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# BIOSORPTION OF AMOXICILLIN FROM CONTAMINATED WATER ONTO PALM BARK BIOMASS

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## ABSTRACT

The adsorption of amoxicillin (AMX) onto palm bark from aqueous solutions was studied in a batch adsorption system. Factors influencing AMX adsorption such as initial AMX concentration (10–100 mg/L), contact time (10–180 min), and adsorbent dosage (0.5–5 g/L) were investigated. The maximum removal efficiency of AMX was 98.1% under optimum conditions of adsorbent dose 3 g/L, contact time of 90 min and temperature 25 $^0$C and initial AMX concentration 10 mg/L. Adsorption isotherms models including Langmuir, Freundlich and Temkin were tested. It was inferred that the Langmuir models (with very high $R^2$ values) were most suited to describe the sorption of AMX in aqueous solutions and the monolayer adsorption capacity of AMX was found to be 35.92 mg/g.

**Keywords:** Adsorption, palm bark, Batch studies, Isotherm,

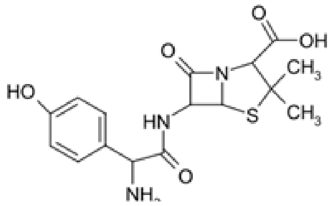
## INTRODUCTION

Pollution of water resources by different pollutants is nowadays a global environmental issue[1, 2]. For several decades now Pharmaceuticals constitute have been used in veterinary and human medicine, yet these compounds when released into the environment have potential risks for aquatic and terrestrial organisms[3, 4]. An important source of these organic compounds is the discharge of effluents from wastewater treatment plants into surface water bodies[5, 6]. They also come from solid waste disposal, spills and uncon-trolled discharges from industries, spreading of manure and sewage sludge as organic fertilizer in agricultural soils, surface run-off, etc. Their concentrations are usually in the ng/L to μg/L range[7, 8]. Among the various pharmaceutical compounds, antibiotics have been paid particular attention because of their potential role in the development of antibiotic-resistant bacteria[9-10]. Antibiotics are used extensively in human and veterinary medicine, as well as in aquaculture to prevent or treat microbial infections[11-13]. Most antibiotics tested to date are known to be biorecalcitrant under aerobic conditions[14]. Amoxicillin (AMX) is a drug belonging to the class of semi-synthetic b-lactam antibiotic that has a broad spectrum against both Gram-negative and Gram-positive bacteria[15, 16]. AMX is one of the top-priority human and veterinary pharmaceuticals, and should receive greater attention in the management of environmental systems in Iran due to its high consumption[17, 18]. AMX belongs to a group of drugs that are predominantly excreted in an un-metabolized form, and some investigations have reported that AMX might present a possible chronic risk in the aquatic environment[19, 20]. Various treatment technologie have been proposed for antibiotics removal including chemical oxidation, precipitation, biological treatment, ion exchange, coagulation–flocculation and so on[21-23.] However, these treatment processes present a number of drawbacks in terms of low efficiency, usually produce large amounts of sludge and cannot effectively be used to treat a wide range of antibiotic wastewater[24, 25]. Among the numerous techniques of antibiotic removal, the adsorption technique has been found to be superior to other techniques as it can be used to remove antibiotics from wastewater, due to its simple design, easy operation, and relatively simple regeneration[26, 27]. In this investigation, Palm bark (PB) was chosen as biosorbent due to being of its natural, renewable and thus cost-effective biomass. The objective of the present work is to investigate the potential of PB biomass for the removal of AMX antibiotics from contaminated water by biosorption. Optimum biosorption conditions biomass dosage, contact time and initial AMX concentration were determined. The Langmuir and Freundlich and Temkin models were used to describe equilibrium isotherms.

## MATERIALS AND METHODS

### *Materials*

Amoxicillin (AMX) (formula mass 365.4 g/mol) with purity higher than 99% was supplied by Sigma–Aldrich. Its $pKa_1$ and $pKa_2$ and $pKa_3$ values are 2.67 and 7.11 and 9.55. The chemical molecular formulae and structure of the AMX are $C_{16}H_{19}N_3O_5S$ is given in Fig. 1. The acetonitrile (ACN, 99%, Aldrich), HCl, NaOH were also provided by Sigma–Aldrich. All the chemicals used for the study were of analytical grad.




### *Biosorbent preparation and characterization*

For the present investigation, Palm bark biomass collected from the Palm groves in Zahedan sity, Iran, was used for the experiment. The grime contents were removed from PB biomass surface by repeated washing with boiling water. The wet form of PB bimass was initially airdried for 5 hour and then kept in the oven at around 60 $^0$C for another 10 hours. The dried biomass was ground, sieved to particles size 1.18 mm and stored in polythythene bags. Morphology and characterization of PB biomass were determined by using Scanning Electron Microscopy (SEM) and Energy Dispersive X- ray (EDX). The Brunauer–Emmett–Teller (BET) of the PB biomass was analyzed by nitrogen adsorption instrument in an ASAP 2020 surface area.

### *Adsorption equilibrium isotherm*

The adsorption of AMX on PB adsorbent was studied using the batch adsorption technique. The adsorption experiments have been conducted using 50 mL of AMX solution of different initial concentrations (10, 25, 50, 75 and 100 mg/L). The solutions were mixed with 3 g PB biomass in 100 mL Erlen meyer flasks. All experiments were performed at the optimum pH (pH 6.5) by adding 0.1 M HCL and NaOH solutions. The flasks were placed in a shaker at a constant speed of 200 rpm and 30 °C for 1.5 h to reach equilibrium. Then, the samples were placed in a centrifuge for 15 min at 4000 rpm. The concentration of AMX in a solution was measured using a Knauer HPLC ($C_{18}$ ODS column) with a UV detector 2006 at a wavelength of 190 nm. The mobile phase was a mixture of buffer phosphate with pH = 4.8 and acetonitrile with a volumetric ratio of 60/40 with an injection flow rate of 1 mL/min.The amount of AMX adsorbed onto PB biomass ($q_e$) can be calculated as below[28, 29]:

$$q_e = \frac{(Co - Ce) \times V}{M}$$

Where $C_0$ and $C_e$ (mg/L) are the initial and the equilibrium concentrations of AMX, respectively. V (L) is the volume of the solution and W (g) is the mass of the adsorbent. The optimum amount of the adsorbent dosage was investigated using different amounts of the adsorbent (0.5–5 g/L) at a concentration of 50 mg/L.

The reaction order and rate constants are important factors in the design of adsorption process that are determined using adsorption isotherms and kinetics. The pH values, temperature and adsorbent dosage were identical for all of the equilibrium experiments. The amount of AMX adsorbed on PB biomass can be calculated as below[30, 31]:

$$q_t = \frac{(Co - C_t) \times V}{M}$$

where Ct (mg/L) is the concentration of the AMX solution at time t (min). The standard deviations (SD) of all experimental data points were calculated according to the equation below and the values were shown graphically as error bars in the figures[32, 33]:

$$SD = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(X_i + \mu)^2}$$

Where N and μ are the number and the average of the experimental data, respectively.

## RESULTS AND DISCUSSION

Characterization of the absorbent was studied using SEM micrograph of biosorbent as depicted in the Fig. 1. It shows that the adsorbent have an irregular and porous surface. The PB biomass was cellulose in nature-based material containing tannin and lignin based organic compounds Physico-chemical analysis of PB biomass was conducted to analyse the percentage removal of moisture content of biosorbent as shown in Table 1.

**Table 1**
***Physiochemical characteristics of PB biomass***

| Proximate analysis | Moisture (%) | Ash (%) | Volatile (%) | Fixed carbon (%) |
|---|---|---|---|---|
| | 7.9 | 8.1 | 49.2 | 34.8 |
| BET surface area ($m^2/g$) = 124.36 | | | Bulk density ($kg/m^3$) = 17.42 | |

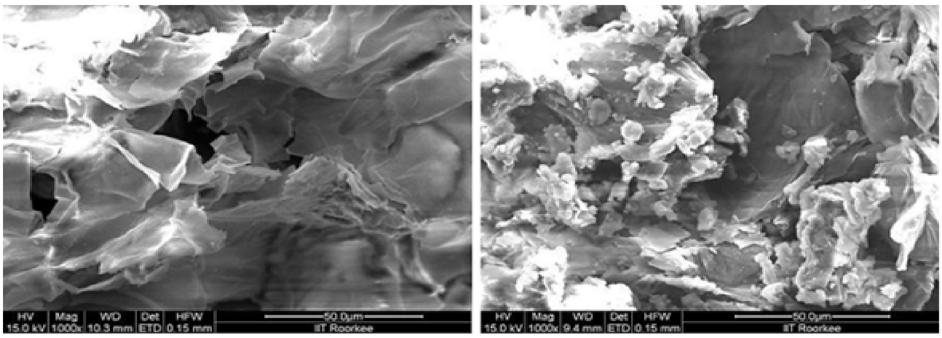



**Figure 1**
***Scanning electron micrograph of PB biomass***
***a: before biosorption b: after biosorption***

***Effect of adsorbent dose***

Biosorbent dose study was performed ranges from 0.5 to 5 g of biomass represented in Fig. 2. As the amount of sorbent dose increased, the percentage of AMX sorbed increased. This indicates the increase in available binding sites[34, 35]. However, further increase in sorbent dose (more than 3 g) did not have any significant effect on AMX removal. Hence, the present investigation found that 3 g of biosorbent was the optimum dose and effective percentage removal of AMX from liquid phase. Beyond 3 g there was lesser removal of AMX due to saturation of pores at the surface of biosorbent[36, 37].

**Effect of Contact time and initial AMX concentration**

The effect of contact time for the adsorption of AMX by PB biomass was studied for aperiod of 3 h for initial AMX mass concentrations of 10-100 mg/L at 298 K. The effect of contact time on removal of AMX is shown in Fig. 3. As concentration of AMX increases efficiency (%) removal decreases for same contact time. The uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to benearly constant. This is obvious from the fact that alarge number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases[38-40]. The effect of initial AMX mass concentration on the removal of AMX by PB biomass is shown in Fig. 3. The efficiency AMX removal decreased with increase in initial AMX mass concentration. The necessary driving force to overcome the resistance to the mass transfer of AMX between the aqueous and the solid phases is provided by initial AMX concentration. The increases in initial AMX mass concentration also enhance the interaction between AMX and PB biomass[41, 42].

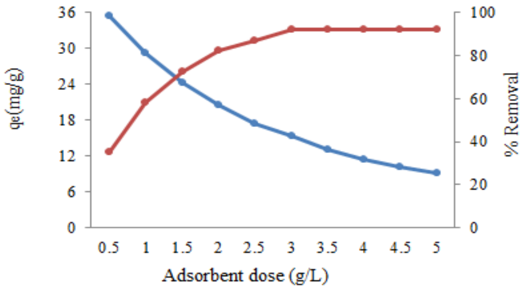



**Figure 2**
***Effect of adsorbent dosage***
***($C_0$ = 50 mg/L, Contact time = 75 min, pH = 7, temp= 25 ∘C)***

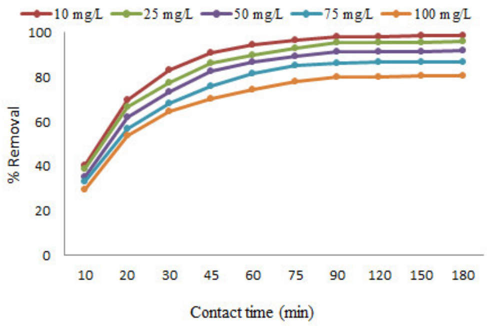



**Figure 3**
***Effect of contact time and AMX concentration***
***(pH =7, Adsorbent dosage 3 g/L and temp= 25 ∘C)***

***Equilibrium***

Various isotherm equations like Freundlich, Langmuir and Temkin have been used to describe the equilibrium characteristics of adsorption. The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. Whereas in the Langmuir theory basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. Temkin isotherm contains a factor that explicitly takes into the account adsorptive-adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coveragedue to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. Freundlich and Langmuir isotherms Linearised form of Freundlich and Langmuir isotherm equations are given a[43-45]:

$$\mathrm{Ln}\ q_e = \frac{1}{n} \ln Ce + \log K_F$$

$$\frac{Ce}{qe} = \frac{1}{q_m K_L} + \frac{Ce}{q_m}$$

Fig. 4a shows the Freundlich isotherm plots (log $q_e$ VS. log $C_e$) for adsorption of AMX onto PB biomass. Langmuir isotherm plot ($C_e/q_e$ VS. $C_e$) are shown in Fig. 4b for adsorption onto PB biomass. Temkin isotherm for adsorption is given as[46, 47]

$$q_e = \frac{RT}{b} \ln (KC_e)$$

which can be linearized as:

$$q_e = B \ln K + B \ln C_e \quad \text{and } B = \frac{RT}{b}$$

A plot of $q_e$ versus ln Ce enables the determination of the isotherm constants B and K from the slope and the intercept, respectively. K is the equilibrium binding constant (l/mol) corresponding to the maximum binding energy and constant B is related to the heat of adsorption. Fig. 4 c shows the Temkin isotherm plot for PB biomass. Freundlich and Langmuir and Temkin isotherm constants are given in Table 2. It can be seen from the Table 2 that the calculated correlation coefficients are also closer to unity for Langmuir isotherm than the Freundlich and and Temkin model. Therefore, the sorption of AMX can be approximated more appropriately by the Langmuir isotherm. Also Lower SD values and good correlation coefficient were observed for Langmuir isotherm model, which indicates the best fit model and significant in describing the AMX adsorption process.

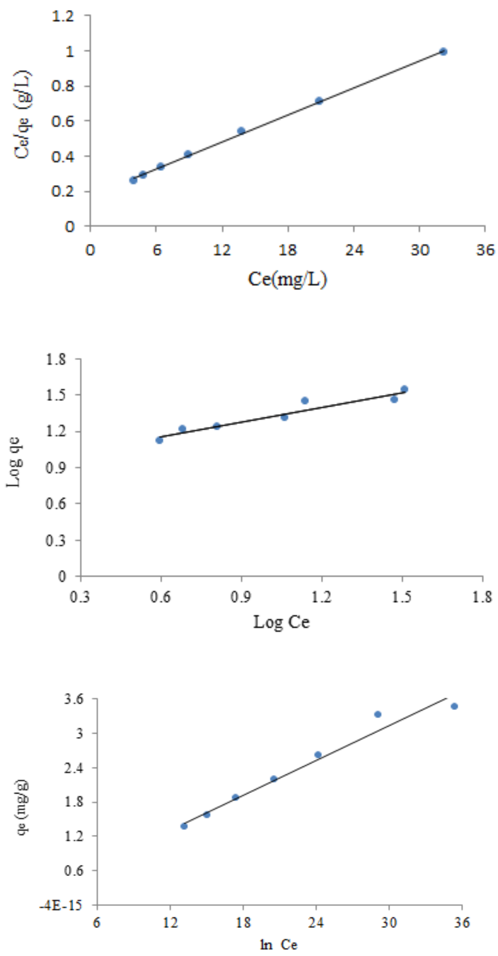



**Figure 4**
***(a) Langmuir model***
***(b) Freundlich model***
***(c) Temkin isotherm model.***

**Table 2**
***Isotherm parameters for adsorption of AMX onto PB biomass***

| Langmuir model | | | | | Freundlich model | | | | Temkin model | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $q_m$ (mg/g) | $R_L$ | $K_L$ | $R^2$ | SD | n | $K_F$ | $R^2$ | SD | B | K | $R^2$ | SD |
| 35.92 | 0.0684 | 0. 272 | 0.998 | 0.0241 | 2.798 | 0.364 | 0.914 | 0.782 | 4.271 | 0.483 | 0.927 | 0.446 |

## CONCLUSION

In this study a new PB biomass is used for the removal of AMX from synthetic water. The SEM, EDS analysis confirms the AMX adsorption. The lowest particle size obtained for the PB biomass was 1.18 mm with maximum surface area of 124.36. The maximum removal efficiency of AMX was 98.1% under optimum conditions with adsorption equilibrium time of 90 min. The adsorption data are best supported to langmuir model with correlation coefficient 0.998 adsorption capacity was found to be 35.92 mg/g.

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