



Removing amoxicillin antibiotic from aqueous solutions by *Saccharomyces cerevisiae* bioadsorbent: kinetic, thermodynamic and isotherm studies

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Received 7 November 2018; Accepted 12 February 2019

ABSTRACT

Antibiotics are used throughout the world and enter the water resources in different ways after consumption and have turned into one of the important concerns for humans due to their adverse effects of which amoxicillin (AMX) could be referred to. Thus, present research aims to study the efficiency of bioadsorbent produced from *Saccharomyces cerevisiae* in removing AMX antibiotic from aqueous solutions. The present experimental study was carried out in a discontinued reaction chamber with an optimal volume of 100 cc. The physical and structural specifications of the produced bioadsorbent were analyzed using FTIR, SEM and BET techniques. This study was carried out by culturing *Saccharomyces cerevisiae* strain on the culture medium of potato dextrose agar and the yeast was transferred to potato dextrose broth culture, 5–7 d after the primary growth of the yeast in order to produce yeast extensively. The effects of pH (2–8), initial concentration of AMX (5–25 mg L⁻¹), the amount of bioadsorbent (0.1–1.5 g L⁻¹) and contact time (10–240 min) were studied in this process. The isothermal models of Langmuir, Freundlich and Dubinin–Radushkevich were used to determine the balance isotherms, pseudo-first and pseudo-second-order kinetic model adsorption process kinetics. Results revealed that the highest efficiency of AMX removal was obtained by bread yeast bioadsorbent at initial antibiotic concentration of 5 mg L⁻¹, bioadsorbent concentration, 0.75 g L⁻¹ and optimal conditions including pH of 5 and contact time of 120 min (93%). Also, results indicate that the adsorption of AMX with the correlation coefficient of 0.939 follows the Freundlich model. Experimental data showed that AMX follows the pseudo-second-order kinetics with the correlation coefficient of 0.99. It can be concluded that the use of the bread bioadsorbent yeast for reducing the pollution load of hospital and manufacturing industries' sewage before entering into conventional treatment units and also before the final discharge of wastewaters containing antibiotic pollutants.

Keywords: Bioadsorbent; *Saccharomyces cerevisiae*; Amoxicillin; Aqueous solutions; Isotherm

1. Introduction

Presence of antibiotics in the environment especially in aquatic ones is considered a major concern. These antibiotics

are used to improve the health of human and livestock and to raise the growth in fish and livestock farms [1,2]. These medicines are usually absorbed in the body weakly. A major part of these materials is removed from the body through urine or stool without any changes or with slight changes and is

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mostly entered into the sewage networks and, ultimately, into the sewage treatment plants [3–5]. The low concentration of these antibiotics leads to antibiotic resistance in the bacteria and genes [6]. Moreover, livestock medicines and antibiotics in low concentrations result in disorder in reproduction and endocrine glands [7]. Studies show that the concentration of antibiotics is at 0.3–200 $\mu\text{g L}^{-1}$ or higher in the hospital and urban wastewater [8]. The standard determined by the US Environmental Protection Agency (EPA) for the presence of these pharmaceutical ingredients is 1 mg L^{-1} in treated wastewaters [9]. Amoxicillin (AMX) is a broad spectrum β -lactam antibiotic (aminopenicillin antibiotic), used as veterinary medicine for treatment of infections encountered in gastrointestinal and systemic infections, and also, commonly used as the human prescription medicine (against infections caused by bacteria) [10,11]. AMX consumption is higher than the other types in the penicillin family because of the oral absorption ability [10], and unfortunately, it is non-biodegradable and also an inhibitor of the photosynthesis mechanism of algae *Synechocystis* sp. [10,11].

This compound has the least metabolism among all medicines; so that 10%–20% of them are absorbed in the body after consumption and 80%–90% of them are discharged into the environment through urine and stool with no changes [12,13]. The concentration of antibiotics in this group is equal to 48 ng L^{-1} in surface waters and the concentration of AMX is in the range of 28–82.7 mg L^{-1} in hospital wastewater [14]. This antibiotic has been identified in surface waters, and the wastewater released from hospital and pharmacy factories and it could be adsorbed in sludge and in case of being used as a fertilizer, it is accumulated in the soil and enters into the soil and vegetables such as lettuce, cucumber and barley [15,16].

Different methods such as ion exchange, biological treatment, reverse osmosis, adsorption and advanced oxidation could be used in order to remove antibiotics from water resources [17]. Fungi and yeasts are large and various groups of eukaryotic organisms that have a considerable effect on the growing trend of other organisms. Also, fungi are used to manufacture the industrial materials such as ethanol, citric acid, antibiotics, poly-saccharides, enzymes and vitamins and the bioadsorbent could be used to remove heavy metals, radioactive substances and other materials [18]. The removal of pollutants from aqueous solutions using methods such as ion exchange, chemical depositing, electrochemical depositing and membrane filters by means of bioadsorbent process is advantageous compared with other conventional methods due to its advantages such as low implementation cost, high efficiency in removing materials with low concentration and lack of producing secondary pollution [19]. In regard to bioadsorbent, the molds, yeasts and other types of fungi have considerably been used. Yeasts are mono-cellular fungi, mostly being among the ascomycetes group [20]. The most important commercial yeasts consist of bread and beer yeasts that are mostly of *Saccharomyces* type [21].

The main habitat of yeasts is certainly the fruits and fruit juices. But the commercial yeasts are really different from its wild type because, during years of studying, these yeasts have genetically been changed and their production has been improved qualitatively and quantitatively [22]. Pre-treatment and modification of consumptive yeast could significantly

raise efficiency [23]. Nowadays, the methods applied for the modification of *Saccharomyces cerevisiae* include the use of autoclave state, dry ice, vacuum, mechanical disorder, methanol, formaldehyde and caustic soda [24].

The present study aims at preparing the bioadsorbent from *Saccharomyces cerevisiae* for the removal of AMX from aqueous solutions. Effective parameters in the adsorption process including pH, contact time, amount of bioadsorbent, concentration of pollutant, the temperature of the process were studied and the characteristics of prepared bioadsorbents, isotherms, kinetics and thermodynamics of the adsorption in this investigation were determined.

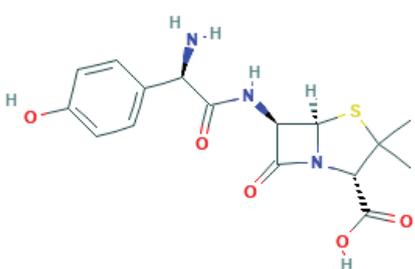
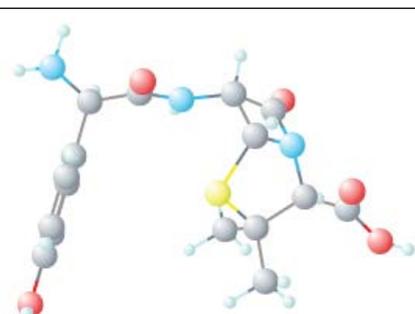
2. Materials and methods

This experimental study was conducted to investigate the removal of amoxicillin (AMX) antibiotic from aqueous solutions by *Saccharomyces cerevisiae* bioadsorbent.

2.1. Chemicals and analytical procedure

All materials required such as NaOH and HCl were purchased from Merck. AMX with chemical formula $\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}_5\text{S}$ (purity $\geq 99\%$) was purchased from Sigma-Aldrich (St. Louis, MO, USA), and its characteristics are summarized in Table 1. For modification of pH, 0.1 N HCl and NaOH were applied. Culture media such as potato dextrose agar (PDA) and

Table 1
Amoxicillin chemical structure and its related information

| Component | Information/schematic/value |
|--|---|
| Compound | Amoxicillin |
| Molecular (chemical) formula | $\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}_5\text{S}$ |
| 2D structure |  |
| 3D structure |  |
| Molecular weight (g mol^{-1}) | 365.4 |
| Melting point ($^{\circ}\text{C}$) | 194 |

potato dextrose broth (PDB) were purchased from Merck (Germany). *Saccharomyces cerevisiae* was purchased from collections of fungi and bacteria available in Biotechnology Research Institute of Iran. All chemicals used in this study were of analytical grade type and used without further purification. A stock solution of 100 mg L⁻¹ containing amoxicillin was prepared, and dilution was performed for the calibration solutions and adsorption study solutions.

After adjusting all components of the freshly prepared solution, samples were collected at predetermined time intervals by passing through the 0.45 µm membrane filter and measured for the final AMX content by using a spectrophotometer (model 1700, HACH, USA) at a wavelength of 230 nm. At the first, the samples were centrifuged using a centrifuge for 5 min to eradicate the disturbance of bioadsorbent in determining the concentration. Then, the syringe filter was used for more assurance and safety of the samples.

2.2. Culture and preparation of bioadsorbent

Having been received in the form of dry ice in 10 mL of sterilized water 45 min before transferring to the PDA culture medium, the fungal species were activated. Approximately 2 mL of the suspension was transferred to the plates. These plates were kept in an incubator at 25°C for 7–10 d. This yeast was cultured using the shake-flask method in a liquid culture medium. Spores and mycelium were transferred from the growth medium of PDB. After inoculation, the dishes were put on a rotating shaker with 150 rpm at 25°C for 4 d. The yeast was grown through filtering the culture medium using a 150 µm filter. This washed yeast is called living yeast. This yeast was kept in an oven at 60°C for 12 h until it was dried completely, then it was turned into a powder and mashed up.

2.3. Effect of contact time

Samples of AMX with a fixed concentration of 10 mg L⁻¹, 0.5 g of adsorbent at pH = 5 were prepared and were mixed in 100 cc reactor at 150 rpm and were sampled at different time intervals of 10–240 min and their concentration was measured.

2.4. Effect of pH

Samples with initial pH values of 2–8 with a fixed concentration of AMX (10 mg L⁻¹) and the adsorbent dose of 0.5 g L⁻¹ were prepared in order to determine the optimum pH. The concentration of antibiotic was measured after the retention time of 120 min and the optimum pH was determined given the removal efficiency. To adjust the pH of the solution, 0.01 M HCl and NaOH were applied.

2.5. Effect of the amount of adsorbent

In this stage, samples with fixed concentrations (10 mg L⁻¹) were prepared and the adsorbent dose was changed from 0.1 to 1.5 g L⁻¹ and the samples were analyzed at optimum contact time and optimum pH according to previous stages in order to study the effect of the amount of adsorbent on the adsorption process.

2.6. Effect of the initial concentration of AMX

In this stage, 5, 10, 15, 20 and 25 mg L⁻¹ of AMX solutions were prepared and experimented in order to optimize the initial concentration of AMX.

2.7. Kinetics of the reaction

The pseudo-first-order and pseudo-second-order models were used in this stage and the results obtained from the effect of contact time on the kinetics of the reactions were studied and in the end, the best kinetic model of the process was determined based on the correlation coefficient.

2.8. Adsorption studies

Experiments were carried out under discontinued conditions in this study. To carry out each experiment, 100 mL of AMX solution was used at different concentrations in a 250 mL Erlenmeyer, with 0.5 g adsorbent. The Erlenmeyer was put on to a shaker with 100 rpm at room temperature and moisture conditions. The 1 N NaOH and 1 N HCl were used for pH adjusting. After mixing, all samples were prepared by filtering with a 0.45 mm cellulose acetate filter and vacuum pump.

The adsorption capacities of adsorbent (q_e , mg g⁻¹) were calculated by the Eq. (1). C_0 and C_e (mg L⁻¹) are initial concentration and equilibrium concentration of amoxicillin, respectively; V (L) is the volume of the solution; m (g) is the amount of adsorbent. The removal efficiency was calculated by Eq. (2).

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (1)$$

$$\text{Removal \%} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

2.9. Isotherms of adsorption

Adsorption in a solid–liquid system consists of removing soluble material from the solution and its accumulation on the surface of the solid material. This is a balance between the concentration of the given soluble material in the solution, its concentration and the characteristics of competitive soluble substances, characteristics of the solution and so on. The isotherm models of Freundlich, Langmuir and Dubinin–Radushkevich were studied in this investigation.

2.9.1. Freundlich adsorption isotherm

Freundlich equation states adsorption at a heterogeneous surface in terms of adsorption energy and this equation is experimental and applicable for the interpretation of laboratory data. Freundlich equation could be calculated in the form of Eq. (3) [25].

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

In this equation, $\log k_p$ the intercept of the Freundlich model, is an index of adsorption capacity and, $1/n$, slope of the Freundlich model, is representative of adsorption intensity. Freundlich model is well in agreement with Langmuir equation and laboratory data at average concentrations of adsorbed substance but it does not conform to the Langmuir equation at very high concentrations of adsorbed substance [26,27].

2.9.2. Langmuir adsorption isotherm

Langmuir equation isotherms are as follows: (1) when the surface of adsorbent is covered with a single-molecular layer of soluble substance, the highest adsorption is obtained. (2) The adsorption energy is the same and fixed in all points. (3) The molecules of adsorbent are not able to move at the surface of the adsorbent. Langmuir equation is stated in the form of Eq. (4).

$$\frac{C_e}{q_e} = \frac{1}{K_a Q_m} + \frac{C_e}{Q_m} \tag{4}$$

where C_e is the concentration of AMX at equilibrium (mg L^{-1}), q_e is the adsorption capacity at equilibrium (mg g^{-1}), Q_m is the maximum adsorption capacity (mg g^{-1}) and K_a is the constant of Langmuir equation (mg L^{-1}) [28].

2.9.3. Dubinin–Radushkevich isotherm

The linear figure has been shown in Eqs. (5) and (6) where ϵ is the Polanyi potential that is obtained according to Eq. (7), R is the general constant of gases ($\text{kJ mol}^{-1} \text{K}^{-1}$), T is temperature (K), q_m is adsorption capacity (mg g^{-1}) and β is adsorption energy (kJ mol^{-1}) that is obtained by drawing the q_e diagram against ϵ^2 [29].

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \tag{5}$$

$$\log Q_e = \log Q_m - \beta \epsilon \log Q_e = \log K_f + \frac{1}{n} \log C_e \tag{6}$$

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \tag{7}$$

2.10. Thermodynamics of AMX adsorption

The thermodynamic parameters for achieving the best conditions of AMX adsorption were studied in this investigation. It is necessary to determine parameters such as enthalpy (ΔH), entropy (ΔS) and Gibb’s free energy (ΔG) in studying thermodynamics and it is conducted based on Eqs. (8)–(10).

$$K_d = \frac{q}{C_e} \tag{8}$$

$$\Delta G = -RT \ln K_d \tag{9}$$

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{10}$$

where k_d is the balance constant, ΔG is free adsorption energy (kJ mol^{-1}), T is reaction temperature in Kelvin and R is universal constant of gases ($8/314 \text{ J mol}^{-1} \text{K}^{-1}$). In Eq. (10), the slope and intercept were indicative of diagram of ΔS and $-\Delta H$ in $\text{Ln } k_d$ against $1/T$, given its line equation [30–32].

2.11. FTIR, BET, SEM experiments

Scanning electron microscope (SEM) is an appropriate tool to study the appearance and morphology of the adsorbent. This tool is used to determine the shape and presence of pores. BET test was used to measure the specific surface of bioadsorbent, mean diameter of pores and its volume. FTIR spectrum was used to study and identify the functional groups on the adsorbent.

3. Results and discussion

3.1. Characterization of adsorbents

The specific surface of bioadsorbent was achieved to be $36.6 \text{ m}^2 \text{g}^{-1}$ based on the results of BET test (Table 2). This amount of specific surface is more than that of other adsorbents such as nuts and almond shells [33]. Based on the method of Barrett, Joyner, and Halenda results, the mean diameter of the pores was determined to be 6.49 nm . According to IUPAC classification, the structure of porous materials given the mean of pore dimensions could contain pores smaller than 2 nm called micro-pore, between 2 and 50 nm , meso-pore and pores larger than 50 nm , micro-pore. Given the results, the bioadsorbent produced is of meso-pore type.

The SEM and FTIR patterns before and after the treatment are presented in Figs. 1 and 2, respectively. The SEM is a good method and widely used to investigate the morphological features of adsorbent materials.

Given the SEM images, the noncrystalline surface of bioadsorbent contains pores and is also layered and this feature results in adsorbing amoxicillin (AMX) on the given bioadsorbent (Fig. 1(b)).

An FTIR spectroscopy was used to determine the vibrational characteristics of chemical functional groups in the biosorbent [34]. Results of FTIR showed that spectrums between 400 and $1,200 \text{ cm}^{-1}$ belong to mineral materials in bioadsorbents such as carbonate, phosphate, sulfate and nitrate. *Saccharomyces cerevisiae* bioadsorbent consists of different functional groups such as amines, alcohols, carbonyl and hydroxyl [34].

Table 2
Characteristics studied bioadsorbents

| Characteristics | BET |
|---------------------------------------|--------------------------------------|
| Vm | $0.843 \text{ cm}^3 \text{g}^{-1}$ |
| Special level, BET | $36.692 \text{ m}^2 \text{g}^{-1}$ |
| Total pore volume ($p/p_0 = 0.990$) | $0.59588 \text{ cm}^3 \text{g}^{-1}$ |
| Mean pore diameter | 6.496 nm |

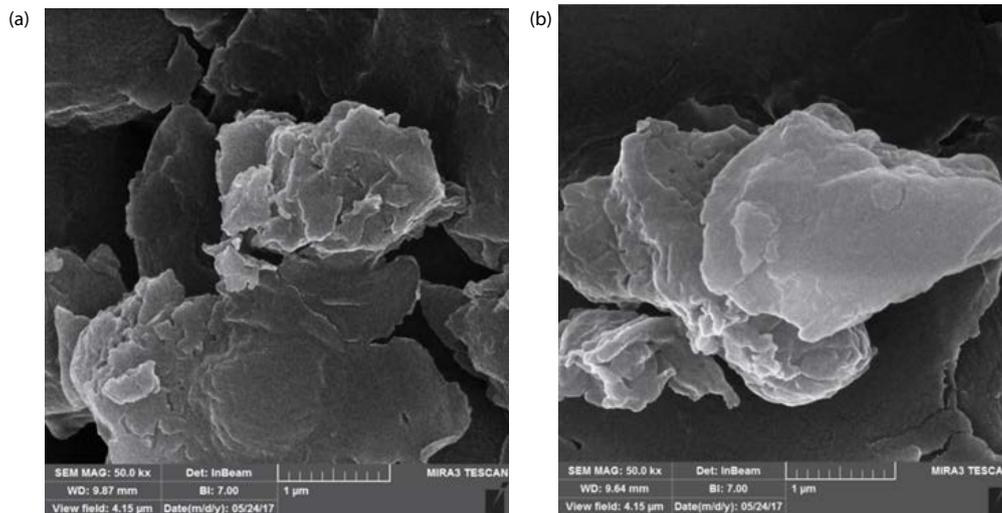


Fig. 1. SEM images bioadsorbents yeast (a) before adsorbing and (b) after adsorption.

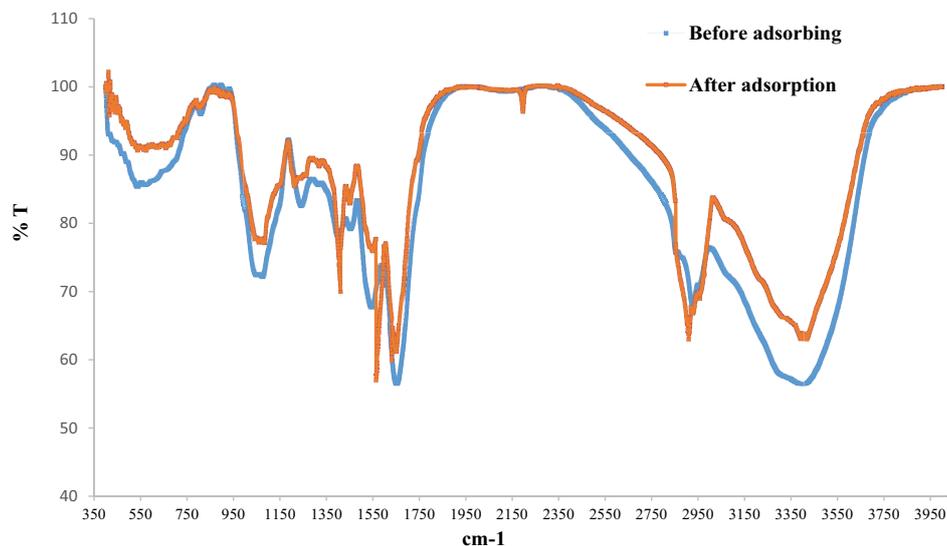


Fig. 2. FTIR images bioadsorbents yeast.

Spectrums between 3,200 and 3,600 cm^{-1} are related to stretching area functional groups of O–H and N–H [35]. Spectrums between 2,400 and 2,950 cm^{-1} are related to stretching area of C–H. Peaks between 3,449 and 2,999 cm^{-1} are related to functional groups of hydroxyl and amines. Also, peaks between 2,190 and 2,928 cm^{-1} are indicative of the presence of C–H groups. Two peaks of 1,594 and 1,665 cm^{-1} indicate the presence of functional group of amines. Peak of 1,649 cm^{-1} proves the presence of carbonyl group on the surface of bioadsorbent. Given the results, the preference of shifts and shortening and widening of peaks after the adsorption process is indicative of AMX adsorption on the bioadsorbent.

3.2. Effect of time

Contact time is one of the effective factors in the adsorption process. The results associated with the effect

of contact time on the adsorption rate of AMX are shown in Fig. 3. In this investigation, 0.5 g of bioadsorbent in 100 cc of 10 mg L^{-1} of AMX solution at pH 5 and the contact time of 10–240 min was studied. Results showed that the amount of AMX adsorption rises with increasing contact time. This increase in adsorption was rapidly done up to 90 min, but then a considerable increase in adsorption was not observed up to 120 min and indeed the amount of antibiotic adsorption was balanced and desorption was observed after 240 min.

The presence of empty places on the surface of bioadsorbent indicates an increase in adsorption rate in the first 90 min that is consistent with the results of the study conducted by Ersan (2016) [36]; in their study, the *Saccharomyces cerevisiae* biocomposite was used to remove tetracycline (TC) from aqueous solutions. It was revealed that the highest rate of TC adsorption was obtained at the retention time of 160 min [36].

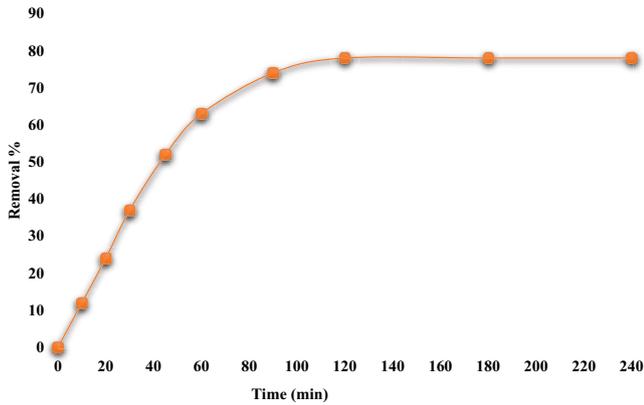


Fig. 3. Effect of time on the removal of AMX (pH 5, $m_{\text{sorbent}} = 0.5 \text{ g L}^{-1}$, $C_0 = 10 \text{ mg L}^{-1}$).

3.3. Effect of pH

The pH value of the aqueous solution plays an important role in the adsorption and biosorption processes. It affects the speciation of AMX, the surface characteristics of the biosorbent, and the chemical properties of the biosorbent during reaction [37].

pH influences adsorption capacity and the surface charge of the adsorbent and leads to ionization of substance in the solution and separation of functional groups on the active sites of the bioadsorbent. The functional groups on the cell wall of bioadsorbent and active sites are the main factors in the adsorption of AMX on the bioadsorbent of bread yeast. Amines are proteinurized and their electrostatic charge becomes positive [38] and results in the adsorption of AMX on the adsorbent. The effect of the initial pH on the AMX removal at the range values of 2–8 is presented in Fig. 4. Varying the initial pH value has an important effect on the efficiency of AMX removal. The optimum removal efficiency was obtained at a pH of 5 (81%). Fazelirad et al. [39] showed the optimum pH was 4.62 for amoxicillin adsorption by multi-walled carbon nanotubes. At lower pH, bioadsorbent functional groups and sulfur atoms will be protonated and adsorbent acquires positive charge and finally, AMX antibiotic adsorbs onto the bioadsorbent via attractive forces.

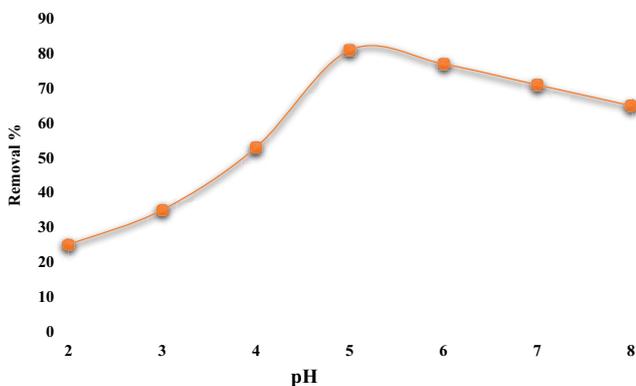


Fig. 4. Effect of the pH on the removal of AMX ($m_{\text{sorbent}} = 0.5 \text{ g L}^{-1}$, time = 120 min, $C_0 = 10 \text{ mg L}^{-1}$).

The pH_{ZPC} of bioadsorbent was measured to be 6.91, meaning that the electrostatic charge of the solution is positive at pH lower than pH_{ZPC} and it is negative above it [40] and given the type of pollutant, adsorption is done better at pH lower than that of pH_{ZPC} . Another reason for the highest adsorption at pH = 5 could be attributed to the transformation of the bioadsorbent at other pHs. In fact, the greatest strength of the cell wall structure is achieved at pH = 5 and its structure is decomposed at other pHs. The results of this study are in agreement with those of Maurya et al. [41] and Nguyen and Juang [42].

3.4. Effects of the initial AMX concentration

The effects of the initial AMX amount on the removal of AMX were studied by varying the AMX amount (5–25 mg L⁻¹) and the results are presented in Fig. 5. The results show that by increasing the AMX concentration, the removal AMX efficiency decreased. The highest removal efficiency was obtained in amoxicillin concentration of 5 mg L⁻¹ (93%).

3.5. Effect of bioadsorbent dosage

The effect of bioadsorbent dosage on the AMX adsorption was studied by varying the bioadsorbent dose from 0.1 to 1.5 g L⁻¹ and the results are presented in Fig. 6.

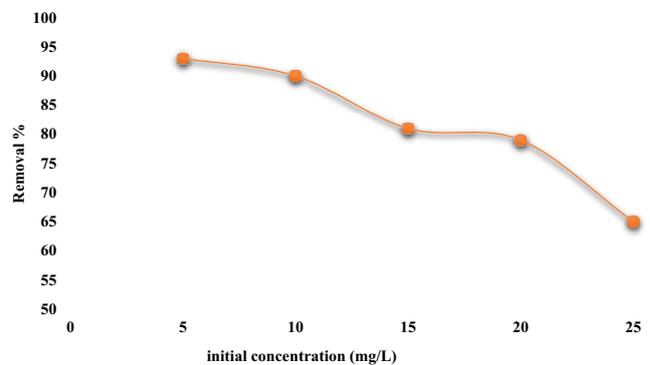


Fig. 5. Effect of initial AMX concentration on the removal of AMX (pH = 5, $m_{\text{sorbent}} = 0.75 \text{ g L}^{-1}$, time = 120 min).

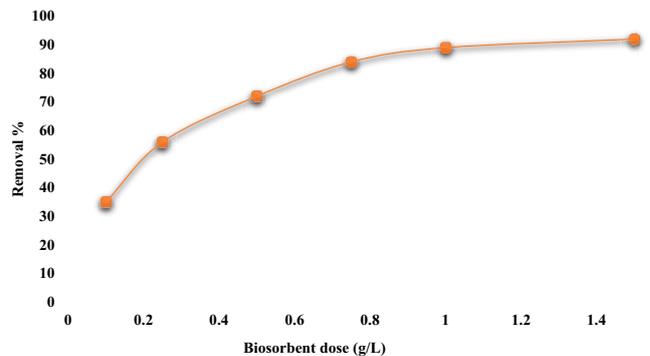


Fig. 6. Effect of the bioadsorbent dosage on the removal of AMX ($C_0 = 10 \text{ mg L}^{-1}$, time = 120 min, pH = 5).

Results revealed that the efficiency of AMX rises by increasing the value of bioadsorbent and this increase in efficiency could be attributed to an increase in the contact surface of the bioadsorbent which in turn results in an increase in active sites that leads to the adsorption of antibiotic onto the bioadsorbent (Chen et al., 2013). But an increase in the amount of bioadsorbent results in decreasing the capacity of adsorption. This could be attributed to lack of saturation of the active sites of bioadsorbent during the adsorption process [43]. According to Fig. 6, the adsorption of AMX has had appropriate speed up to 0.75 g L^{-1} of the bioadsorbent and a significant increase was not observed in the adsorption rate at higher values of bioadsorbent. Thus, 0.75 g L^{-1} of bioadsorbent was considered the optimal dose of bioadsorbent.

3.6. Determination of adsorption isotherms

Adsorption isotherm could be used to describe the reaction between the absorbed matter and adsorbent and to optimize the rate of adsorbent application; the compliance of each system is determined by drawing the curve associated with each balance and comparing correlation coefficient with experimental results. Each of these isotherms consists of specific features that are used to compare and evaluate the models. Important parameters that must be determined for predicting whether the adsorption is appropriate are the dimensionless coefficients of R_L , n and E that are derived from Langmuir, Freundlich and Dubinin–Radushkevich (D–R) equations. Equilibrium parameter of R_L is defined in the form of Eq. (11).

$$R_L = \frac{1}{1 + bC_0} \quad (11)$$

where b is the Langmuir constant and C_0 is the initial concentration of AMX. The value of R_L shows the type of the isotherm; $R_L = 0$, the irreversible isotherm, $0 < R_L < 1$, desirable isotherm, $R_L = 1$, linear isotherm and $R_L > 1$, undesirable isotherm.

In Freundlich, $1/n$, the values from 0 to 1, indicate the surface heterogeneity. In other words, $1/n$ value smaller than 1 is indicative of this point that the adsorption of AMX on the bioadsorbent is better at lower concentrations compared with higher ones and results of present study support this fact. In the D–R equation, the value of apparent adsorption energy (E) is calculated from Eq. (12),

$$E = \frac{1}{\sqrt{2\beta}} \quad (12)$$

β is the coefficient of activity that is associated with the mean energy of adsorption and is calculated using the D–R slope diagram. The results from adsorption isotherms in this study have been presented in Fig. 7 and Table 3. The comparison of E obtained from this process is mostly physical. Given the results of the adsorption process in this study, it is more proportionate for the Freundlich model and the value of R_L less than 1 is indicative of desirable adsorption of AMX and the highest value of adsorption capacity was obtained 12 mg g^{-1} according to Langmuir equation that is consistent with the results of the study by Erşan [36].

3.7. Kinetics of AMX adsorption

One of the most important factors in designing adsorption system for determining contact time and calculating the dimensions of the discontinued Reactor is

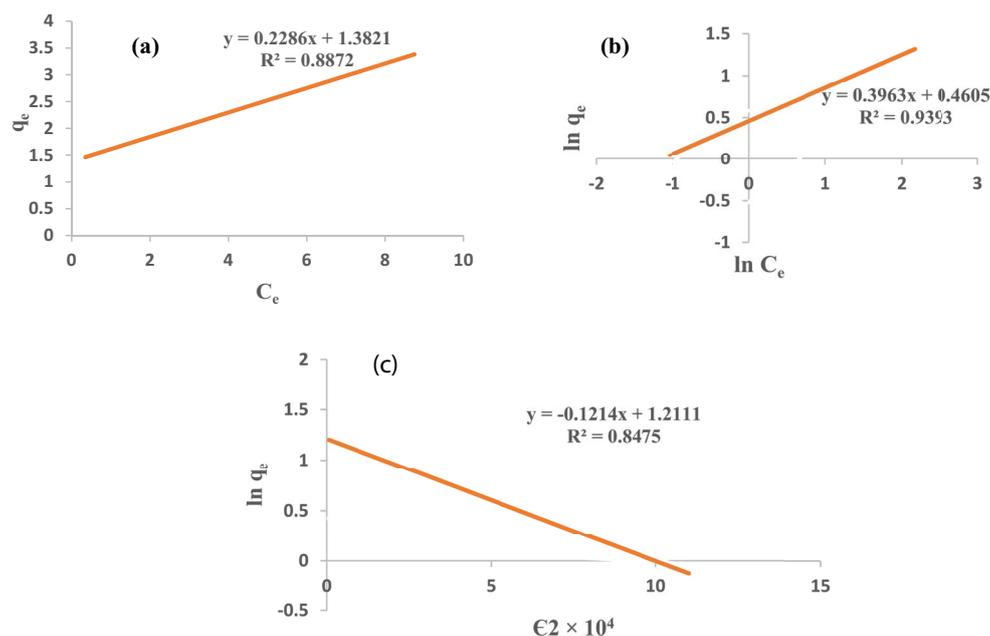


Fig. 7. AMX adsorption isotherm models: (a) Langmuir, (b) Freundlich and (c) Dubinin–Radushkevich.

Table 3
Parameters of AMX adsorption isotherm models by the bioadsorbent

| Freundlich | | | Langmuir | | | | Dubinin–Radushkevich (D–R) | | | |
|------------|---|------|----------|-----------------------------|-----------------------------|-------|----------------------------|--|-----------------------------|-----------------------------|
| R^2 | K_f (mg g ⁻¹)(L mg ⁻¹) ^{1/n} | 1/n | R^2 | Q_m (mg g ⁻¹) | K_a (L mg ⁻¹) | R_L | R^2 | β (kJ ² mol ⁻²) | E (kJ mol ⁻¹) | q_m (mg g ⁻¹) |
| 0.939 | 0.46 | 0.39 | 0.887 | 6.27 | 0.724 | 0.121 | 0.847 | 0.12 | 2.04 | 0.83 |

predicting the speed of adsorption in adsorption process that is controlled by the kinetics of the system. The adsorption constants could be calculated by using the Lagergren equation pseudo-first-order mechanism and pseudo-second-order mechanism in order to study the adsorption mechanism [44]. The linear form of pseudo-first-order model equation is based on Eq. (13).

$$\log(q_e - q_t) = \log q_e - k_1 t \tag{13}$$

In this equation, q_e is the value of adsorbed AMX in the moment of balance (mg g⁻¹) and q_t is the value of AMX adsorbed at time t (mg g⁻¹) and k_1 is the constant of adsorption balance speed related to pseudo-first-order model mechanism (min⁻¹).

If the diagram is drawn on the basis of t , a straight line is achieved that the rate constant of k_1 and the correlation coefficient of R^2 could be calculated based on the diagram. The linear form of the pseudo-second-order kinetic model equation is according to Eq. (14).

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{1}{q_e} t \tag{14}$$

where q_e is the value of AMX adsorbed in the moment of balance (mg g⁻¹) and k_2 is the constant of second-order kinetic model of balance speed (g mg⁻¹ min⁻¹). The speed constant of k_2 and the correlation coefficient of R^2 are obtained by drawing t/q_t diagram based on t . The results obtained from studying adsorption kinetics of AMX are demonstrated in Fig. 8 and Table 4. According to results, the values of correlation coefficient in pseudo-first and pseudo-second-order model were 0.957 and 0.99, respectively, and this indicates that the process of AMX adsorption follows pseudo-second-order kinetic model. Given the fact that the dominant process in

Table 4
AMX antibiotic uptake kinetic parameters

| $q_{e,exp}$ (mg g ⁻¹) | Pseudo-second-order | | | Pseudo-first-order | | |
|-----------------------------------|-----------------------------------|---|-------|-----------------------------------|----------------------------|-------|
| | $q_{e,cal}$ (mg g ⁻¹) | K_2 (g mg ⁻¹ min ⁻¹) | R^2 | $q_{e,cal}$ (mg g ⁻¹) | K_1 (min ⁻¹) | R^2 |
| 1.56 | 2.5 | 0.005 | 0.99 | 1.404 | 0.016 | 0.957 |

the adsorption of AMX is physical but the presence of a little chemical adsorption process could be the main factor in controlling speed.

3.8. Determination of thermodynamic parameters

To investigate the thermodynamic parameters, the effect of temperature on the AMX adsorption process was studied in the temperature range of 25°C–55°C at the optimum conditions, that is, pH 5, bioadsorbent of 0.5 g/100 cc, AMX concentration of 10 mg L⁻¹ and reaction time of 120 min. The results showed that, by increasing the ambient temperature from 25°C to 55°C, the AMX removal efficiency was decreased. Also, according to Table 5, the negative values of the ΔG indicate that the AMX adsorption process by bioadsorbent is possible and spontaneous in terms of stoichiometry and, as the results show, by increasing the temperature, the amount of ΔG decreases, which is indicative of higher adsorption capacity at lower temperatures; these results are in agreement with the results of Vega et al. [45]. The positive values of ΔS represent an increase in irregularities with increasing temperature at the solid–liquid interface level during the adsorption process. Also, negative values of ΔH illustrate that the adsorption process is a physical process and the process is exothermic, and the removal efficiency is increased by decreasing ambient temperature. Moreover,

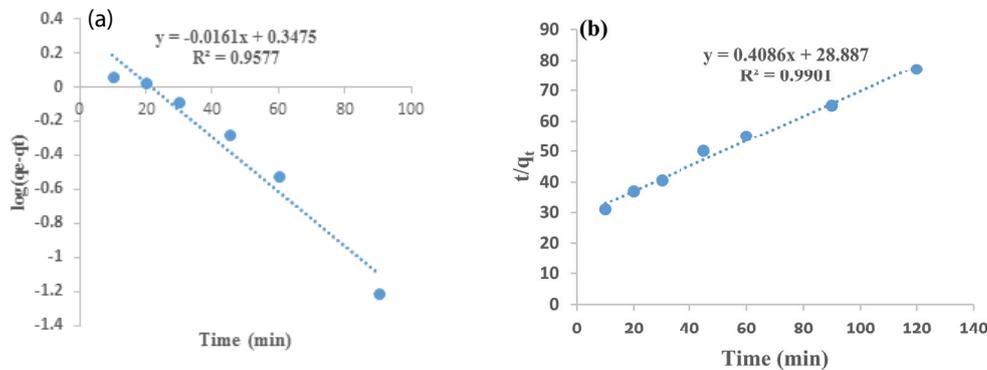


Fig. 8. Kinetic model (a) pseudo-first-order and (b) pseudo-second-order.

Table 5
AMX antibiotic uptake dynamic parameters

| Temperature (K) | ΔG (kJ mol ⁻¹) | ΔH (kJ mol ⁻¹) | ΔS (J mol ⁻¹ K ⁻¹) |
|-----------------|------------------------------------|------------------------------------|---|
| 298.15 | -1.235 | | |
| 308.15 | -1.251 | 5.66 | 1.9 |
| 318.15 | -1.163 | | |
| 328.15 | -1.157 | | |

the positive values of ΔH represent the endothermic nature of the process and the formation of a strong chemical bond between the pollutant molecules and the adsorbent surface, and it suggests that the adsorption process is a chemical process [46,47]. According to the results, ΔH is positive in the present study, which indicates that the adsorption process is chemisorption.

4. Conclusion

In general, it can be concluded that the maximum adsorption of AMX is obtained at optimum conditions including pH of 5, the initial concentration of AMX of 5 mg L⁻¹, the adsorbent dosage of 0.75 g L⁻¹, the contact time of 90 min and the temperature of 25°C. The results showed that adsorption of AMX on the bioadsorbent follows the Freundlich isotherm ($R^2 = 0.939$). The results of the kinetic equations also confirmed that the adsorption behavior of AMX per unit time follows a pseudo-second-order kinetic model ($R^2 = 0.99$). The thermodynamic parameters revealed that AMX adsorption on the *Saccharomyces cerevisiae* bioadsorbent has endothermic nature. According to the results, the *Saccharomyces cerevisiae* bioadsorbent, as the cost-effective adsorbent, in comparison with other natural adsorbents, can be used in the removal of AMX antibiotic.

Acknowledgments

This study has been adapted from an MSc thesis at Hamadan University of Medical Sciences. The study was funded by Deputy of Research and Technology, Hamadan University of Medical Sciences (No. 960115131).

References

- [1] A. Almasi, A. Dargahi, M. Mohammadi, A. Azizi, A. Karami, F. Baniamerian, Z. Saeidimoghadam, Application of response surface methodology on cefixime removal from aqueous solution by ultrasonic/photooxidation, *Int. J. Pharm. Technol.*, 8 (2016) 16728–16736.
- [2] M. Samarghandi, A. Rahmani, G. Asgari, G. Ahmadidoost, A. Dargahi, Photocatalytic removal of cefazolin from aqueous solution by ac prepared from mango seed+ZnO under UV irradiation, *Global Nest J.*, 20 (2018) 399–407.
- [3] A. Dargahi, M. Mohammadi, F. Amirian, A. Karami, A. Almasi, Phenol removal from oil refinery wastewater using anaerobic stabilization pond modeling and process optimization using response surface methodology (RSM), *Desal. Wat. Treat.*, 87 (2017) 199–208.
- [4] M.R. Samarghandi, T.J. Al-Musawi, A. Mohseni-Bandpi, M. Zarrabi, Adsorption of cephalexin from aqueous solution using natural zeolite and zeolite coated with manganese oxide nanoparticles, *J. Mol. Liq.*, 211 (2015) 431–441.
- [5] A. Almasi, A. Dargahi, M. Mohammadi, H. Biglari, F. Amirian, M. Raei, Removal of penicillin G by combination of sonolysis and photocatalytic (sonophotocatalytic) process from aqueous solution: process optimization using RSM (response surface methodology), *Electron. Phys.*, 8 (2016) 2878.
- [6] E.H. Ezechi, S.R. bin Mohamed Kutty, A. Malakahmad, M.H. Isa, Characterization and optimization of effluent dye removal using a new low cost adsorbent: equilibrium, kinetics and thermodynamic study, *Process. Saf. Environ. Prot.*, 98 (2015) 16–32.
- [7] Y. Luo, W. Guo, H.H. Ngo, L.D. Nghiem, F.I. Hai, J. Zhang, S. Liang, X.C. Wang, A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment, *Sci. Total Environ.*, 473 (2014) 619–641.
- [8] B. Kasprzyk-Hordern, R.M. Dinsdale, A.J. Guwy, The removal of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs during wastewater treatment and its impact on the quality of receiving waters, *Water Res.*, 43 (2009) 363–380.
- [9] A. Gulkowska, H.W. Leung, M.K. So, S. Taniyasu, N. Yamashita, L.W. Yeung, B.J. Richardson, A. Lei, J.P. Giesy, P.K. Lam, Removal of antibiotics from wastewater by sewage treatment facilities in Hong Kong and Shenzhen, China, *Water Res.*, 42 (2008) 395–403.
- [10] H. Pouretdal, N. Sadegh, Effective removal of amoxicillin, cephalixin, tetracycline and penicillin G from aqueous solutions using activated carbon nanoparticles prepared from vine wood, *J. Water Process Eng.*, 1 (2014) 64–73.
- [11] M.A. Chayid, M.J. Ahmed, Amoxicillin adsorption on microwave prepared activated carbon from *Arundo donax* Linn: isotherms, kinetics, and thermodynamics studies, *J. Environ. Chem. Eng.*, 3 (2015) 1592–1601.
- [12] M. Panizza, A. Dirany, I. Sirés, M. Haidar, N. Oturan, M.A. Oturan, Complete mineralization of the antibiotic amoxicillin by electro-Fenton with a BDD anode, *J. Appl. Electrochem.*, 44 (2014) 1327–1335.
- [13] E. Elmolla, M. Chaudhuri, Optimization of Fenton process for treatment of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution, *J. Hazard. Mater.*, 170 (2009) 666–672.
- [14] L.J. Githinji, M.K. Musey, R.O. Ankumah, Evaluation of the fate of ciprofloxacin and amoxicillin in domestic wastewater, *Water Air Soil Pollut.*, 219 (2011) 191–201.
- [15] S.x. Zha, Y. Zhou, X. Jin, Z. Chen, The removal of amoxicillin from wastewater using organobentonite, *J. Environ. Manage.*, 129 (2013) 569–576.
- [16] T. Pirom, T. Wongsawa, T. Wannachod, N. Sunsandee, U. Pancharoen, S. Kheawhom, Amoxicillin removal from aqueous solutions using hollow fibre supported liquid membrane: kinetic study, *Chem. Pap.*, 71 (2017) 1291–1302.
- [17] Y.x. Liu, J. Zhang, Photochemical oxidation removal of NO and SO₂ from simulated flue gas of coal-fired power plants by wet scrubbing using UV/H₂O₂ advanced oxidation process, *Ind. Eng. Chem. Res.*, 50 (2011) 3836–3841.
- [18] E. Tekay, S. Şen, D. Aydınoğlu, N. Nugay, Biosorbent immobilized nanotube reinforced hydrogel carriers for heavy metal removal processes, *e-Polymers*, 16 (2016) 15–24.
- [19] S. Guiza, Biosorption of heavy metal from aqueous solution using cellulosic waste orange peel, *Ecol. Eng.*, 99 (2017) 134–140.
- [20] S. Peyvandi, H. Faghihian, Biosorption of uranyl ions from aqueous solution by *Saccharomyces cerevisiae* cells immobilized on clinoptilolite, *J. Radioanal. Nucl. Chem.*, 301 (2014) 537–543.
- [21] F. Zan, S. Huo, B. Xi, X. Zhao, Biosorption of Cd²⁺ and Cu²⁺ on immobilized *Saccharomyces cerevisiae*, *Front. Environ. Sci. Eng.*, 6 (2012) 51–58.
- [22] W. Guo, D. Schaefer, X. Guo, L. Ren, Q. Meng, Use of nitrate-nitrogen as a sole dietary nitrogen source to inhibit ruminal methanogenesis and to improve microbial nitrogen synthesis in vitro, *Asian-australas. J. Anim. Sci.*, 22 (2009) 542–549.
- [23] E.E. Oaikhena, D.B. Makaije, S.D. Denwe, M.M. Namadi, A.A. Haroun, Bioremediation potentials of heavy metal tolerant bacteria isolated from petroleum refinery effluent, *Am. J. Environ. Prot.*, 5 (2016) 29–34.

- [24] P. Vasudevan, V. Padmavathy, S. Dhingra, Kinetics of biosorption of cadmium on Baker's yeast, *Bioresour. Technol.*, 89 (2003) 281–287.
- [25] G. Moussavi, R. Khosravi, Preparation and characterization of a biochar from pistachio hull biomass and its catalytic potential for ozonation of water recalcitrant contaminants, *Bioresour. Technol.*, 119 (2012) 66–71.
- [26] A. Naghizadeh, F. Ghasemi, E. Derakhshani, H. Shahabi, Thermodynamic, kinetic and isotherm studies of sulfate removal from aqueous solutions by graphene and graphite nanoparticles, *Desal. Wat. Treat.*, 80 (2017) 247–254.
- [27] B. Hayati, N.M. Mahmoodi, Modification of activated carbon by the alkaline treatment to remove the dyes from wastewater: mechanism, isotherm and kinetic, *Desal. Wat. Treat.*, 47 (2012) 322–333.
- [28] B. Kavitha, D.S. Thambavani, Kinetics, equilibrium isotherm and neural network modeling studies for the sorption of hexavalent chromium from aqueous solution by quartz/feldspar/wollastonite, *RSC Adv.*, 6 (2016) 5837–5847.
- [29] J. Guo, X.-d. Zheng, Q.-b. Chen, L. Zhang, X.-p. Xu, Biosorption of Cd(II) from aqueous solution by *Pseudomonas plecoglossicida*: kinetics and mechanism, *Curr. Microbiol.*, 65 (2012) 350–355.
- [30] A. Naghizadeh, M. Kamranifar, A.R. Yari, M.J. Mohammadi, Equilibrium and kinetics study of reactive dyes removal from aqueous solutions by bentonite nanoparticles, *Desal. Wat. Treat.*, 97 (2017) 329–337.
- [31] A. Naghizadeh, M. Ghafouri, A. Jafari, Investigation of equilibrium, kinetics and thermodynamics of extracted chitin from shrimp shell in reactive blue 29 (RB-29) removal from aqueous solutions, *Desal. Wat. Treat.*, 70 (2017) 355–363.
- [32] A. Özcan, E.M. Öncü, A.S. Özcan, Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite, *Colloids Surf., A*, 277 (2006) 90–97.
- [33] M.A. Zazouli, A.H. Mahvi, S. Dobaradaran, M. Barafrashtehpour, Y. Mahdavi, D. Balarak, Adsorption of fluoride from aqueous solution by modified *Azolla filiculoides*, *Adsorption*, 47 (2014) 349–358.
- [34] W.-J. Liu, F.-X. Zeng, H. Jiang, X.-S. Zhang, Adsorption of lead (Pb) from aqueous solution with *Typha angustifolia* biomass modified by SOCl_2 activated EDTA, *Chem. Eng. J.*, 170 (2011) 21–28.
- [35] F. Pagnanelli, M. Petrangeli Papini, L. Toro, M. Trifoni, F. Veglio, Biosorption of metal ions on *Arthrobacter* sp.: biomass characterization and biosorption modeling, *Environ. Sci. Technol.*, 34 (2000) 2773–2778.
- [36] M. Erşan, Removal of tetracycline using new biocomposites from aqueous solutions, *Desal. Wat. Treat.*, 57 (2016) 9982–9992.
- [37] Q. Peng, Y. Liu, G. Zeng, W. Xu, C. Yang, J. Zhang, Biosorption of copper(II) by immobilizing *Saccharomyces cerevisiae* on the surface of chitosan-coated magnetic nanoparticles from aqueous solution, *J. Hazard. Mater.*, 177 (2010) 676–682.
- [38] S. Chatterjee, S. Chatterjee, B.P. Chatterjee, A.K. Guha, Adsorptive removal of congo red, a carcinogenic textile dye by chitosan hydrobeads: binding mechanism, equilibrium and kinetics, *Colloids Surf., A*, 299 (2007) 146–152.
- [39] H. Fazelirad, M. Ranjbar, M.A. Taher, G. Sargazi, Preparation of magnetic multi-walled carbon nanotubes for an efficient adsorption and spectrophotometric determination of amoxicillin, *J. Ind. Eng. Chem.*, 21 (2015) 889–892.
- [40] M.A. Zazouli, D. Balarak, Y. Mahdavi, Application of Canola residuals in absorption of reactive red 198 (RR198) dye from aqueous solutions, *J. Neyshabur Univ. Med. Sci.*, 2 (2014) 56–66.
- [41] N.S. Maurya, A.K. Mittal, P. Cornel, E. Rother, Biosorption of dyes using dead macro fungi: effect of dye structure, ionic strength and pH, *Bioresour. Technol.*, 97 (2006) 512–521.
- [42] M.L. Nguyen, R.-S. Juang, Modification of crosslinked chitosan beads with histidine and *Saccharomyces cerevisiae* for enhanced Ni(II) biosorption, *J. Taiwan Inst. Chem. Eng.*, 56 (2015) 96–102.
- [43] N.V. Suc, H.T.Y. Ly, Lead (II) removal from aqueous solution by chitosan flake modified with citric acid via crosslinking with glutaraldehyde, *J. Chem. Technol. Biotechnol.*, 88 (2013) 1641–1649.
- [44] Y. Khambhaty, K. Mody, S. Basha, B. Jha, Kinetics, equilibrium and thermodynamic studies on biosorption of hexavalent chromium by dead fungal biomass of marine *Aspergillus niger*, *Chem. Eng. J.*, 145 (2009) 489–495.
- [45] E.D. Vega, G.E. Narda, F.H. Ferretti, Adsorption of citric acid from dilute aqueous solutions by hydroxyapatite, *J. Colloid Interface Sci.*, 268 (2003) 37–42.
- [46] M. Ghaedi, A. Ansari, R. Sahraei, ZnS: Cu nanoparticles loaded on activated carbon as novel adsorbent for kinetic, thermodynamic and isotherm studies of Reactive Orange 12 and Direct yellow 12 adsorption, *Spectrochim. Acta, Part A*, 114 (2013) 687–694.
- [47] B. Hayati, N.M. Mahmoodi, M. Arami, F. Mazaheri, Dye removal from colored textile wastewater by poly(propylene imine) dendrimer: operational parameters and isotherm studies, *Clean – Soil Air Water*, 39 (2011) 673–679.