Biosorption of dicloxacillin from pharmaceutical waste water using tannin from Indian almond leaf: Kinetic and equilibrium studies

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A B S T R A C T

This study focused on the use of Indian almond leaf biomass, a local plant widely found in Thailand, on removal of dicloxacillin from pharmaceutical waste water by biosorption. The biosorption characteristics of dicloxacillin were investigated in terms of equilibrium, kinetics and thermodynamics. Optimum biosorption conditions were determined from pH, initial dicloxacillin concentration, biomass dosage, contact time, and temperature. The maximum adsorption capacity was 86.93 % (pH 6.0, 0.1 g/L biomass, dicloxacillin concentration 20 mg/L, contact time 24 h, temperature 283.15 K). The thermodynamic parameters (298.15 K), free energy change, enthalpy change and entropy change were -3475.79 J/mol, −25.36 kJ/mol, and −73.40 J/mol/K, respectively. The best interpretation for the experimental data was given by the Langmuir isotherm with correlation coefficient of 0.965. The results were found to tie in well with pseudo-second-order kinetics. Considering the cost-effectiveness, Indian almond leaf biomass is considered to be suitable to remove dicloxacillin from pharmaceutical waste water.

1. Introduction

Pharmaceutical waste water treatment presents a real challenge for waste water engineers [1]. Recently, majority of the active pharmaceutical ingredients (APIs) are manufactured through a pharmaceutical manufacturing process [2]. Several reports have revealed that significantly high levels of APIs are being released to the environment daily [2–5]. Among those APIs, antibiotics constitute a significant proportion of APIs found in the environment, and have become a class of contaminants of emerging concern. They have been detected at concentrations between a few ng per L to, g per L, as well as at levels as high as mg per L in both industrial waste water and received water, including surface and groundwater throughout [3]. Nowadays, the evolution of microbial pathogens able to resist antibiotics treatments is seen as one of the most pressing public health crises [6–8]. Antibiotic resistance also imposes a significant financial burden on world economies [9]. The rate of antibiotic discovery has declined over the past decades due to technical and economic challenges, leading up to an "antibiotic crisis" [10]. The antibiotics of pharmaceutical origin are now found in large quantities in human-made environments such as sewage and waste water treatment plants [10]. Moreover, because

antibiotic pollution is poorly regulated on both local and global scales, antibiotic molecules are increasingly found in terrestrial, freshwater, and marine environments [11].

The most widely used antibiotic, both in human and livestock production, are penicillins [12]. Penicillins are a group of antibiotics that were among the first medications to be effective against many bacterial infections caused by staphylococci and streptococci [12]. Penicillins are still widely used today, though many types of bacteria have developed resistance following extensive use [12]. Dicloxacillin (Fig. 1a) is a β-lactamic antibiotic belongs to penicillins group which is used for treatment of gram positive bacterial infections [13,14]. Dicloxacillin is classified as penicillinase-resistant penicillin used to treat infections caused by certain types of bacteria. It works by inhibiting cell wall synthesis and therefore effectively killing the bacteria [13–15]. High amount of dicloxacillin, as well as other kinds of antibiotics, is released into the waste water and may promote development of antibiotic resistant bacteria (ARB) and antibiotic resistant genes (ARGs), which eventually find their way into natural environments [16]. Emerging microbial pathogens and increasing antibiotic resistance among them is a global public health issue. The presence of the antibiotic residues in the sewage treatment plants poses a problem due to the reasons such as increased risks to human health from the development of antibiotic-resistant microorganisms if antibiotics are present in sub lethal concentrations of the pathogens in sewage [17]. A proper treatment of waste water is essential before its discharge into rivers, lake, or sewage system to prevent the

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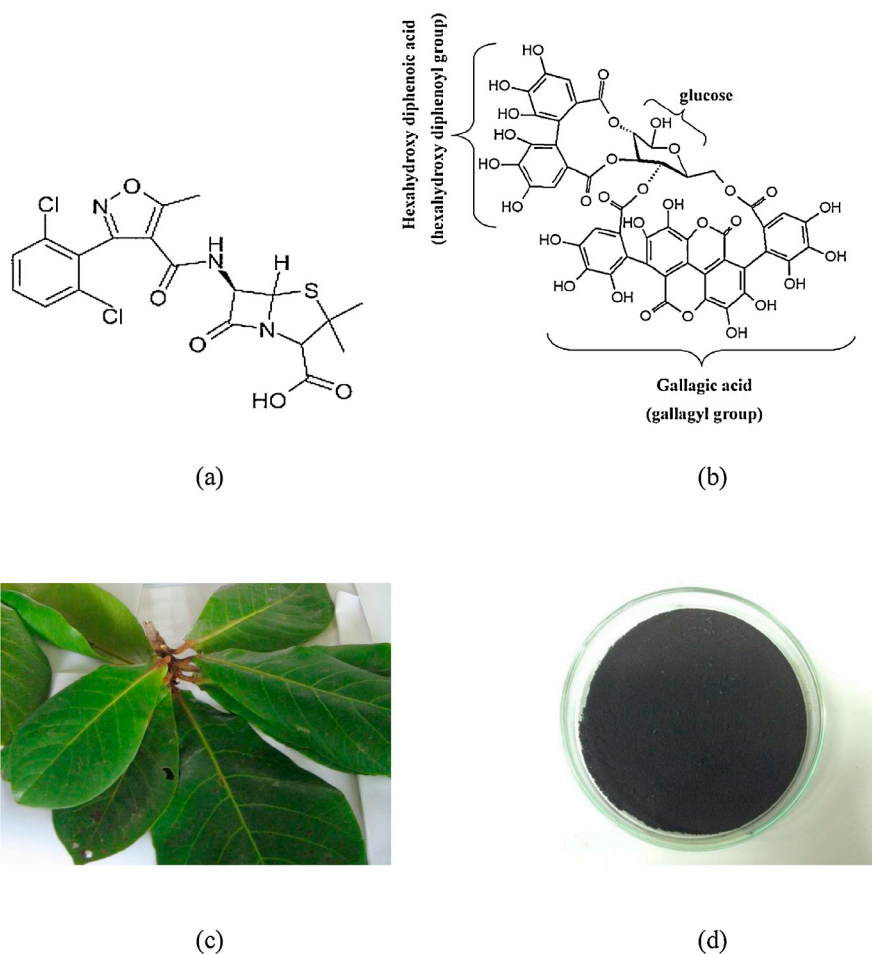
Fig. 1. The picture of (a) chemical structure of dicloxacillin [13]. (b) chemical structure of tannin [38]. (c) leaves of *Terminalia catappa* L. (d) extracted tannin.

spread of ARB and ARGs into the environment [18]. Antibiotic concentrations in natural environments such as soil or water range from a few nanograms to hundreds of nanograms per litre or kg soil. The highest quantities are usually found in areas withstrong anthropogenic pressures such as hospital effluents. In waste waters, antibiotic concentrations are correlated with variations in annual consumption data. Low concentrations are usually detected in natural environments in which antibiotic concentrations in some Italian rivers are reported was 0.1−230 ng/L [19]. In Thailand, the reported concentration of penicillins in the environment was 130-18,000 ng/L [20,21]. Dicloxacillin is a β-lactamic antibiotic of penicillins.

In order to find solutions to control dissemination of antibiotic resistance in the environment, it is important to study various treatment options applied for combating the spread of ARB and ARGs in waste water treatment plants [22]. The effluent containing antibiotics need to be treated by chemical, physical, or physico-chemical method to prevent global public health issues [23]. There are several techniques have been developed to purify industrial effluent before being discharged to the main streams such as ozonation, membrane, filtration, and solvent extraction [24]. However, many of these techniques are not practical due to high operating cost and high energy consumption. Therefore, physico-chemical using biosorption method with a low-cost biomass as adsorbent is an alternative technique to solve these problems [25].

This research approaches to develop the method in order to treat this compound from pharmaceutical waste waters.

Biosorption using biomass as adsorbent has been known for a few decades but using tannin as low cost adsorbent has only been introduced in recent years [25–27]. Tannins compose of multiple adjacent hydroxyl groups. It is found in the bark, roots, stalks of plants and fruits [28]. Tannin (Fig. 1b) is an important class of secondary plant metabolites, water-soluble polyphenolic compounds of molecular weight ranged between 500 and some thousands Daltons [29]. In the present study, tannin was synthesized from Indian almond (*Terminalia catappa* L.) leaves (Fig. 1c). The advantage of tannins from Indian Almond leaves is due to the fact that Indian Almond is a plant widely found in Thailand, which has higher amount of tannins that can be extracted than other local plants [30]. From extensive literature review, similar studies using biosorbents mostly applied in removing metal-ion waste. According to a review article by Silva et al. [31], there are a number of studies addressing pharmaceutical waste using biosorption method from algae and fungi. The studies used waste containing various types of pharmaceutical chemicals. However, most of them are non-antibiotics, or antibiotics from different chemical group. There is also one recently published study by using biosorbents from mushroom stems for removing pharmaceutical waste [32]. The study focused on paracetamol and 17 α-ethynyl estradiol as pharmaceutical waste. The selected

mushroom is not locally available in Thailand. In addition, there is few studies using other natural biosorbents apart from algae and fungi. Therefore, using a source available locally and selecting a commonly used antibiotic for our study would be beneficial and cost-effective in real-world application in the region.

Indian almond tree is a Combretaceous plant (tropical almond family), is a large tropical tree in the lead wood tree family, which grows mainly in the tropical regions of Asia. Indian almond has a vast natural distribution in tropical regions of the world, and it is widely grown in Southeast Asia especially in Thailand [30]. Indian almond presenting throughout any region of Thailand [33]. This tree was chosen as a biosorbent for this study because of it's naturally and readily availability, and thus a low-cost biomass for adsorption process. [29]. The chemical compositions of this plant consist of high concentration tannins [34]. The leaves of this tree contain several flavonoids, saponins and phytosterols [35] and a high tannin content of around 13 % [36,37]. Tannin, a polyphenolic compound commonly found in most herbs, has antibacterial properties. [38]. The chemical compositions of indian almond leaves consist of high concentration tannins [38,39]. Tannins contain many hydroxyl groups and are especially well known for their ability to complex with some metal ions and chemical compound [39]. A great deal of research has been conducted on the study of tannins binding with metal ions and chemical compound such as aluminum [39] iron [40] mercury [41] palladium and platinum [42]. Tannins have also been chemically modified to enhance chelation ability for use as bio-absorbance for environmental remediation [38].

In this study, we present a new approach to remove an antibiotic, dicloxacillin, from pharmaceutical waste water by biosorption method using a locally available Indian Almond Leaf biomass, resulting in an economical alternative suitable for widespread application. Biosorption method with a low-cost biomass as adsorbent is an alternative technique to remove dicloxacillin, from pharmaceutical waste water. Several parameters were investigated in attempt to obtain maximum biosorption ability including pH, initial dicloxacillin concentration, biomass dosage, contact time, and temperature of solution. Langmuir and Freundlich models were used to describe equilibrium isotherms. The mechanisms of biosorption of dicloxacillin onto tannin were also demonstrated in terms of thermodynamics and kinetics. This research aims to develop the method and the optimum condition in order to treat this compound from pharmaceutical wastewaters using a locally available biomass.

2. Experimental procedures

2.1. Biomass preparation

Indian almond (*Terminalia catappa* L.) leaf samples were washed by water and then dried in an oven at 343.15 K for 48 h. The dried Indian almond leaf biomass was mixed with concentrated sulfuric acid at 373.15 K for 24 h, then neutralized with sodium bicarbonate solution, washed with distilled water, and dried in an oven at 343.15 K for 48 h. Finally, the adsorbent synthesized from Indian almond leaf biomass (Fig. 1d) was crushed and sieved through mesh of different sizes. Adsorbent sizes in a range of 100–150 μm were used in all experiments. This method for biomass adsorbent preparation was proposed by Parajuli et al. [43]. Total tannin concentration was determined by colorimetric method [33].

2.2. Reagents and equipment

Pharmaceutical waste water used in this study was taken from pharmaceutical plant of Sevenstar Pharmaceutical Company,

Thailand. The waste water was generated from the manufacturing processes of dicloxacillin, and contained a variety of solvents, additives, reactants, and high-value finished dicloxacillin products. The generation rate of the waste water was 20 L per batch. The properties of the waste water are shown in Table 1. The concentration of dicloxacillin from real wastewater was analyzed by HPLC analytical procedure followed USP 41 [44]. The concentration of dicloxacillin from real waste water was approximately 400−600 mg/L. Therefore, we chose concentration 500 mg/ L of dicloxacillin for our study.

Other chemicals – hydrochloric acid, sodium hydroxide, sodium bicarbonate, and sulfuric acid – were also supplied by Merck. All chemicals used in this study were analytical grade. The list of chemical and reagents with purity are shown in Table 2. Double-deionized water (Milli-Q; Millipore, Billerica MA, USA), 18.2 MΩ·cm^{-1} conductivity, was used for all dilutions. The pH values in aqueous phase were measured by pH meter with glass-tip electrode (pH Spear; Eutech Instruments, Singapore). Zeta meter System 3.0+ (Zeta-Meter, Staunton VA, USA) was used to analyze zeta potential values in aqueous phase. The biosorption mechanism was also studied by measuring the zeta potential of *T. catappa* L. biomass before and after adsorption by using a Zeta Meter microelectrophoretic apparatus.

The chromatographic system consisted of Agilent® 1100 Compact LC system series (Agilent Technologies, Palo Alto, CA, USA) was used to determine dicloxacillin concentrations. This system contained quaternary pump with degasser, autosampler, column compartment, and DAD (photodiode array detector). Agilent software (ChemStation Version B.04.01) was used to analyzed the experimental data.

Analytical procedure followed USP 41 [44]. Chromatographic column was Inertsil® ODS-3 column (5 μm, 4.6 mm x 250 mm) USP Code L1. Column heater was set at 318.15 K to control temperature. Mobile phase was a mixture of 75 % volume by volume of 2.72 g/L of monobasic potassium phosphate in water, adjusted with 8 N potassium hydroxide to a pH of 5.0 ± 0.1 and 25 % volume/volume of acetonitrile. The flow rate of mobile phase was 2.0 mL/min. The injection volume was 10 μL. The photodiode array detector was set as UV 225 nm. The time of sample analysis set at 20 min per sample. The acid and basic values of the solution were measured with SevenMulti™ Mettler-Toledo pH meter, Switzerland.

Fourier transform infrared (FT-IR) spectra of dried unloaded biomass and dicloxacillin-loaded biomass were recorded using an Equinox 55 FT-IR spectrometer (Bruker Optics, Billerica MA, USA). Analytical procedure followed USP 41 general chapter prospectus

Table 1
Characteristics of the raw pharmaceutical waste water and Indian almond leaf biomass.

Parameter	Value
Raw pharmaceutical waste water	
Dicloxacillin (mg/L)	∼ 400–600
Color	Yellowish
Temperature (K)	298.15
pH	5.5
TSS (mg/L)	720
BOD (mg/L)	1,780
COD (mg/L)	3,270
Conductivity (μs/cm)	2,990
Indian almond leaf biomass	
Total tannin (mg/ml)	∼ 13
Moisture (%)	8.5
Ash (%)	10.2
Volatile (%)	38.2
Fixed carbon (%)	35.7
BET surface area (m^2/g)	131.41

Table 2
The list of chemical and reagents with purity.

Chemical and reagents	Dicloxacillin	Hydrochloric acid	Sulfuric acid	Sodium hydroxide	Sodium bicarbonate
Chemical formula	$C_{19}H_{17}Cl_2N_3O_5S$	HCl	H_2SO_4	NaOH	$NaHCO_3$
Molecular weight	470.33	36.46	98.08	40.00	84.00
CAS Number	3116-76-5	7647-01-0	7664-93-9	1310-73-2	144-55-8
Purity (%)	98.5	36.9	96.5	97.0	99.5
Analysis method of purity (%)	HPLC	GC	Titration	Titration	Titration

<197> Spectroscopic Identification Tests [44]. The method is indicated for the preparation of previously dried specimens and reference standards for analysis follow sub-general chapter prospectus <197 K> signifies that the substance is mixed intimately with potassium bromide. Record spectra of the test specimen and the corresponding USP reference standard over the range from about 2.6 μm to 15 μm (3800 to 650 cm – 1) unless otherwise specified in the individual monograph. The IR absorption spectrum of the preparation of the test specimen, previously dried under conditions specified for the corresponding reference standard unless otherwise specified, or unless the reference standard is to be used without drying, exhibits maxima only at the same wavelengths as that of a similar preparation of the corresponding USP reference standard.

Scanning electron microscopy (SEM) (JSM-5410LV; JEOL, Tokyo, Japan) was used to analyze the surface morphology of the adsorbent. Analytical procedure followed Scanning electron microscopy (SEM) standard method [45]. In this study, the adsorbent morphology such as surface texture, pore organization and pore structure of prepared adsorbents before and after biosorption were examined.

2.3. Batch biosorption procedure

The concentration of dicloxacillin from real wastewater was approximately 400−600 mg/L. Therefore, we chose concentration 500 mg/L of dicloxacillin for our study. Dicloxacillin solutions were prepared by dissolving pharmaceutical waste water in deionized water and then further diluting to the various concentrations used in the experiments. Biosorption experiments were carried out using solutions of 100 mg/L dicloxacillin, with an optimal biomass concentration of 0.1 g/L. Solution samples (20 mL) including the biomass were shaken at 250 rpm for the desired contact times by an electrically thermostatic reciprocating shaker (Selecta Multi-matic-55; Barcelona, Spain).

Batch studies were performed under a range of conditions: initial dicloxacillin concentration (20−500 mg/L), contact time (1−48 h), pH (2.0−8.0), biomass concentration (0.025–0.3 g), and temperature (278.15–323.15 K). The equilibrium time was estimated by drawing samples at regular time intervals until equilibrium was reached. The contents of the flasks were filtered through a 0.25 μm filter (Double-Ring; Hangzhou, China). The concentrations of dicloxacillin in the filtrate were analyzed by High Performance Liquid Chromatography (HPLC). Experiments were done in duplicate, and the averaged results were determined. The percentages of biosorption of dicloxacillin were defined by Eq. (1a):

$$\%Biosorption = \frac{C_f - C_i}{C_i} X100 \tag{1a}$$

where C_i and C_f are the initial and final dicloxacillin concentrations, respectively. The amount of dicloxacillin adsorbed on the adsorbent [46] were defined by Eq. (1b)

$$\left(q = \frac{(Ci - Ct) \times V}{m} \right) \tag{1b}$$

where q is biosorption capacities (mg/g), C_i is the initial concentration of dicloxacillin (mg/L), C_t is the concentration of dicloxacillin at time t (mg/L), V is volume of dicloxacillin solution, and m is mass of biosorbent used in the reaction mixture (g).

2.4. Biosorption kinetics

In order to investigate the mechanism of the adsorption process, models of pseudo-first-order adsorption and pseudo-second-order adsorption were applied to test the adsorption rate data. The pseudo-first-order rate model [47] is expressed in Eq. (2) as:

$$\ln(q_e - q_t)q_t = \ln(q_e) - k_1 t \tag{2}$$

where q_e is equilibrium biosorption capacities (mg/g) and q_t is the amounts of dicloxacillin adsorbed on the adsorbent at time (mg/g), t is time, and k_1 is the pseudo-first-order rate constants (min^{-1}).

The pseudo-second-order rate model [48] is given in Eq. (3):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} t \tag{3}$$

where k_2 is the constant of the pseudo-second-order rate (g/mg/min), which is obtained by plotting $\frac{t}{q_t}$ versus t.

2.5. Biosorption isotherm models

Biosorption equilibrium data were fitted for linear Langmuir, and Freundlich isotherms. The Langmuir model represents one of the first theoretical treatments of nonlinear sorption, and suggests that the uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. This means that once a site is filled, no further sorption can take place at that site. The Langmuir equation is represented by [48]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{k_L q_{max}} \tag{4}$$

where q_e is equilibrium biosorption capacities (mg/g), C_e is the concentration at equilibrium (mg/L), q_{max} is maximum biosorption capacities (mg/g), and K_L is Langmuir equations constants (L/mg) which can be determined from linear plot of $\frac{C_e}{q_e}$ versus C_e.

2.6. Biosorption thermodynamics

The thermodynamic behavior of the biosorption of dicloxacillin onto *T. catappa* L. biomass can be described by thermodynamic parameters including the changing of free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) which were calculated from the following equation:

$$\Delta G^0 = -RT \ln K_D \tag{5}$$

where R is the universal gas constant (8.314 J/mol K), T is the temperature (K) and K_D is the distribution coefficient [49,50].

However, since activity coefficients have not been incorporated, the shifted free energy, ΔG^0 can be calculated. The Gibbs free

energy change (ΔG^0) is related to the standard enthalpy and extraction entropy changes $(\Delta H^0 \text{and} \Delta S^0)$ through the Gibbs–Helmholtz equation. The relationship of Gibbs free energy with the enthalpy and entropy is as follows in Eq. (6).

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (6)$$

Substituting Eq. (6) into Eq. (5) results in van't Hoff's equation [51,52] in linear form, and is shown as Eq. (7):

$$\ln K_D = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (7)$$

The enthalpy $(\Delta H°)$ and entropy $(\Delta S°)$ are estimated from Eq. (7) by plotting K_D against $\frac{1}{T}$. A plot of ln K_D versus $1/T$ should give a straight line, and the values of $\Delta H°$ and $\Delta S°$ can be calculated from the slope and coordinate, respectively [53].

3. Results and discussion

Characterization of the absorbent was studied using SEM micrograph of biosorbent as depicted in the Fig. 2. It shows that the adsorbent has an irregular and porous surface. The Indian almond leaf biomass was cellulose in nature-based material containing tannin and lignin based organic compounds Physico-chemical analysis of Indian almond leaf biomass was conducted to analyse the percentage removal of moisture content of biosorbent as shown in Table 1.

3.1. Influence of initial pH

Experiments were performed using solutions of different pH values, ranging from 2.0 to 8.0. The concentration of dicloxacillin was fixed at 100 mg/L, while biomass adsorbent dosages were 0.1 g/L and solution volumes were 20 mL at 298.15 K. The results are shown in Fig. 3. The adsorption capacity of dicloxacillin on tannins can vary according to pH control by 2 reasons.

1 According to Fig. 3, when the pH of solution increased from 2.0 to 6.0, the %biosorption also increased. The degree of ionization of phenolic hydroxyls of tannin increases with increasing pH value [38,39,42], thereby increases its ability to react with dicloxacillin compound. This resulted in higher adsorption capacity.
2 When the pH of solution increased from 6.0 to 8.0, the % biosorption decreased. Dicloxacillin starts to ionize from pH 5 to

pH 9 [13,14]. Therefore, the adsorption capacity of dicloxacillin concentration is reduced.

Fig. 3 also indicated that the optimal pH for biosorption of dicloxacillin using biomass adsorbent was 6.0. The pH for biosorption of dicloxacillin using biomass adsorbent for all experiment was fixed at pH 6.0.

3.2. Influence of contact time

Experimental studies were carried out by varying contact times. The initial dicloxacillin concentration was 100 mg/L, with 0.1 g/L of biomass adsorbent dosage, 20 mL solution volume, and pH of 6.0 at 298.15 K. As shown in Fig. 4, the adsorption occurs very rapidly during the initial contact time and then it is almost constant. The fast dicloxacillin bisorption rate was attributed to the surface binding and the following slower sorption was attributed to the interior penetration [54,55]. The results also demonstrated that adsorption capacity increased with increasing contact time, and reached equilibrium after 24 h. The capacity of biomass adsorbent for dicloxacillin will be establish when the system is in the equilibrium state. Therefore, the optimal contact time for complete separation of dicloxacillin was 24 h.

3.3. Influence of initial dicloxacillin concentration

The effect of different initial dicloxacillin concentrations of 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 250, 300, 350, 400, 450 and 500 mg/L on its removal using *Terminalia catappa* L. biomass was studied. As shown in Fig. 5, when the initial concentrations of dicloxacillin increased from 20 to 500 mg/L, the biosorption (removed dicloxacillin (mg/L)) increased continuously due to insufficient binding sites for excessive dicloxacillin at high initial concentration. However, the removal rate of biosorbents comparatively increased faster but reached equilibrium at the concentrations of dicloxacillin was 140 mg/L (removed dicloxacillin was 64.21 mg/L). In general, at low concentration values, a larger surface area of adsorbent is available for the adsorption of dicloxacillin at specific sites. However, with increasing initial concentration of dicloxacillin, the available sites of adsorption become less, the specific sites are saturated and filled with exchange sites, and thus the adsorption capacity reached equilibrium [56]. From the result, it can be concluded that the maximum adsorption capacity was 86.93 % (removed dicloxacillin was 17.39 mg/L). The initial dicloxacillin concentration was
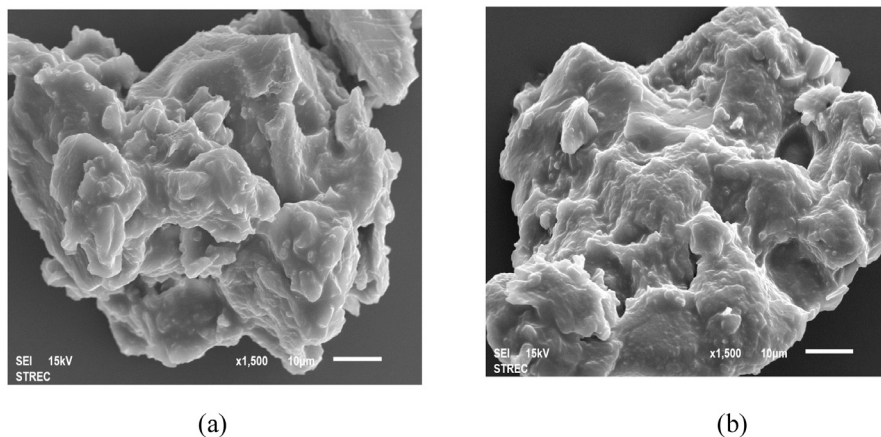

(a)   (b)

Fig. 2. (a) SEM micrograph of biomass adsorbent before adsorption; (b) SEM micrograph of biomass adsorbent after adsorption (0.1 g/L biomass, dicloxacillin concentration 100 mg/L, pH 6.0, contact time 24 h, temperature 298.15 K.).
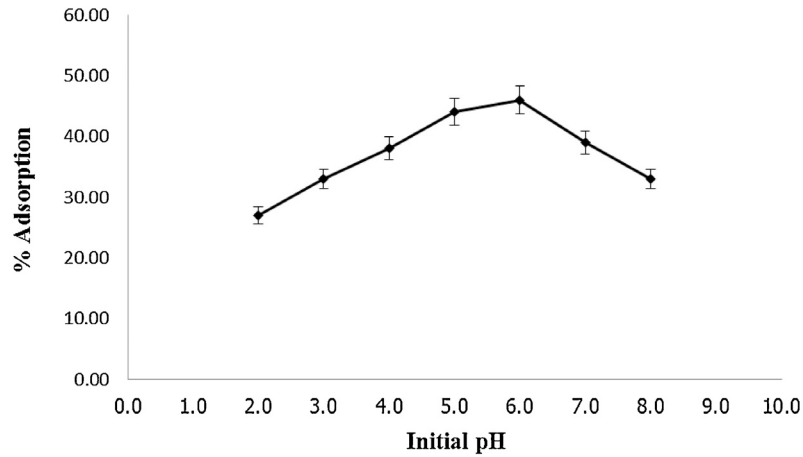
Fig. 3. The influence of pH on the biosorption of dicloxacillin onto *T. catappa* L. biomass (0.1 g/L biomass, dicloxacillin concentration 100 mg/L, contact time 24 h, temperature 298.15 K.).
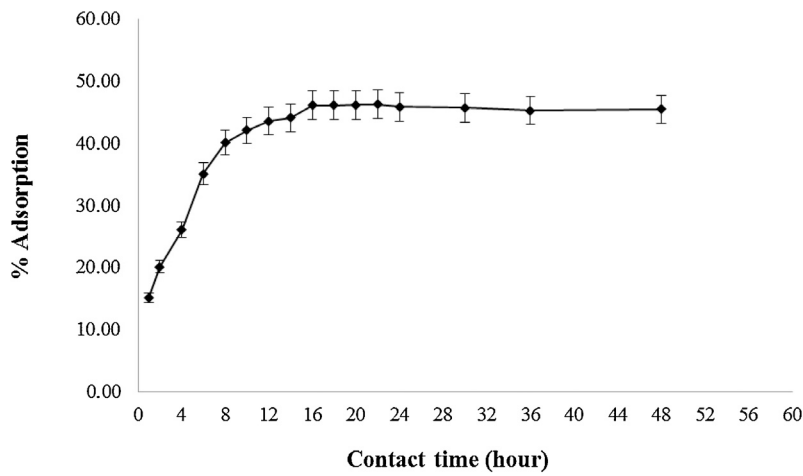

Fig. 4. The influence of contact time on the biosorption of dicloxacillin onto *T. catappa* L. biomass (0.1 g/L biomass, dicloxacillin concentration 100 mg/L, pH 6.0, temperature 298.15 K.).
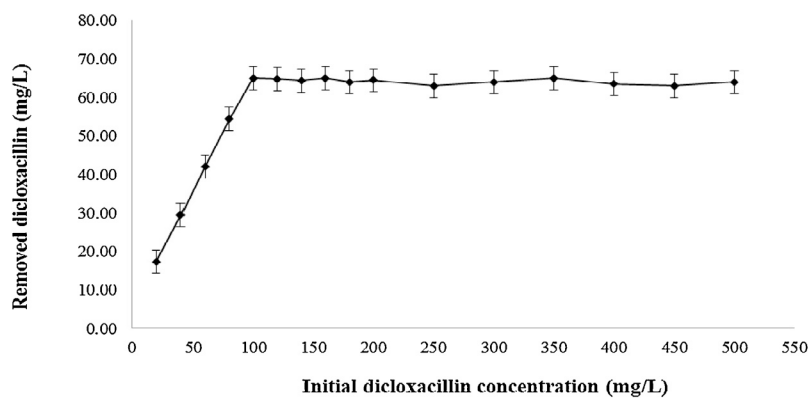

Fig. 5. The influence of initial dicloxacillin concentration on biosorption of dicloxacillin onto *T. catappa* L. biomass (0.1 g/L biomass, pH 6.0, contact time 24 h, temperature 298.15 K.).
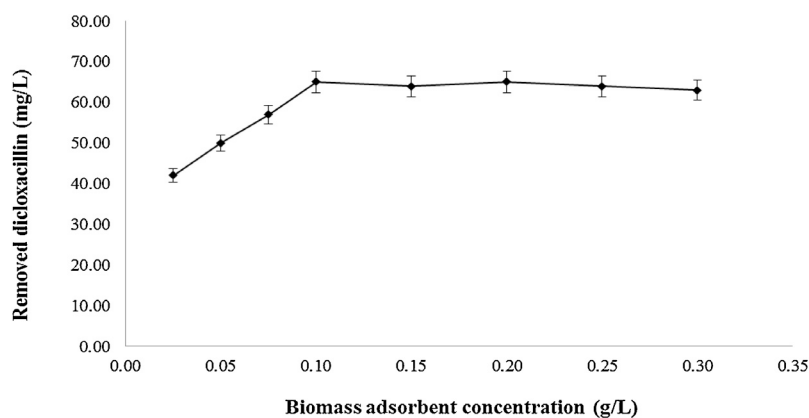
Fig. 6. The influence of biomass adsorbent concentration on the biosorption of dicloxacillin onto *T. catappa* L. biomass (dicloxacillin concentration 100 mg/L, pH 6.0, contact time 24 h, temperature 298.15 K.).
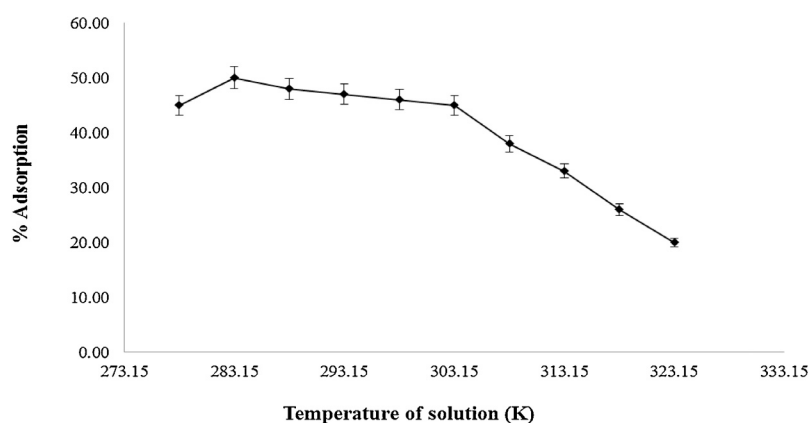

Fig. 7. The influence of temperature on the biosorption of dicloxacillin onto *T. catappa* L. biomass (0.1 g/L biomass, dicloxacillin concentration 100 mg/L, pH 6.0, contact time 24 h.).

100 mg/L, with 0.1 g/L of biomass adsorbent dosage, 20 mL solution volume, and pH of 6.0 at 303.15 K. This strongly suggests that *Terminalia catappa* L. is an effective biomass adsorbent for adsorption of dicloxacillin from pharmaceutical waste water.

3.4. Influence of biomass adsorbent concentration

Biomass adsorbent provides binding sites for the sorption of dicloxacillin, and hence its concentration strongly affects the adsorption of dicloxacillin from the solution. In this study, the effect of biomass adsorbent dosage on the adsorption capacity of dicloxacillin was investigated. As shown in Fig. 6. The adsorption capacity increased when the biomass dosage increased from 0.025 to 0.3 g/L due to the availability of more empty binding sites as compared to lower dosage which has less binding sites to adsorb the same amount of dicloxacillin in solution [56]. As the amount of biomass adsorbent increases, the total adsorbed dicloxacillin increased until ultimately becoming constant. Therefore, the relationship between the amount of biomass adsorbent and dicloxacillin adsorbed is close to a hyperbolic curve [57]. The optimal initial biomass concentration for complete separation of dicloxacillin using 100 mg/L of initial dicloxacillin concentration was 0.1 g/L biomass adsorbent.

3.5. Influence of temperature

The data of dicloxacillin adsorption onto biomass adsorbent at different temperatures (from 278.15 to 323.15 K) are shown in Fig. 7. The result demonstrated that the increase of temperature from 278.15 to 303.15 K, the adsorption capacity increased, and then decreased continuously until reaching 323.15 K. This may be attributed to the actions of bonds between dicloxacillin and active sites of adsorbent being weakened at high temperature. This indicated that the adsorption of dicloxacillin by biomass was controlled by exothermic process [58].

3.6. Biosorption kinetics

In order to examine the mechanism of adsorption process, a suitable kinetic model is needed to analyze the rate data. In this research, the models include the pseudo-first order, and pseudo-second orders were also applied. The kinetic process of dicloxacillin biosorption on pH 6.0, using 0.1 g/L of biomass adsorbent dosage, with 20 mg/L of initial dicloxacillin concentration at 298.15 K were investigated at different contact times. Fig. 6 shows a plot of log $(q_{e,1} - q_t)$ vs. t for biosorption of dicloxacillin for the pseudo-first order equation. The values of pseudo-first-order rate constants (k_1), and equilibrium biosorption capacities ($q_{e,1}$) were
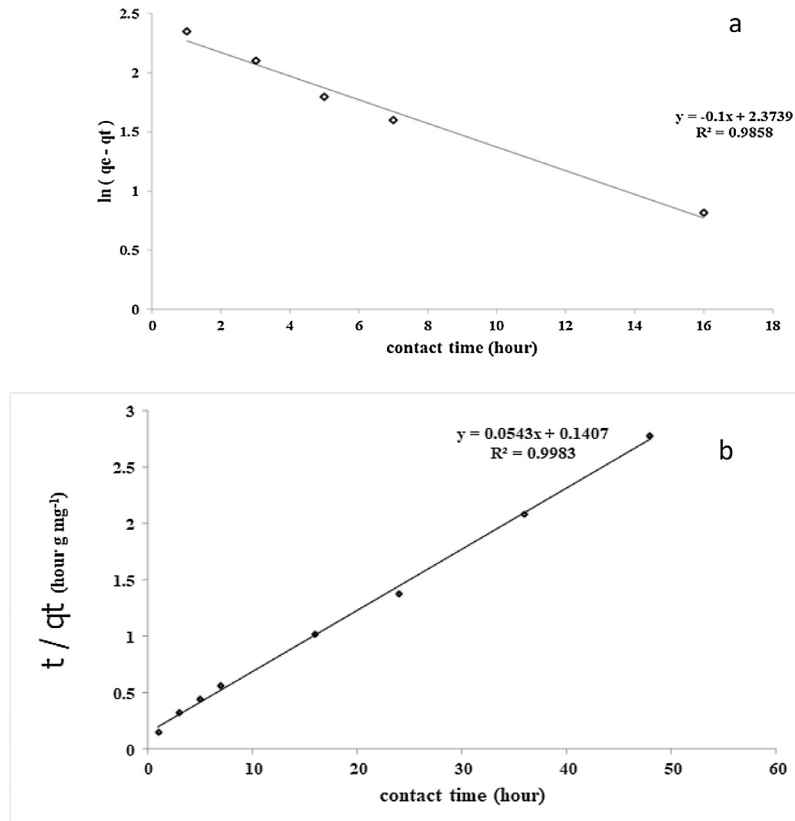
Fig. 8. a) Plot of the pseudo-first order equation for biosorption kinetics of dicloxacillin on *T. catappa* L. biomass at different contact times. b) Plot of the pseudo-second order equation for biosorption kinetics of dicloxacillin on *T. catappa* L. biomass at different contact times.
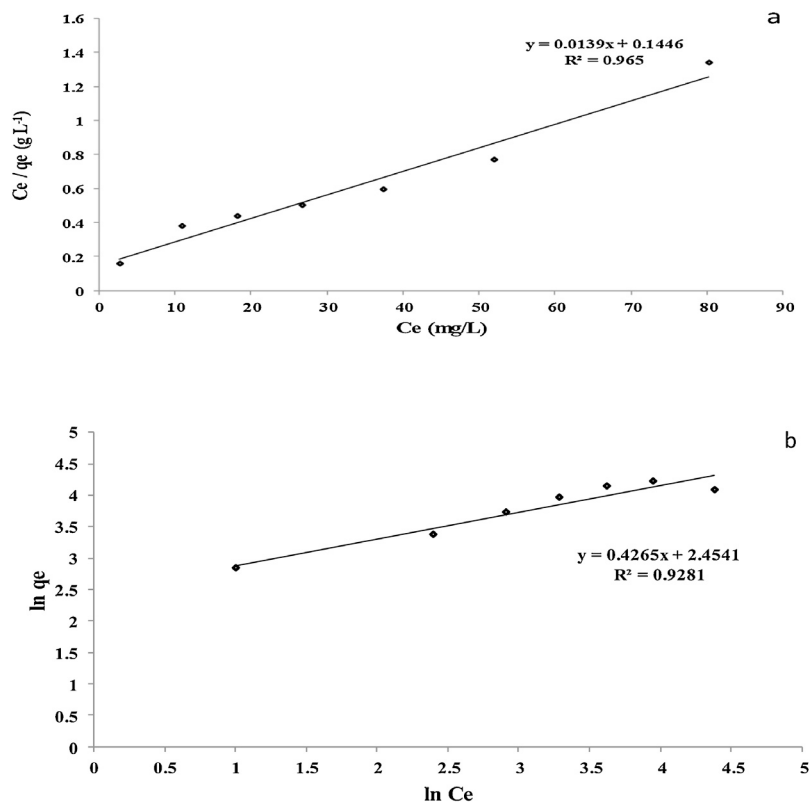

Fig. 9. a) Langmuir isotherm equations of dicloxacillin on *T. catappa* L. biomass at various initial dicloxacillin concentrations. b) Freundlich isotherm equations of dicloxacillin onto *T. catappa* L. biomass at various initial dicloxacillin concentrations.

Table 3
The results of rate constant investigated by pseudo-first order equation and pseudo-second order equation.

	k	q_e (mg/g)	R^2
Pseudo-first order	k_1 (hour^{-1}) = 0.1	10.74	0.9858
Pseudo-second order	k_2(gmg^{-1} hour^{-1}) = 0.021	18.42	0.9983

calculated from slopes and intercepts of straight lines in Fig. 8. The values of pseudo-first-order equation parameters together with correlation coefficients are given in Table 1. The correlation coefficient for pseudo-first order equation was 0.9858. Fig. 9 also shows typical plots of pseudo-second order equation for dicloxacillin adsorption as t/q_t vs. t. The values of pseudo-second-order equation parameters together with correlation coefficients are also listed in Table 3. The correlation coefficient for the pseudo-second order equation (R^2 = 0.9983) which approaches to 1.0 more than the value from pseudo-first order equation (R^2 = 0.9858). The calculated $q_{e,2}$ value (18.42 mg/g) is in agreement with the experimental data (17.28 mg/g) as well. This strongly suggests that the biosorption of dicloxacillin onto *T. catappa* L. biomass is most appropriately represented by a pseudo-second order rate process. Similar result was reported [59,60]. The dicloxacillin adsorption process behavior was enplaned by pseudo-second order kinetics chemical reaction from chemical structure of tannin

and dicloxacillin. The major functional group of tannin was hydroxyl group. The adjacent phenolic hydroxyls of tannins are able to react with dicloxacillin compound. In the pseudo-second order model, the rate-limiting step is the surface adsorption that involves chemisorption, where the removal from a solution is due to physicochemical interactions between the two phases [60]. The model is usually represented by its linear form as shown in Fig. 8 and Table 3. Fitted pseudo-second-order-model kinetic parameters for the removal of dicloxacillin by hydroxyl group of tannin are presented in Table 3.

3.7. Biosorption isotherm models

In this study, the equilibrium isotherm models were fit to biosorption experimental data in order to study the nature of adsorption process including Langmuir, and Freundlich models. To investigate the suitability of these two models, they were applied in the results of this research. Fig. 9 show Langmuir and Freundlich adsorption isotherms of dicloxacillin on biomass at 298.15 K and optimal pH value, using 0.1 g/L of biomass with various initial dicloxacillin concentrations (20–500 mg/L), and the simulated equations were also given in Table 4. This suggests that the experiment data were agree well with Langmuir isotherm model due to higher value of regression coefficient value (R^2 = 0.965). However, the Freundlich isotherm model did not fit well to the

Table 4
Langmuir equations and Freundlich equations of dicloxacillin on *T. catappa* L. biomass at various initial dicloxacillin concentrations.

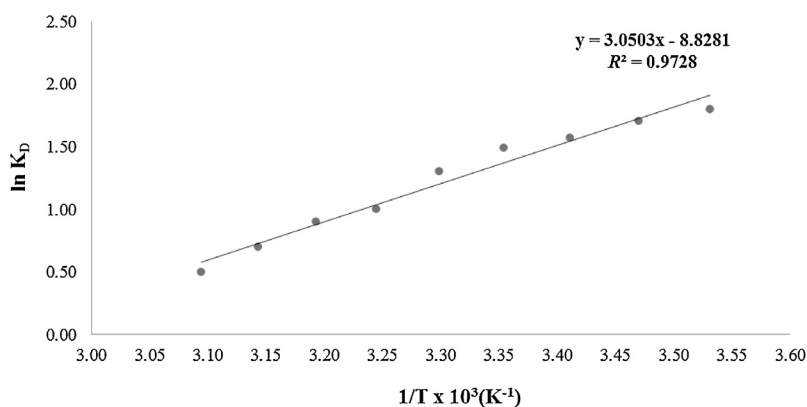| Langmuir equations				Freundlich equations			
q_0 (mg/g)	K_L (L/mg)	R^2	Deviation (%)	K_F (mg/g)	1/n (L/g)	R^2	Deviation (%)
71.94	0.0961	0.9650	2.11	6.98	0.4265	0.9281	7.17

Fig. 10. Plot of $\ln K_D$ vs. $\frac{1}{T}$ for the estimation of thermodynamic parameters for biosorption of dicloxacillin onto *T. catappa* L. biomass.

Table 5
Thermodynamic parameter for biosorption of dicloxacillin onto *T. catappa* L. biomass.

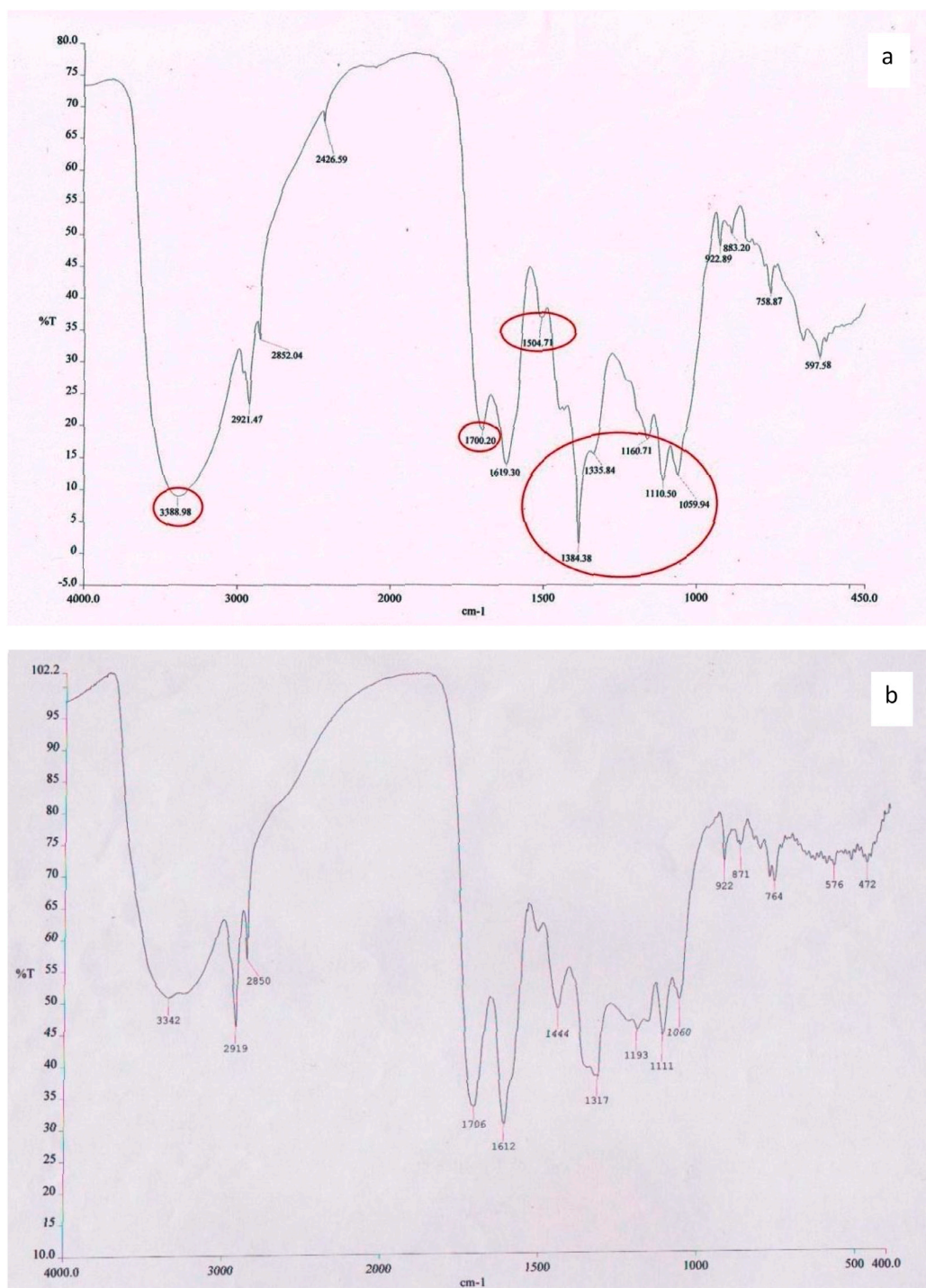| Temperature (K)	Gibbs free energy change (ΔG^0) (J/mol)	Enthalpy change (ΔH^0) (kJ/mol)	Entropy entropy (ΔS^0) (J/mol/K)
283.15	−4576.79	−25.36	−73.40
288.15	−4209.79		
293.15	−3842.79		
298.15	−3475.79		
303.15	−3108.79		
308.15	−2741.79		
313.15	−2374.79		
318.15	−2007.79		
323.15	−1640.79		

Fig. 11. a) FT-IR spectra of the biomass adsorbent particles before adsorption process. b) FT-IR spectra of the biomass adsorbent particles after adsorption process (0.1 g/L biomass, dicloxacillin concentration 100 mg/L, pH 6.0, contact time 24 h, temperature 298.15 K.).

experimental data with showing the R^2 values of 0.784 at the same conditions.

The dicloxacillin adsorption adjusted well to Langmuir model. This suggests that the surface of *T. catappa* L. biomass contains homogeneous binding sites, equivalent sorption energies, and that there is no interaction between adsorbed species. Similar effect was reported by Mahmut Ozacar et al. showing that the adsorption of lead onto tannin resin was demonstrated by

Langmuir isotherm [61]. The solubility and stability of dicloxacillin in aqueous solution was reported [13,14]. In aqueous solution, dicloxacillin was freely soluble in water and methanol in free form. There is no evidence regarding dicloxacillin-dicloxacillin molecules interactions. Our investigation showed that dicloxacillin compound are able to react with phenolic hydroxyls of tannins on the surface of *T. catappa* L. biomass contain homogeneous binding sites.

3.8. Biosorption thermodynamics

The Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$), are important parameters that are used to describe the thermodynamic behavior of the biosorption of dicloxacillin onto *T. catappa* L. biomass. Fig. 10 shows the plot of $\ln K_D$ vs. $\frac{1}{T}$ according to Eq. (7) for different temperatures (283.15, 288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K), a straight line is obtained with a slope of $-\frac{\Delta H^0}{R}$ and an ordinate of b$\frac{\Delta S^0}{R}$. Thus the values of $\Delta H°$ and $\Delta S°$ can be calculated from the slope and ordinate, respectively [62]. Gibbs free energy change ($\Delta G°$) can be calculated by Eq. (6) as shown in Table 5. It was found to be -4209.79, -3842.79, -3475.79, -3108.79, -2741.79, -2374.79, -2007.79, and -1640.79 J/mol for dicloxacillin biosorption at 283.15, 288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K, respectively. The reaction occurs spontaneously due to the negative values of $\Delta G°$ [62]. The $\Delta H°$ parameters were also found to be -25.36 kJ/mol for dicloxacillin biosorption. The negative $\Delta H°$ indicates the exothermic nature of the biosorption processes. Furthermore, the $\Delta S°$ parameter was found to be -73.40 J/mol/K. The negative $\Delta S°$ value suggests a decrease in randomness at the solid–solution interface during adsorption process [63].

3.9. Mechanism of reaction between dicloxacillin and biomass adsorbent FT-IR analysis

The biomass adsorbent before and after adsorption were characterized by using the Fourier transform infrared (FT-IR) spectrophotometer as shown in Fig. 11. The functional groups that may be involved in the biosorption process were analyzed. In accordance with the literature [33,37,38], the FT-IR spectrum (Fig. 11a) of the biomass adsorbent particles before adsorption process showed a broad and strong peak of tannin particles at 3389.98 cm^{-1} (3600$-$3000 cm^{-1}), indicating the presence of a hydroxyl (—OH) or amine (—NH) group. The peak at 1700.20 cm^{-1} (1720$-$1706 cm^{-1}) could be due to the strong stretching vibration of the carboxylic acid (C=O dimer) group, and those at 1504.71 cm^{-1} (1550$-$1500 cm^{-1}) could be due to the strong stretching vibration of the nitro compound (N—O) group. The peak at 1384.48 cm^{-1} (1450$-$1375 cm^{-1}) could be due to the medium stretching vibration of the alkane methyl group (C—H) group. The FT-IR spectrum represent the major functional group of tannin was hydroxyl group.

Fig. 11b shows FT-IR spectra of the biomass adsorbent particles after adsorption process. The band at 1706 cm-1 (1720-1706 cm-1) increased. This result indicates that the hydroxyl groups of the biomass adsorbent are oxidized to carbonyl groups [61,64]. It was found that a strong broad peaked at 3342 cm-1 (3550-3200 cm-1), indicating the presence of a broad hydroxyl stretching alcohol with intramolecular bond. This suggests that the functional group of hydroxyl group of tannin was reacted with dicloxacillin by intermolecular bond, which mediate interaction between molecules and other types of neighboring particles, including forces of attraction or repulsion.

According to FTIR and SEM method, it was found that the interaction between functional groups of dicloxacillin and the adsorbent was intermolecular interaction, such as hydrogen bonds or van der Waals forces. The appearance of broad hydroxyl stretching alcohol with intramolecular bonded confirms the binding between the dicloxacillin and hydroxyl group of tannin. This reveals that the intermolecular interaction such as hydrogen bonds, van der Waals forces can be the main interaction for the dicloxacillin and the surface properties of adsorbent.

4. Conclusion

This study evaluated the feasibility of using Indian almond leaves (*Terminalia catappa* L.), a locally available low-cost biosorbent for biosorption of dicloxacillin from pharmaceutical waste water. The thermodynamic parameters (298.15 K), free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were -3475.79 J/mol, -25.36 kJ/mol, and -73.40 J/mol/K, respectively. The negative $\Delta G°$ value of indicated that the biosorption process was feasible and spontaneous. The interactions between dicloxacillin and functional groups on the biomass surface were estimated by FT-IR. The SEM analysis confirms dicloxacillin adsorption. The intermolecular interaction such as hydrogen bonds or Van der Waals forces can be the main interaction for the dicloxacillin and the surface properties of adsorbent. The adsorption data are best supported by Langmuir model with correlation coefficient of 0.965. Kinetics for the removal of dicloxacillin were obtained and fitted to different kinetics models. Kinetics data were best fitted by the pseudo-second-order model and the result indicated that Indian almond leaves adsorbent is excellent in the removal of dicloxacillin (penicillin antibiotics) from pharmaceutical waste water.

Author contribution statement

Suphot Phatanasri and Ura Pancharoen conceived the experiments. Niti Sunsandee conducted the experiments. Data analyses were done by Niti Sunsandee with consultation with Suphot Phatanasri, Ura Pancharoen and Prakorn Ramakul. The paper was written by Niti Sunsandee, Suphot Phatanasri, and all authors contributed to the subsequent drafts. All authors reviewed the manuscript.

Declaration of Competing Interest

The authors declare no competing interests and conflict of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.btre.2020.e00488.

References

[1] A. Angelakis, S. Snyder, Wastewater treatment and reuse: past, present, and future, Water 7 (2015) 4887–4895.
[2] Z. Chen, N. Ren, A. Wang, Z.P. Zhang, Y. Shi, A novel application of TPAD–MBR system to the pilot treatment of chemical synthesis-based pharmaceutical wastewater, Water Res. 42 (2008) 3385–3392.
[3] N. Nakada, K. Kiri, H. Shinohara, A. Harada, K. Kuroda, S. Takizawa, H. Takada, Evaluation of pharmaceuticals and personal care products as water-soluble molecular markers of sewage, Environ. Sci. Technol. 42 (2008) 6347–6353.

[4] Y.A. Oktem, O. Ince, P. Sallis, T. Donnelly, B.K. Ince, Anaerobic treatment of a chemical synthesis-based pharmaceutical wastewater in a hybrid up flow anaerobic sludge blanket reactor, Bioresour. Technol. 99 (2007) 1089–1096.

[5] A.B.A. Boxall, The environmental side effects of medication, Eur. Mol. Biol. Org. 5 (2004) 1110–1116.

[6] J.M. Smith, E.J. Feil, N.H. Smith, Population structure and evolutionary dynamics of pathogenic bacteria, BioEssays 22 (2000) 1115–1122.

[7] S.C. Davies, T. Fowler, J. Watson, D.M. Livermore, D. Walker, Annual report of the chief medical officer: infection and the rise of antimicrobial resistance, Lancet 381 (2013) 1606–1609.

[8] D.M. Livermore, Discovery research: the scientific challenge of finding new antibiotics, J. Antimicrob. Chemother. 66 (2011) 1941–1944.

[9] M.L. Cohen, Epidemiology of drug resistance: implications for a post-antimicrobial era, Science 257 (1992) 1050–1055.

[10] H.C. Neu, The crisis in antibiotic resistance, Science 257 (1992) 1064–1073.

[11] P.J.G. Henriksson, A. Rico, M. Troell, D.H. Klinger, A.H. Buschmann, S. Saksida, M.V. Chadag, W. Zhang, Unpacking factors influencing antimicrobial use in global aquaculture and their implication for management: a review from a systems perspective, Sustain. Sci. 13 (2018) 1105–1120.

[12] M. Lobanovska, G. Pilla, Penicillin's discovery and antibiotic resistance: lessons for the future? Yale J. Biol. Med. 90 (1) (2017) 135–145.

[13] S.D. Bhinge, S.M. Malipatil, Development and validation of a stability-indicating method for the simultaneous estimation of cefixime and dicloxacillin using the RP-HPLC method, J. Taibah Univ. Sci. 10 (5) (2016) 734–744.

[14] N.G. Donskaya, V.L. Lapidus, G.S. Libinson, P.S. Braginskaya, Stability of dicloxacillin in aqueous solution, Pharm. Chem. J. 10 (1976) 518–521.

[15] P. Villegas-Guzman, J. Silva-Agredo, Ana L.G. Aguirre, O. Flórez-Acosta, C. Petrier, A. Ricardo, Torres-Palma Enhancement and inhibition effects of water matrices during the sonochemical degradation of the antibiotic dicloxacillin, Ultrason. Sonochem. 22 (2015) 211–219.

[16] M.L. Richardson, J.M. Bowron, The fate of pharmaceutical chemicals in the aquatic environment, J. Pharm. Pharmacol. 37 (1985) 1–12.

[17] R. Hirsch, T. Ternes, K. Haberer, K.L. Kratz, Occurrence of antibiotics in the aquatic environment, Sci. Total Environ. 225 (1999) 109–118.

[18] D.I. Andersson, D. Hughes, Evolution of antibiotic resistance at non-lethal drug concentrations, Drug Resist. Updat. 15 (2012) 162–172.

[19] P. Grenni, V. Ancona, A.B. Caracciolo, Ecological effects of antibiotics on natural ecosystems: a review, Microchem. J. 136 (2018) 25–39.

[20] FDA, Annual Per Capita PPCP Consumption Were Calculated Considering the Population Data in Each Country in the Particular Year and Based on the Annual PPCPs' Consumption Thailand, (2009) .

[21] V. Sawaittayotin, Department of Environmental Quality Promotion, Contamination of Pharmaceutical and Health Care Products in the Bang Pakong River, (2016) .

[22] K. Kümmerer, Antibiotics in the aquatic environment - A review - Part II, Chemosphere. 75 (2009) 435–441.

[23] B. Spellberg, Antibiotic resistance and antibiotic development, Lancet Infect. Dis. 8 (2008) 211–212.

[24] S.Z. Li, X.-y. Li, D.-z. Wang, Membrane (RO-UF) filtration for antibiotic wastewater treatment and recovery of antibiotics, Sep. Purif. Technol. 34 (2004) 109–114.

[25] A. Berrazoum, R. Marouf, F. Ouadjenia, J. Schott, Bioadsorption of a reactive dye from aqueous solution by municipal solid waste, Biotechnol. Rep. 7 (2015) 44–50.

[26] N. Das, Recovery of precious metals through biosorption - a review, Hydrometallurgy 103 (2010) 180–189.

[27] J.M. do Nascimento, J.D. de Oliveira, A.C.L. Rizzo, S.G.F. Leite, Biosorption Cu (II) by the yeast Saccharomyces cerevisiae, Biotechnol. Rep. 21 (2019)e00315.

[28] I.A. Sengil, M. Özacar, H. Türkmenler, Kinetic and isotherm studies of Cu(II) biosorption onto valonia tannin resin, J. Hazard. Mater. 162 (2009) 1046–1052.

[29] S. Hassanpour, N. Maheri-Sis, B. Eshratkhah, F.B. mehmandar, Plants and secondary metabolites (Tannins): a Review, Int. J. Forest Soil Erosion 1 (2011) 47–53.

[30] C. Somta, A. Winotai, P. Ooi, Fruit flies reared from Terminalia catappa in Thailand, J. Asia-Pac. Entomol. 13 (2010) 27–30.

[31] A. Silva, C. Delerue-Matos, S.A. Figueiredo, O.M. Freitas, Review the use of algae and Fungi for removal of pharmaceuticals by bioremediation and biosorption processes. A review, Water 11 (8) (2019) 1555–1591.

[32] J.J. Menk, A.I.S. do Nascimento, F.G. Leite, R.A. de Oliveira, A.F. Jozala, J.M. de Oliveira Junior, M.V. Chaud, D. Grotto, Biosorption of pharmaceutical products by mushroom stem waste, Chemosphere 237 (2019).

[33] N. Chansue, N. Assawawongkasem, The in vitro antibacterial activity and ornamental fish toxicity of the water extract of indian almond leaves (*Terminalia catappa* Linn.) KKU, Vet. J. 18 (2008) 36–45.

[34] S.M. Ahmed, V. Swamy, P.G.R. Dhanapal, V.M. Chandrashekara, Anti-diabetic activity of Terminalia catappa Linn. leaf extracts in alloxan-induced diabetic rats, Iran. J. Pharmacol. Ther. 4 (1) (2005) 36–39.

[35] D.F. Hayward, The phenology and economic potential of Terminalia catappa L. in south-central Ghana, Vegetatio 90 (1990) 125–131.

[36] T.C. Lin, F.L. Hsu, Tannin and related compounds from Terminalia catappa and Terminalia parviflora, J. Chin. Chem. Soc. 46 (1999) 613–618.

[37] Y.L. Lin, Y.H. Kuo, M.S. Shiao, C.C. Chen, J.C. Ou, Flavonoid glycosides from Terminalia catappa L, J. Chin. Chem. Soc. 47 (2000) 253–256.

[38] P. Insain, S. Khonyoung, P. Sooksamiti, S. Lapanantnoppakhun, J. Jakmunee, K. Grudpan, K. Zajicek, S. Kradtap, Green analytical methodology using indian almond (Terminalia catappa L.) leaf extract for determination of aluminum ion in waste water from ceramic factories, Anal. Sci. 29 (2013) 655–659.

[39] K.T. Chung, Z. Lu, M.W. Chou, Mechanism of inhibition of tannic acid and related compounds on the growth of intestinal bacteria, Food Chem. Toxicol. 36 (12) (1998) 1053–1060.

[40] M. Karamać, R.B. Pegg, Limitations of the tetramethylmurexide assay for investigating the Fe(II) chelation activity of phenolic compounds, J. Agric. Food Chem. 57 (14) (2009) 6425–6431.

[41] B.S. Inbaraj, N. Sulochana, Mercury adsorption on a carbon sorbent derived from fruit shell of Terminalia catappa, J. Hazard. 133 (2006) 283–290.

[42] P. Ramakul, Y. Yanachawakul, N. Leepipatpiboon, N. Sunsandee, Biosorption of palladium(II) and platinum(IV) from aqueous solution using tannin from Indian almond (Terminalia catappa L.) leaf biomass: kinetic and equilibrium studies, Chem. Eng. J. (2012) 102–111.

[43] D. Parajuli, H. Kawakita, K. Inoue, K. Ohto, K. Kajiyama, Persimmon peel gel for the selective recovery of gold, Hydrometallurgy 87 (2007) 133–139.

[44] The United States Pharmacopeia 41 National Formulary 36, Webcom Limited. The United States Pharmacopeia Convention, Canada, 2018.

[45] J. Goldstein, D. Newbury, D. Joy, C. Lyman, P. Echlin, E. Lifshin, L. Sawyer, J. Michael, Scanning Electron Microscopy and X-ray Microanalysis, 3rd ed., Springer, New York, NY, 2003.

[46] M.A. Hashim, K.H. Chu, Biosorption of cadmium by brown, green, and red seaweeds, Chem. Eng. J. 97 (2004) 249–518.

[47] M.S. Chiou, H.Y. Li, Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads, Chemosphere 50 (2003) 1095–1105.

[48] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[49] A.D. Westland, E.O. Otu, The thermodynamics of extraction of some lanthanide and other ions by 2-ethylhexylhydrogen-p-phenylphosphonate, Solvent Extr. Ion Exch. 9 (1991) 607–621.

[50] E.O. Otu, A.D. Westland, The thermodynamics of extraction of some lanthanides and other ions by dinonylnaphthalene sulfonic acid, Solvent Extr. Ion Exch. 8 (1990) 827–842.

[51] F. Gritti, G. Guiochon, Adsorption mechanisms and effect of temperature in reversed-phase liquid chromatography. Meaning of the classical Van't Hoff Plot in chromatography, Anal. Chem. 78 (2006) 4642–4653.

[52] F. Angulo-Brown, L. Arias-Hernández, Van't Hoff's equation for endoreversible chemical reactions, J. Phys. Chem. 100 (1996) 9193–9195.

[53] E.O. Otu, The thermodynamics of synergistic extraction of bismuth by 2-ethylhexyl phenylphosphonic acid and micelles of dinonyl naphthalene sulfonic acid, Thermochim. Acta 329 (1999) 117–121.

[54] A. Sarı, M. Tuzen, Biosorption of cadmium (II) from aqueous solution by red algae (Ceramium virgatum): equilibrium, kinetic and thermodynamic studies, J. Hazard. Mater. 157 (2008) 448–454.

[55] A. Lodi, C. Solisio, A. Converti, M. Del Borghi, Cadmium, zinc, copper, silver and chromium(III) removal from wastewaters by Sphaerotilus natans, Bioproc. Eng. 19 (1998) 197–203.

[56] N. Das, Recovery of precious metals through biosorption – a review, Hydrometallurgy 103 (2010) 180–189.

[57] A. Nakajima, T. Sakaguchi, Uptake and recovery of gold by immobilised persimmon tannin, J. Chem. Technol. Biotechnol. 57 (1993) 321–326.

[58] M. Yurtsever, i.A. Sengil, Adsorption and desorption behavior of silver ions onto valonia tannin resin, Trans. Nonferrous Met. Soc. China 22 (2012) 2846–2854.

[59] C.W. Oo, M.J. Kassim, A. Pizzi, Characterization and performance of Rhizophora apiculata mangrove polyflavonoid tannins in the adsorption of copper (II) and lead (II), Ind Crop Prod. 30 (2009) 152–161.

[60] H. Wang, A. Zhou, F. Peng, H. Yu, J. Yang, Mechanism study on adsorption of acidified multi-walled carbon nanotubes to Pb(II), J. Colloid Interface Sci. 316 (2007) 277–283.

[61] M. Özacar, İ.A. Şengil, H. Türkmenler, Equilibrium and kinetic data, and adsorption mechanism for adsorption of lead onto valonia tannin resin, Chem. Eng. J. 143 (2008) 32–42.

[62] X. Han, W. Wang, X. Ma, Adsorption characteristics of methylene blue onto low cost biomass material lotus leaf, J. Chem. Eng. 171 (2011) 1–8.

[63] A. Fakhri, S. Adami, Adsorption and thermodynamic study of Cephalosporins antibiotics from aqueous solution onto MgO nanoparticles, J. Taiwan Inst. Chem. Eng. 45 (2014) 1001–1006.

[64] T. Ogata, Y. Nakano, Mechanisms of gold recovery from aqueous solutions using a novel tannin gel adsorbent synthesized from natural condensed tannin, Water Res. 39 (2005) 4281–4286.