK[2]
[1]Department of Environmental Sciences, Cyprus International University, Nicosia 99010, Turkey
[2]Department of Environmental Engineering, Faculty of Engineering, Cyprus International University, Nicosia 99010, Turkey
Corresponding author: Murad M. KHAMAYSEH, murad.kha32@gmail.com

ABSTRACT:

Antibiotic removal poses a serious risk to the environment due to its intricate structure. Consequently, scientists are developing new and efficient techniques to remove antibiotic compounds from wastewater. The goal of this study is to employ green Pithophora macroalgae to remove the antibiotic amoxicillin (AMX) from a water-based solution. With a focus on understanding the process, this study assesses the application of reacting AMX biosorption on the biomass of Pithophora algae in aqueous solutions using thermodynamic modeling. The determined thermodynamic characteristics show that an endothermic process is used in the biosorption of the antibiotic AMX considering that AMX has a positive electrical charge of ΔH^o at 49.796 KJ mol^{-1}. As ΔG^o has a positive charge (2.982 kJ mol^{-1}, 3.718 kJ mol^{-1}, and 4.793 kJ mol^{-1}) for AMX at (298 K, 303 K, and 308 K, respectively; This positive result indicates that the reaction is not feasible or spontaneous. The decrease in chaos at the liquid/solid interface caused by AMX biosorption on Pithophora macro algae is reflected in the negative charge of ΔS^o, which was -176.735 kJ mol^{-1}. The effect of temperature on the biosorption of AMX was investigated for different initial AMX concentrations. At a lower temperature of 298 K, the AMX molecules were more likely to diffuse into the internal pores of the Pithophora algae. This suggests that the diffusion rate of the adsorbate (AMX) across the bulk and pore boundaries of the biosorbent particles may be increased at lower temperatures. The findings of this study indicate that the biomass of the macroalgae Pithophora is a valuable biosorbent for the biosorption of AMX antibiotics, and it may have potential applications in the treatment of wastewater.

Key Words	Amoxicillin, Biosorption, Biosorbent, Pithophora Macroalgae
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1. INTRODUCTION

Biosorption is a sustainable method for removing contaminants and heavy metals from aqueous solutions (Balarak et al., 2017). It is a process where contaminants are extracted from water or wastewater using a biosorbent. Biosorbents are materials that can be found naturally or produced artificially, and they have the ability to selectively bind contaminants and other chemicals from aqueous solutions (Arihilam and Arihilam, 2019). They are frequently employed in the cleanup of polluted soils and water. Because of its straightforward operation, low cost of raw materials, ability to reduce spent water, and ability to keep contaminants out of natural resources, bio sorption has become a viable method for removing toxins from water and soil (Abd and Mohammed, 2021).

Amoxicillin (AMX) is a beta-lactam antibiotic that is used for the treatment of bacterial infections. Because amoxicillin is so inexpensive, it is prescribed extensively all throughout the world. With a half-life of roughly one to two hours, it is known that this antibiotic is very vulnerable to hydrolytic and oxidative degradation in aqueous solutions (Aljeboree et al., 2020). It is well known that this antibiotic is extremely reactive, acting much like hydroxyl radicals. Due to its reactivity, using it in water systems may cause the creation of hazardous intermediates, which may have an impact on aquatic life (Matsubara et al., 2020).

One potential method for removing AMX from water systems is biosorption. The majority of AMX is allegedly released into the sewage system unaltered, as stated by Jung et al (2012). Water samples contain about 1.3 μg mL^{-1} of it (Välitalo et al., 2017). Before AMX is released into the environment, the sewage system does not adequately remove it (Lai et al., 2017). On the other hand, amoxicillin can be removed more successfully via genetic engineering, and the biological process of removing antibiotics from macroalgae does not require chemical intervention (Chakhtouna et al., 2021). Many methods, including as adsorption, coagulation, electrolysis, filtration, photocatalysis, coagulation, accelerated oxidation, and biological degradation, have been used to eradicate antibiotics (Yan et al., 2022).

The high energy consumption, high material costs, and additional pollution caused by the addition of additional chemicals are some of the disadvantages of these technologies (Boukhelkhal et al., 2016). Adsorption is the most widely used and successful technique for removing contaminants from wastewater (Asim et al., 2021). Its uncomplicated appearance and ease of usage make it simple to install. Because biosorption is inexpensive, efficient, and safe for the environment, it has attracted a lot of attention as an alternative to antibiotics. This method binds and concentrates pollutants in water by using biological material from live and dead biomass that has been heat-dried and chemically treated (Dimitrakopoulou et al., 2012). Because of its straightforward operation, low cost of raw materials, ability to minimize spent water, and ability to keep contaminants out of natural resources, biosorption has become a promising method for removing pollutants from soil and water (Limousy et al., 2017). With a focus on comprehending its mechanism, this paper reviews some recent developments in equilibrium and kinetics research on the biosorption of reactive Amoxicillin Antibiotic (AMX) on Pithophora Macroalgae in aqueous solutions. Pithophora is a type of filamentous green algae. It can grow in dense mats either on the surface or at the bottom. This algae is often described as having a rough, coarse texture, and its growth pattern resembles a tangled mass of cotton

or wool. One of the most economical adsorbents is green algae, which contains cellulosic polysaccharides that react with a large number of proteins to form glycoproteins. Numerous functionalized groups, such as amino, carboxyl, sulphate, and hydroxyl, are present in these materials and are essential to the biosorption process (Romera et al., 2007). The thermodynamic values obtained from the study suggest that the sorption of levofloxacin (LVX) antibiotics is governed by an endothermic process. The findings indicate that the biomass of Pithophora macroalgae serves as an effective biosorbent for the removal of LVX antibiotics, presenting a promising alternative method for the elimination of antibiotics from aqueous environments. Furthermore, Pithophora demonstrates potential applicability in real-world wastewater treatment scenarios, having proven its efficacy as a biosorbent for antibiotic compounds (Khamayseh and Kidak, 2023According to the study conducted by Kalyani et al. (2021), the thermodynamic analysis revealed that the biosorption processes are both exothermic and spontaneous. The biosorbents derived from Pithophora cleveana Wittrock and Mimusops elengi exhibited maximum removal efficiencies of 74.11% and 73.11%, respectively, with corresponding maximum uptake capacities of 13.58 mg/g and 12.96 mg/g. Furthermore, the thermodynamic parameters, including $\Delta G°$, $\Delta H°$, and $\Delta S°$, indicated that the biosorption process is spontaneous and exothermic. These findings suggest that the biosorbents derived from Pithophora cleveana Wittrock and Mimusops elengi possess significant potential for the removal of lead metal ions from aqueous solutions, attributable to their effective absorption capabilities (Gaddam et al., 2020). Additionally, Pithophora has demonstrated its applicability in real-world wastewater treatment scenarios and has proven to be an effective biosorbent for the biosorption of antibiotics.

Algal biomass treated with an alkaline solution will bio-absorb pharmaceutical chemicals. The primary goal of this research is to use the readily available green Pithophora macroalgae to extract AMX from aqueous solutions. The starting pH, temperature, agitation speed, and adsorbent dosage all have an impact on how well the green macroalgae biosorb antibiotic. For equilibrium studies, the isotherm biosorption and kinetics models and thermodynamic modelling are also assessed. Therefore, our objective was to examine the effectiveness of Pithophora macroalgae in the removal of AMX from aqueous solutions. Pithophora is a filamentous green alga, creates free-floating mats which refers to Cladophorales member (O'Neal et al. 1985).

2. Materials and Methods

2.1 Materials and Instruments

The following materials and instruments were used in this experiment: 10 L distilled water; 10 L tab water; 1 L Methanol; 1 g Amoxicillin antibiotic; 8 Erlenmeyer flasks; 8 Lab shaker bottles; one measuring cylinder; 2 Pipettes; 1 Flask; 1 beaker; volumetric cylinder; 0.1 NaOH; 0.1 HCL solution; and weighing Scale (Saturius CP, model CPA 2250). In addition, 1 mortar and pestle; 1 magnetic stirrer or batch; Bath water shaker; and UV- visible spectrophotometer were used. (National Center for Biotechnology Information, 2022)

2. 2 Procedure of Preparing the Stock Solution

Amoxicillin (AMX) antibiotic component was obtained from a local pharmacy in Istanbul, Turkey, for analytical reference purposes without undergoing any further processing. The antibiotics' characteristics are listed in Table 1; the following process was used to use the AMX: The antibiotic was precisely weighed by weighing scale. The stock solution (1g/L) was prepared by grounding the antibiotics, 1 g of AMX antibiotic using mortar and pestle to make them as powders in the lab. Dissolving accurately weighted amount of the antibiotics in suitable solvents. The AMX antibiotic was dissolved in methanol and water. Then the antibiotic powders were added on the magnetic stirrer around 2 hours at 70 ºC to speed the dissolving, after that, the stock solutions were put in the refrigerator at 4º C further to use it. 0.1 M NaOH and 0.1 M HCl were used to adjust the pH.

A number of standards calibration chart were prepared for a wide range of concentrations that were close to the anticipated concentration of the analyte measuring the absorbance of different Antibiotic (AMX) concentrations at different (λ) nanometers and unknown concentrations of antibiotics before and after adsorption were computed from the calibration chart. In this work, the calibration curve was plotted using different wavelengths as given for the AMX at 231 nm. UV spectrometer, which would be based on the wavelength obtained during spectrum research. As shown in the Figure 1, the calibration curve was obtained for the range of 10 to 150 mg/L. N.B: experiment was repeated three times and the mean values and standard deviations from the mean values were recorded. Table 2 presents the various concentrations of AMX alongside their corresponding absorbance values. A double beam/visible spectrophotometer (Shimadzu UV-2450) was employed to measure absorbance at the specific wavelength characteristic of the compound, facilitating the determination of an unknown antibiotic concentration.

The measurement of antibiotic concentration is widely regarded as one of the most commonly utilized methodologies. When appropriately calibrated, this technique can exclusively analyze the UV-visible spectral properties of the substance, thereby providing accurate estimations of AMX concentration. The UV spectrophotometer utilized in the laboratory during the experiments is depicted by the spectrophotometer device (Figure 2). The standard deviation of the measurements is reported to be 1.41. The best-fitting isotherm has been found in recent years using a variety of error analysis techniques, including the coefficient of determination (R^2), the sum of the errors squared, a hybrid error function, Marquardt's percent standard deviation, the average relative error, and the sum of absolute errors which noted that the R^2 of linear regression analysis alone is not a suitable metric for assessing an isotherm model's fit quality (Allen et. al., 2003)

2.3 Determination of pH and Zeta Potential Charge

The pH of the growth media was assessed at the commencement and conclusion of each trial, as well as on designated sample days and during the preparation of the medium, utilizing a pH meter (WTW Inolab pH 7110 masa Tipi pH meter). Additionally, the pH of the metal removal media was adjusted prior to the initiation of the experiment. To ensure accurate pH measurements, a two-point calibration

with buffer solutions was routinely conducted. The determination of the zero-point charge (ZPC) of the Pithophora algae was carried out at a pH of 7.6, following the mass titration method as described by Cristiano et al. (2011). Specifically, fifty milliliters of 0.01 M $NaNO_3$ were placed in Erlenmeyer flasks, and appropriate biosorbent dosages ranging from 0.1 to 1.5 grams were introduced. The samples were agitated in a mechanical shaker for a duration of twenty-four hours, after which the residual pH value was measured.

The neutral charge of the bio-sorbent was assessed utilizing the pH drift method. Under optimal conditions, the kinetic profiles illustrating the biosorption removal of AMX, employing non-linear forms across varying solution pH levels, are presented in Figure 3. A gradual biosorption process was observed, characterized by an increase in contact time across all pH levels investigated. The AMX antibiotic was effectively removed at an initial pH level, reaching equilibrium after 120 minutes, beyond which no further sorption occurred. The influence of pH on the adsorption process can be attributed to the solubility of pollutants and the presence of active functional groups on the adsorbents, which facilitate electrostatic interactions between the antibiotic molecules and the surface of the algae. (Khamayseh and Kidak, 2024)

3. Collection and Identification of Algae

This study made use of the (seaweed) Green Pithophora Macroalgae (GPM) as in Figure 4. Between October and November 2021, during the winter months, they were gathered from the pond at Cyprus International University (CIU). To create the 40 g powdery form, around 8 kg of pond-harvested material were pulverized in a milling machine. After which they were dried at 40 degrees and grounded at 45 microns.

Under electron microscope shown in Figure 5, Pithophora was seen which is made up of filaments irregularly branching and frequently include akinetes; they are many inflated reproductive cells that resemble spores. From lime green to a dark greenish brown, it can be any color. When gas bubbles created by the plant are caught within the thick algal growth, they become buoyant and the surface mats typically form in warmer weather. These mats may momentarily sink to the bottom if they are disturbed by significant wind or rain events.

4. Results and Discussion

4.1 Effects of Temperature

The temperature is typically affected by processes involving heat or mass transport. A thermodynamic process is one that alters the thermodynamic state of a system. r is defined as the degree of chaos or uncertainty in a system. Enthalpy is a key concept in thermodynamics. It is the overall amount of heat in the system. This indicates that as more energy is provided, the enthalpy rises. To determine whether antibiotic adsorption by Pithophora algae occurs spontaneously, entropy and energy factors should be considered. An experimental investigation was conducted to examine the influence of temperature on the adsorption of AMX by Pithophora algae. The findings indicated that the capacity for antibiotic adsorption diminishes as the temperature increases. (Khamayseh and Kidak, 2023).

At temperature ranges of 298 K to 308 K, the removal effectiveness of AMX medication at various start concentrations was investigated. A 100 ml solution was applied to 0.5 g of biomass in Erlenmeyer flasks. After that, it was shaken in a temperature-controlled shaker at 150 rpm. Samples were taken anywhere from five to eighty-one minutes apart at various times. The equations were used to calculate Gibb's free energy (ΔGº). (4.1), (4.2), and (4.3) (Aravindhan et al., 2009).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{..... 4.1}$$

$$\Delta G^\circ = -RT \ln Kd \quad \text{..... .4.2}$$

$$K_d = \frac{q_e}{C_e} \quad \text{..... 4.3}$$

Where T is the absolute temperature (K), R is the gas constant (8.314 J mol^{-1} K^{-1}), qe is the amount of antibiotic absorbed onto the biosorbent at equilibrium time (mg/g), and Ce is the equilibrium concentration of the sorbate present antibiotics (mg/L).

Van't Hoff plots ln Kd vs 1/T (Figure 6) can be used to determine entropy (ΔSº) and enthalpy (ΔHº) based on their slope and intercept. Also, entropy (ΔS) and enthalpy (ΔH) can be determined using the following equations (4.4) and (4.5)

ΔHº = Slope * R gas constant 4.4

ΔSº = Intercept * R gas constant 4.5

The Langmuir isotherm equilibrium constants at 298 K, 303 K and 308 K were used to calculate ΔG°, ΔH°, and ΔS° for AMX adsorption by Pithophora (Table 3). At increasing temperatures, the biosorption % shows a trend toward decline. This decrease may be explained by an increase in the propensity of ions to break bonds and move from the solid to the bulk state, the destruction or deactivation of active sites on the surface of the biosorbent as a result of bond breaks, or the mobilization of ions in solution as a result of highly energized metal ions (Sulaymon, et al., 2013). The coefficient of correlation value, R^2, of the van't Hoff plot in Figure 6 was deemed satisfactory 0.996 for AMX. For the necessary system, the thermodynamic parameters ΔGº, ΔSº, and ΔHº were measured. As can be shown in Table 3, the charge of ΔGº for AMX is positive (2.982 kJ mol^{-1}, 3.718 kJ mol^{-1}, and 4.793 kJ mol^{-1}) at (298 K, 303 K, and 308 K, respectively. This positive value suggests that the reaction is neither possible nor spontaneous.

According to the ΔHº values, the biosorption process could be viewed as a physical sorption that is facilitated by a chemical reaction. Given that the electrical charge of ΔHº for AMX is positive at 49.796 KJ mol^{-1}. This shows that the method of biosorption was endothermic, indicating that the antibiotics and biomass have a significant interaction. This finding indicates that the biosorption process is endothermic, suggesting a significant interaction between the biomass and the antibiotics. Consequently, algal biomass can be effectively utilized for the removal of AMX at ambient temperature.

Entropy effects can be considered as the driving force of the biosorption process Consequently, the biomass of algae demonstrates efficacy in the removal of AMX at ambient temperature. It can be

posited that entropy effects are instrumental in driving the biosorption process. The reduction in disorder at the liquid/solid interface, resulting from the biosorption of AMX onto Pithophora macro algae, is indicated by the negative value of ΔS^o, which is measured at -176.735 kJ $mol^{-1.}$

The measured qe values of the biomass of AMX decreased substantially from 18.0 to 12.1 mg/g when the temperature of an antibiotic solution rose to 298 K to 308 K, as depicted in Figure 7's plot of the influence of the biosorption of AMX antibiotic. This may indicate a decrease in the viscosity of the antibiotic-containing aqueous solution. As a result, the total volume of the biosorbent particles and the adsorbate's diffusion rate across pore borders may both rise (Mohammed et al., 2020).

3.2 Biosorption Isotherm at Defferent Temperatures

At all the temperatures investigated, Table 4 demonstrates that the adsorption data of AMX can be better described by the Langmuir isotherm than the Freundlich isotherm. According to the Langmuir isotherm's values for qm, the two antibiotics under study have a significant amount of adsorption capacity for algae biosorbent, and adsorption capacity for AMX. The experimental qm values of the biomass of AMX dramatically dropped from 25.83 to 15.69 mg/g. This may indicate a decrease in the viscosity of the antibiotic-containing aqueous solution. As a result, the adsorbate's diffusion rate may rise through the biosorbent particles' pore and bulk borders (Mohammed et al., 2020). The greater R^2 of the Langmuir isotherm model in Table 4 for all AMX values indicates that it provides the best fitting for the experimental data. Having a 25.83 mg/g maximal capacity for sorption, the experimental data for AMX biosorption most closely resembles the Langmuir isotherm model (khamayseh and Kidak, 2024).

4.4 Biosorption Kinetics at Different Temperatures

The Biosorption kinetics determine the sorption mechanism which involves mass transfer, diffusion, and reaction on the biosorbent surface, as well as the reaction rate. This involves how the system sorption qualities vary over time, and how much of the surface is covered which in turn provides information about how quickly a process is happening. The design and regeneration of the biosorbent rely heavily on the rates of adsorption since sorption and desorption processes are both time-dependent. The experimental data are analyzed using dynamic models to study the component of biosorption, the potential rate and governing steps, mass transfer, and chemical reaction process (Ho and Mckay, 1999). In other word, the sorption equilibrium also reveals details about the adsorption process dynamics. Based on the physicochemical characteristics of the antibiotic and the bio-sorbent, the kinetics of the biosorption process aids in assessing effectiveness and identifying the type of sorption mechanism (Kerkez-Kuyumcu et al., 2016). The capacity for biosorption at equilibrium and the rate of solute binding on the surface of the biological material may both be calculated using biosorption kinetics. This material gives crucial details regarding a potential biosorption mechanism that includes chemical reactions and diffusion (Kratochvil and Volesky, 1998). Three kinetic models—pseudo-first order (PFO), pseudo-second order (PSO), and intraparticle diffusion models—were employed to investigate the biosorption kinetics of AMX. The rate constants for these models were determined through linear

regression analysis of the experimental data, as presented in Table 5. The experiment was conducted under optimal conditions, utilizing an initial concentration of 50 mg/L, and the kinetics were examined at a temperature of 25°C.

The pseudo-second-order (PSO) model demonstrated a superior fit to the experimental data, exhibiting a regression coefficient (R^2) of 0.999 and a rate constant of 0.0641 g/mg·min^{-1} at an initial amoxicillin (AMX) concentration of 10 mg/L. Additionally, at the maximum AMX concentration of 150 mg/L, the PSO rate constant (K_2) was determined to be 0.0029 g/mg·min^{-1}, with an R^2 value of 0.998 at a temperature of 25 °C. The PSO model was more obvious to fit with the experimental data (Table 5) demonstrates that the PSO model was fitted better with the experimental data than the PFO model and the intraparticle diffusion model in terms of regression coefficients for all AMX concentrations. This is further shown by contrasting the experimental data's qe values with the one inferred from the plots (qe.CAL). The intraparticle diffusion method was then used to examine the data in order to gain additional insight into the adsorption mechanism. The potential of intra-particle diffusion was explored using experimental data and the Weber-Morris intra-particle diffusion model. The lower R^2 values obtained corroborate the conclusion drawn from Table 5 data analysis: intraparticle diffusion is not able to explain the experimental results, the intraparticle diffusion cannot explain the experimental results, which is confirmed by the lower R^2 values attained in the AMX antibiotic. All things considered, the PSO model appears to have the greatest match to the study data, indicating that the biosorption of AMX onto Pithophora algae is caused by chemisorption interaction which is responsible for the biosorption of AMX. This correlates with previous researches (Oba and Aydinlik, 2022; Dan et al., 2021; Hamadeen et al., 2021; Pezoti et al., 2016). Pseudo-first-order and pseudo-second-order kinetic model equations were used to model the experimental data (Figure 8 a, b). In order to determine whether film diffusion or intraparticle diffusion is the rate-controlling step, kinetic parameters were calculated using the Weber and Morris kinetic model to investigate intraparticle diffusion Figure 8 (c). It can be said that the pseudo-second order kinetic model and the experimental data closely match each other Additionally, $qe_{,calc}$ based on the pseudo-second-order isotherm has values that are comparable to $qe_{,exp.}$ Temperature has an impact on parameter values like k_2, $qe_{,calc}$, but not in a way that makes it necessary to treat it less than 298 K. For Kinetic analyses, Table 6 displays the values for the K_{diff} and C parameters from the modeling along with the rate constants, k, and adsorption capacity. The regression coefficient, or R^2, values are also displayed in the same table. According Table 6, the expirement was carried out on the optimal condition at 50 mg/L initial concentration and the kinetic was studied at different temperatures. It was seen the qe decreased by increasing the tempreature in all types of the kinetiks under 298 K, 303K and 308 K. So, the best fit tempreature is 298 K which indicates high qe in pseudo second order as the following order 9.48 , 9.18 and 8.40 (mg/g) for AMX at 298 K , 303K and 308K, respectively. We looked at the Freundlich and Langmuir isotherms to see which model fit the experimental data best. The experimental results' kinetic model adheres to the pseudo-second order (R^2 = 0.999). In practical water and wastewater treatment applications, the biomass of the macroalgae Pithophora has been demonstrated in this study to be a potential biosorbent for the biosorption of AMX antibiotics (Khamayseh and Kidak, 2024).

Conclusion

There is significant interest in identifying effective strategies for the removal of highly hazardous organic chemicals from water and wastewater. Among these strategies, adsorption has emerged as a recognized method for eliminating organic contaminants, noted for its efficiency, cost-effectiveness, and ability to yield high-quality treated effluent. Thermodynamic analyses have indicated that the biosorption process is endothermic and nonspontaneous. The findings of this study suggest that Pithophora algae represent a promising biosorbent for the extraction of the antibiotic amoxicillin from aqueous environments in practical wastewater applications. Pithophora was selected for this research due to its prevalence in urban areas, propensity for algal blooms, and natural dominance in nutrient-rich or eutrophic conditions. Furthermore, its filamentous structure contributes to reduced harvesting costs. When compared to other materials, algal biomass is the most frequently utilized biosorbent. Algae possess a high capacity for binding metal ions due to their untreated state and the characteristics of their cell walls, rendering them a cost-effective biosorbent option. Future investigations should focus on the specific functional characteristics of Pithophora's cell wall, particularly the presence of chlorophyll, and its implications for the biosorption process. Additionally, further research is necessary to explore modeling, the regeneration of biosorbent materials, and the testing of adsorbed raw biomasses in relation to antibiotics. Advancements in techniques that enhance biosorbent processing will be essential for optimizing the application of biosorbent technology and regenerating biomass. • It is advised to use modified pithophora algae in a subsequent isotherm study to compare raw, unmodified algae with modified macroalgae treated with NaOH, formaldehyde, and $CaCL_2$ under different tempreatures related to the thermodynamics methods . The potential for biological process improvement is limited because cells are not metabolizing; and there is no ability for biologically changing the metal cationic and anionic state The scientific understanding of the ion-binding mechanisms of these materials remains limited, highlighting the need for ongoing research and development in this area.

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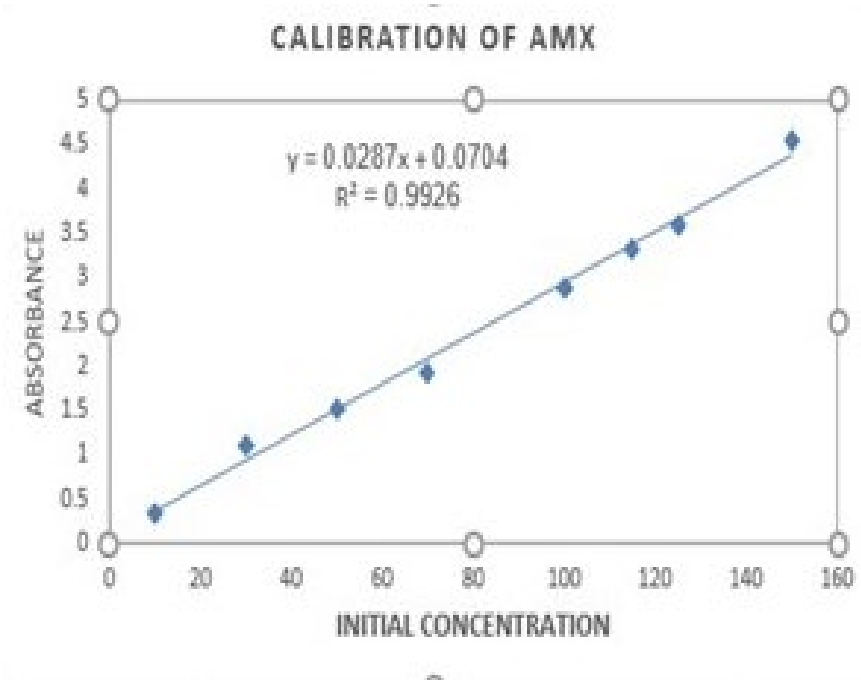


Figure 1: Calibration curve of AMX at different concentrations.

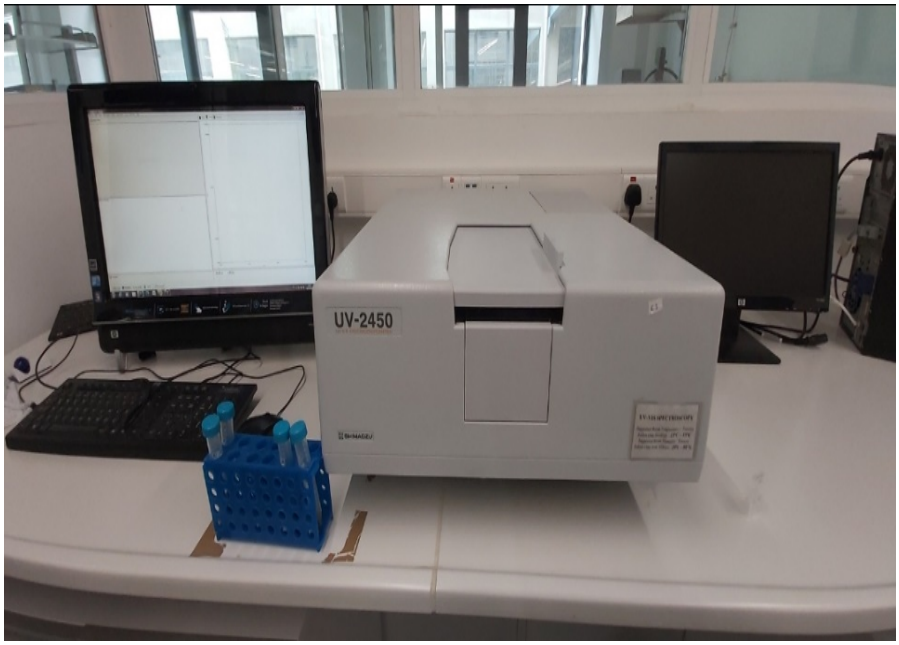


Figure 2: Shimazdu UV-2450 double-beam UV/visible spectrophotometer

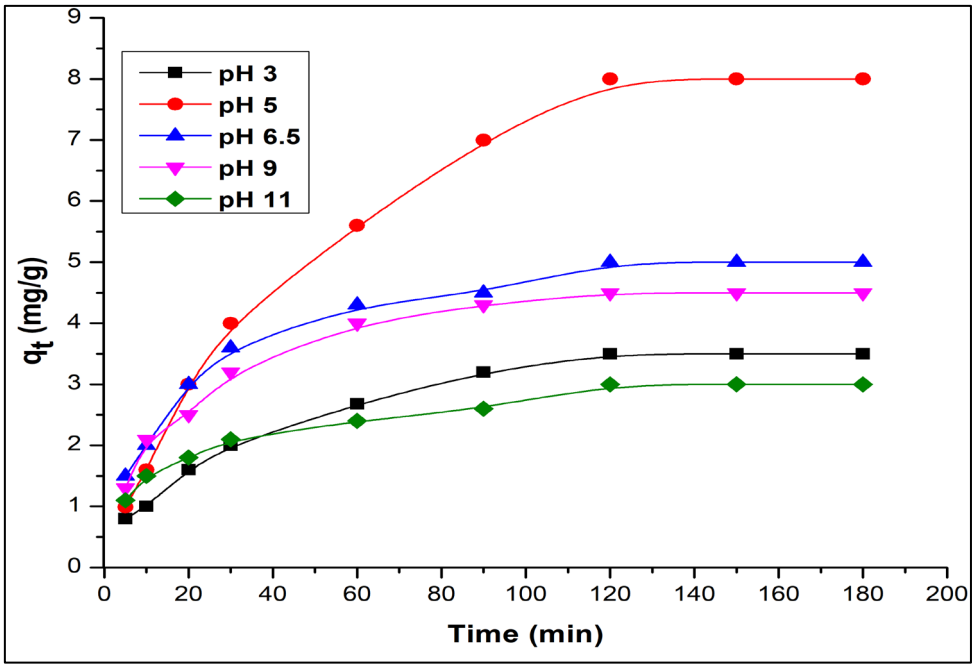


Figure 3: Effect of initial pH and contact time on sorption of AMX (Khamayseh and KIdak, 2024)

Figure 4: Fresh Pithophora macro algae harvested from the CIU university (2022)**.**

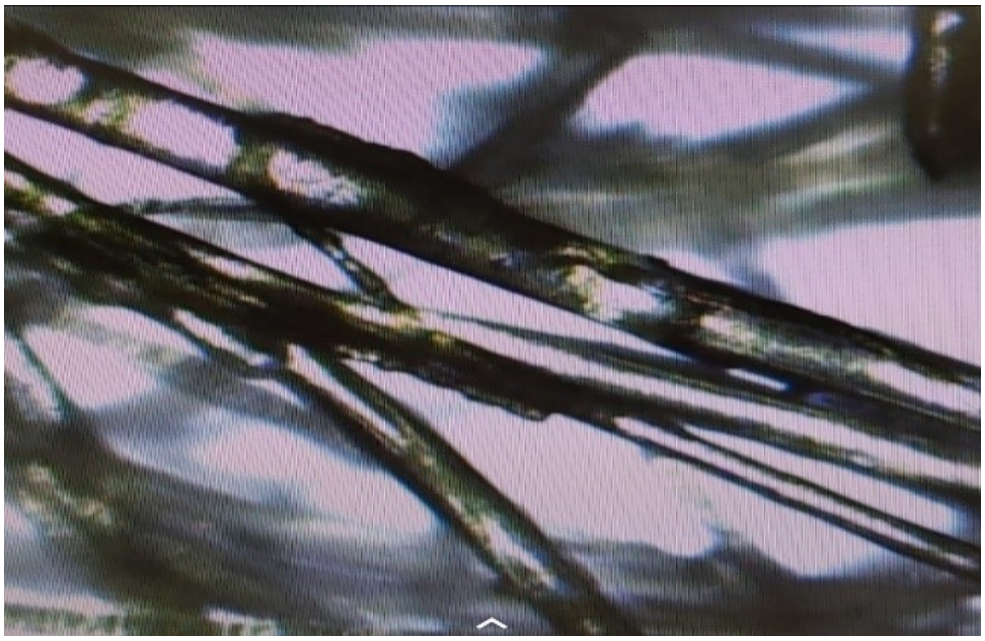


Figure 5: Pithophora cells under electron microscope, CIU labs-North Cyprus.

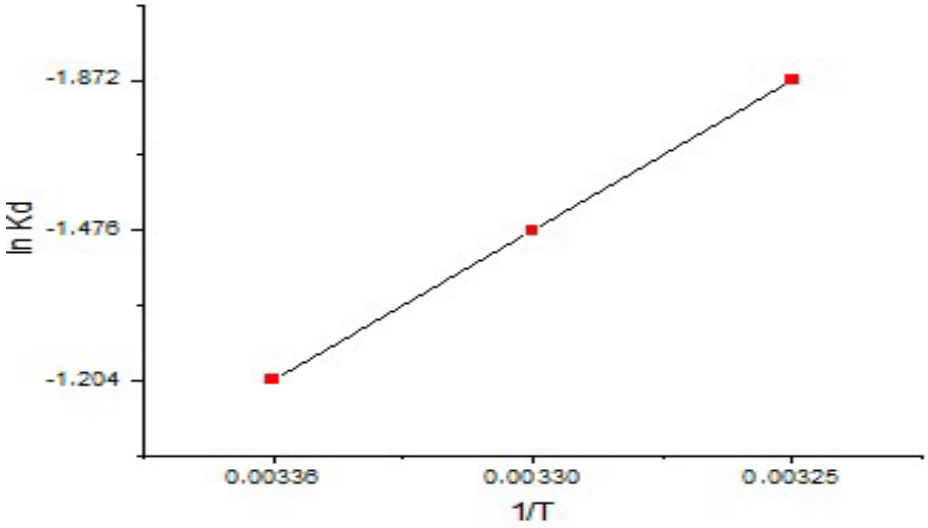


Figure 6: The relation between ln Kd and 1/T of AMX

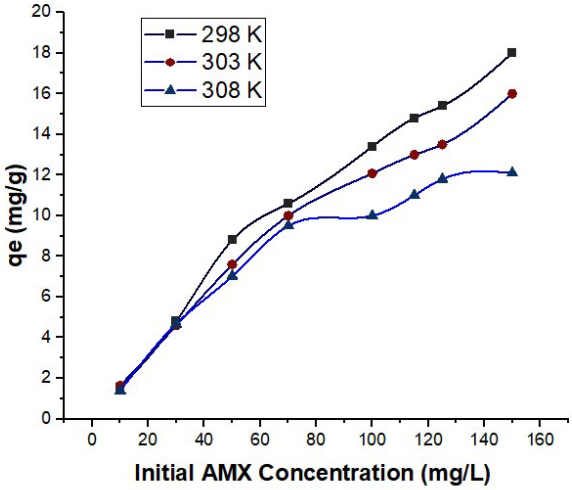
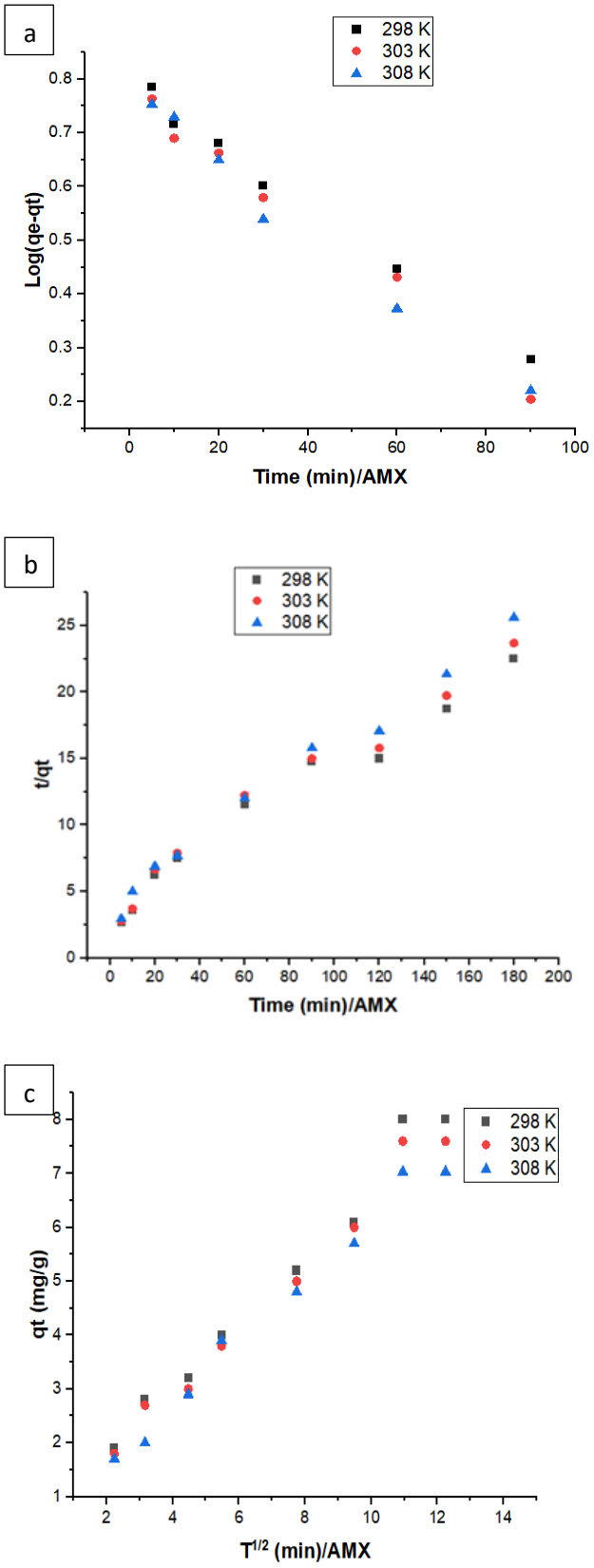


Figure 7: Effect of temperature on the equilibrium AMX and uptake capacity



Figures 8: Biosorption Kinetics at different temperature: (a-c): For AMX biosorption at 298 K, 303 K, and 308 K, pseudo-first order, pseudo-second order, and intraparticle diffusion kinetics are presented. a) Pseudo-first order of AMX b) Pseudo-second- order of AMX, c) intraparticle diffusion

Table 1: The characteristics of the Amoxicillin antibiotic (Khamayseh and Kidak, 2024)

Amoxicillin (AMX)

(penicillin antibiotic)

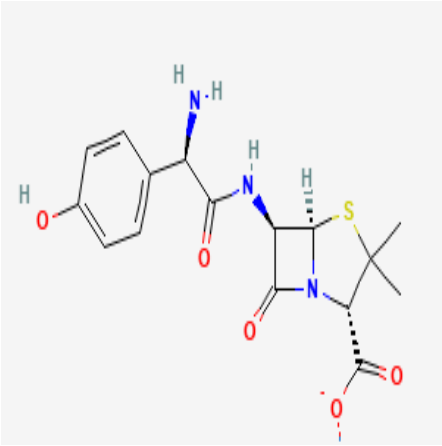
Structure	
Molecular formula	$C_{16}H_{19}N3O5S$
Molecular weight	365.4 g/mol
pKa	2.67, 7.11 and 9.55

Table 2: The concentrations of AMX and its absorptions

Conc. mg/L	absorbance
10	0.345
30	1.108
50	1.512
70	1.912
100	2.89
115	3.31
125	3.59
150	4.56

Thermodynamic parameters

Adsorbate	T (ºC)	qe (mg/g)	ΔGº (kJ mol^{-1})	ΔHº (kJ mol $^{-1}$ k)	ΔSº (J mol^{-1} K)
AMX	**25**	18.0	2.982	49.796	-176.735
	30	16.0	3.718		
	35	12.1	4.793		

Table 3: Thermodynamic for biosorption of AMX at different tempreatures.

Table 4: Biosorption isotherm constants obtained for various models obtained through linear regression analysis for AMX removal by Pithophora biosorbent at different temperature.

Antibiotic	T (K)	qe $_{EXP}$ (mg/g)	Freundlich			Langmuir		
			K_f (mg/g)	N	R^2	Q_m (mg/g)	K(L/mg)	R^2
AMX	298	18.0	1.17	1.43	0.930	25.83	0.0345	0.944
	303	16.0	1.07	1.51	0.921	18.79	0.0367	0.954
	308	12.1	1.03	1.63	0.841	15.69	0.076	0.942

Table 5: Results comparison between Pseudo-first order, pseudo-second order kinetics and Intraparticle diffusion for AMX biosorption at 25 °C (Khamayseh and Kidak, 2024)

Adsorbent	C_o (mg/L)	$q_{e,EXP}$ (mg/g)	Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
Pithophora Algae			K_1 (min^{-1})	$q_{e,cal}$ (mg/g)	R^2	K_2 ($g/mg\ min^{-1}$)	$q_{e,cal}$ (mg/g)	R^2	K_{DIF} (g. g^{-1} $min^{-1/2}$)	C ($g.g^{-1}$)	R^2
	10	1.52	0.0091	1.31	0.985	0.0641	1.60	0.999	0.0687	0.7059	0.965
	30	4.80	0.0047	2.91	0.942	0.0093	5.32	0.993	0.2932	1.2117	0.976
	50	8.00	0.0057	6.18	0.996	0.0031	9.48	0.986	0.5830	0.7619	0.986
	70	10.60	0.0052	7.89	0.988	0.0025	11.79	0.988	0.7532	1.1859	0.984
	100	13.40	0.0094	10.93	0.989	0.0026	15.40	0.994	0.9256	2.3055	0.979
	115	14.80	0.0092	11.70	0.991	0.0025	16.88	0.996	1.0127	2.7025	0.977
	125	15.40	0.0104	11.38	0.993	0.0033	17.08	0.999	0.9851	3.8705	0.956
	150	18.00	0.0135	14.66	0.983	0.0029	20.02	0.998	1.1795	4.4310	0.944

Table 6: Results comparison between Pseudo-first order, pseudo-second order kinetics and Intraparticle diffusion for AMX biosorption at different temperatures

	$Temp.$	$q_{e,EXP}$ **(mg/g)**	**Pseudo-First Order**			**Pseudo-Second Order**			**Intraparticle Diffusion**		
			K_1 (min^{-1})	$q_{e,cal}$ (mg/g)	R^2	$g/K_2($ $mg\ /min)$	$q_{e,cal}$ (mg/g)	R^2	K_{dif} (mg/g $min^{1/2}$)	C (mg/g)	R^2
AMX	298 K	8.00	0.0057	6.18	0.996	0.0031	9.48	0.999	0.5830	0.7619	0.986
	303 K	7.60	0.0064	6.10	0.986	0.0029	9.18	0.975	0.5687	0.593	0.971
	308 K	7.03	0.0062	5.49	0.943	0.0034	8. 40	0.981	0.529	0.546	0.961