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The modelling of biosorption for rapid removal of organic matter with activated sludge biomass from real industrial effluents

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Abstract−Biosorption is becoming increasingly important for the treatment of pollutants due to its cost-effectiveness, environmental friendliness and efficiency. For a more sustainable environment, more studies need to focus on the application of real industrial effluents. Increasing the initial concentration of activated sludge increases the specific surface area of the sludge, which allows for greater sorption of sorbates. The optimal initial concentration of activated sludge in the process of biosorption of pollutants from pharmaceutical effluent was 5.12±0.13 g/L. The biosorption process can be described by the Temkin model, where the estimated values of B_T and A_T ranged from 29.11 to 76.08 and from 1.10 to 1.48 L/g, respectively. The overall efficiency of the biosorption process ranged from 9.5 to 40.2%. The removed toxicity averaged 41.1±7.88% for all experiments.

Keywords: Biosorption, Pharmaceutical Effluent, Activated Sludge, Adsorption Isotherms

INTRODUCTION

Pollution is one of the greatest challenges facing modern society. Industrial development and urbanization have led to increased consumption of potable water and the consequent generation of significant amounts of wastewater [1]. Industrial effluents contain anthropogenic compounds such as pharmaceutical residues, pesticides and dyes [2].

The increase of potentially hazardous pollutants in water can endanger human health and have negative effects on other living organisms [1,3]. Natural or chemical compounds and substances whose emission limits are not regulated by law, whose effects on human health and the environment have been insufficiently studied, or which are potentially harmful are referred to as emerging contaminants. The steady release of emerging contaminants has been predicted to be occurring for a long time and from various sources [4].

Since the 1980s, the presence of pharmaceuticals in the surface waters of many European countries has been reported. This has led to growing concern that some of these persistent products may find their way back into drinking water. Toxic/harmful substances have negative effects on biological organisms [5] and persist over a longer period of time in a natural environment [6]. Effective management of wastewater generated from industrial activities is becoming a serious problem [6].

The biological process is often chosen for the treatment of effluents from pharmaceutical production because it is cost effective and environmentally friendly [7]. One of the most common embodiments of biological treatment is the activated sludge process [7,8], which consists of a mixed community of microorganisms capable of removing a variety of pollutants from a complex system such as pharmaceutical effluent. Microorganisms have the unique ability to interact physically and chemically with a variety of substances, both natural and anthropogenic. It is their specificity that allows structural changes of the target molecule or its complete degradation [2,6].

When microorganisms suddenly encounter nutrients in concentrations too high for their metabolic rate, the cells take them up for storage. Uptake by cells is very rapid, and the process is called biosorption [8,9].

The mechanism of biosorption is a combination of metabolically mediated biological and physicochemical processes involving both biosorption of organic material on the cell surface and storage of soluble organic material within the cell [3,4,9]. The storage of soluble organic material within the sludge flocs can involve surface sorption: metabolically mediated passive uptake of organic material; storage of organic material: metabolically mediated uptake of organic material and accumulation within the cell; and entrapment of organic material: entrapment of larger particles within the open structure of the sludge floc, facilitated by extracellular polymeric substances [10].

The biosorption process plays a key role in the rapid removal of organic compounds in the early stages of biological wastewater treatment by activated sludge [3] and occurs within a short period of time [11]. Sorption of toxic compounds allows sludge to adapt to new environmental conditions for biodegradation. It is important in the removal of pharmaceuticals from wastewater, where these compounds are adsorbed on the surface of the activated sludge [12]

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and then desorbed over a longer period of time, allowing microorganisms to adapt to the environmental conditions and substrate source [11]. Although metabolic processes play a primary role in biological wastewater treatment or remediation, the biosorption process is inevitably integrated into the overall pollutant removal process [3]. This effect is used in a biological waste treatment process known as contact stabilization for rapid removal of organic materials. The removal of organic matter in wastewater is the direct result of biosorption and the permanent removal of organic matter depends on the metabolism of microorganisms. Therefore, biosorption could be a key factor to describe the treatment of organic pollutants [3,8].

In this work, the biosorption mechanism of activated sludge in the removal of organic pollutants from real pharmaceutical effluent was investigated. The binding of pollutants from wastewater to the cellular structure of activated sludge was studied using activated sludge in the endogenous respiration phase. Different models of adsorption isotherms were applied to determine the mechanism of biosorption, and the optimum initial concentration of activated sludge for biosorption of pollutants from pharmaceutical effluent was determined.

MATERIALS AND METHODS

1. Pharmaceutical Effluent and Activated Sludge Samples

Pharmaceutical effluent and activated sludge were collected from the pharmaceutical wastewater treatment plant located on the site of one of the Croatian active pharmaceutical ingredient manufacturing plant. Three original effluent samples were collected from the equalization tank before entering the pharmaceutical wastewater treatment plant (PhWWTP). The concentration of pharmaceutical effluent, S, which represents the total organic pollution of the effluent from pharmaceutical production, is expressed in terms of chemical oxygen demand (COD), representing sorbate in biosorption experiments.

Samples of the activated sludge were collected from the aeration bioreactor of the PhWWTP. The prepared initial concentration of activated sludge is expressed in terms of suspended solids (X) and determined by mixed liquor suspended solids (MLSS). After sampling, the activated sludge and pharmaceutical effluent were stored at 4 °C.

2. Biosorption Studies

The biosorption experiments were carried out with the activated sludge in the endogenous respiration phase, which was achieved by aerating the activated sludge with an aeration pump (Tetratec® APS 100, Germany) for 24 hours. After 24 hours, aeration was stopped, the activated sludge was concentrated by precipitation for three hours and the supernatant was decanted. The concentrated activated sludge was washed with demineralized water, mixed and precipitated while the supernatant was decanted. The procedure was repeated three times.

The experiments were performed in three series, named E1-E3, with three different initial concentrations of pharmaceutical effluent and different initial concentrations of activated sludge in the endogenous respiration phase. The initial concentrations of the real pharmaceutical effluents with different organic load were expressed as chemical oxygen demand (COD), which represents the concentration of organic pollutants (sorbates) S_{01}=1,780±83 mg/L (Exp. E1), S_{02}=2,717±102 mg/L (Exp. E2) and S_{03}=4,007±111 mg/L (Exp. E3). The prepared initial concentration of activated sludge (sorbent) is expressed in terms of suspended solids (X) and determined by mixed liquor suspended solids (MLSS). The initial concentrations of the activated sludge in all three series of experiments were X_{01}=3.18±0.13 g/L, X_{02}=4.14±0.17 g/L, X_{03}=5.12±0.13 g/L, X_{04}=6.04±0.33 g/L and X_{05}=7.02±0.68 g/L.

To investigate the biosorption capacity of activated sludge, batch experiments were carried out on a rotary shaker (Grant-bio PSU-10i, England) in 1,000 mL Erlenmeyer flasks, each containing a suspension of 500 mL of activated sludge in the endogenous respiration phase with initial concentrations from X_{01} to X_{05} and pharmaceutical effluent with initial concentrations from S_{01} to S_{03}, at 160 rpm and contact time of 30 minutes. The experiments were conducted at 25 °C to be representative of relevant conditions in biological wastewater treatment plant. The pH of pharmaceutical effluent was 7.9. Temperature, pH and contact time were kept constant.

3. Analytical Methods

During the experiments, sorbate and the activated sludge concentration in the samples were determined according to APHA Standard Methods [13]. Prior to analysis, all samples of activated sludge suspension and pharmaceutical effluent were filtered through a membrane filter with a pore size of 0.45 μm. All determinations were averages of duplicate samples.

4. Toxicity Studies

Toxicity was determined by bioluminescence inhibition test with *Vibrio fischeri* (ISO 11348-3:2007) [14]. According to the effective concentration of the compound causing 50% of bioluminescence inhibition (EC_{50}), toxicity can be expressed as toxicity impact index (TII), which can be calculated by the equation $TII_{50}=100\times1/(EC_{50})$ [15].

5. Biosorption Isotherm Models

The isotherm equation of biosorption represents the relationship between the amount of solute sorbed and the concentration of the solute in the aqueous phase. Eqs. (1) and (2) were used to calculate the percentage removal and the biosorption capacities (q_e, mg/g) [3,16,17]:

$$\%\ \text{Removal} = \frac{(S_0 - S_e)}{S_0} 100 \tag{1}$$

$$q_e = \frac{(S_0 - S_e)V}{X} \tag{2}$$

where S_0 and S_e are the initial sorbate concentration and the sorbate concentration at equilibrium (mg/L), V is the solution volume (L), and X is the mass of the sorbent (g). The Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models have been used to study and predict biosorption performance at equilibrium [18].

The Langmuir isotherm is an empirical model based on the assumption that sorption occurs until the surface of the sorbent completely covers the monomolecular layer of the sorbent, resulting in a uniform sorption energy on the sorbent surface [19]. The sorption process occurs when a sorbate molecule binds to the sorbent

site, and the adsorbed substances in the monomolecular layer do not interact with each other [18]. The following equation was derived from the above assumptions:

$$q_e = q_m \frac{K_L S_e}{1 + K_L S_e} \tag{3}$$

where K_L is the Langmuir constant relating to the sorption capacity (L/mg), and q_m is the maximum monolayer capacity of sorption (mg/g). The Langmuir equation can be written in the following linear form:

$$\frac{S_e}{q_e} = \frac{1}{q_m K_L} + \frac{S_e}{q_m} \tag{4}$$

The essential properties of the Langmuir isotherm can be expressed by a dimensionless constant called the separation factor R_L [16]:

$$R_L = \frac{1}{1 + K_L S_0} \tag{5}$$

R_L values indicate that sorption is unfavorable when $R_L>1$, linear when $R_L=1$, favorable when $0<R_L<1$, and irreversible when $R_L=0$ [18].

Freundlich sorption is commonly used to describe the sorption characteristics for a heterogeneous surface [20]. These data often fit the empirical equation proposed by Freundlich as follows [20]:

$$q_e = K_f S_e^{1/n} \tag{6}$$

where K_f is the Freundlich isotherm constant (mg/g) $(L/mg)^{1/n}$ and n is the sorption intensity. The linearized Freundlich isotherm is shown in Eq. (7):

$$\log q_e = \log K_f + \frac{1}{n} S_e \tag{7}$$

The constant K_f is an approximate indicator of sorption capacity, while 1/n is a function of the strength of sorption in the sorption process. The favorability of the Freundlich model was determined by n. Values of n in the range of 1-10 represent favorable sorption, while n<1 represents unfavorable sorption [18-20].

The Temkin isotherm considers the influence of indirect interaction of sorbents and sorbates on the sorption process. This model assumes that the heat of sorption of all sorbed molecules in the layer decreases linearly with increasing coverage of the sorbent surface [19]. The nonlinear and linear forms of the Temkin isotherm are shown in Eqs. (8) and (9):

$$q_e = \frac{RT}{b_T} \ln(A_T S_e) \tag{8}$$

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln S_e \tag{9}$$

where:

$$B_T = \frac{RT}{b_T} \tag{10}$$

The expression of Temkin's model follows:

$$q_e = B_T \ln A_T + B_T \ln S_e \tag{11}$$

A_T is the Temkin isotherm equilibrium binding constant (L/g), b_T is the Temkin constant which is related to the heat of sorption (J/mol), R is the universal gas constant (8.314 J/mol K); T is the temperature at 298 K and B_T is a constant related to the heat of sorption.

The Dubinin-Radushkevich (D-R) isotherm [18,19] is an empirical adsorption model that describes the sorption mechanism with a Gaussian energy distribution on a heterogeneous sorbent surface. The equation of the D-R sorption model is expressed as follows:

$$q_e = q_m e^{-K_{DR}\varepsilon^2} \tag{12}$$

The linear form of Eq. (12). is presented:

$$\ln q_e = \ln q_m - K_{DR}\varepsilon^2 \tag{13}$$

Furthermore, ε can be calculated by the following equation:

$$\varepsilon = RT \ln\left(1 + \frac{1}{S_e}\right) \tag{14}$$

where K_{DR} is Dubinin-Radushkevich constant, mol^2/kJ^2, ε is the Polanyi potential. The D-R model is usually used to determine the type of sorption (physical or chemical). It uses the free energy, E, (kJ/mol), or the energy required to remove the sorbate molecule from the active site on the sorbent. The value of the free energy, E, is calculated according to the following equation:

$$E = \frac{1}{\sqrt{2K_{DR}}} \tag{15}$$

The sorption process is physical if the value of E is less than 8 kJ/mol, whereas it is called chemical if the E values are between 8 and 16 kJ/mol [21].

6. Model Analysis

Based on the obtained experimental data, the biosorption process was analyzed. The model parameters were estimated by linear regression analysis using least squares method as an integral part of MS Excel. The results obtained by simulation using the mathematical models were compared with the experimental data and recalculated until a minimum deviation was obtained between the experimental data and the values calculated by the model. A set of optimized model parameters was used for the simulations, which were compared with the experimental results. Statistical analysis (R^2 and Fisher-Snedecor F-test) was performed to compare the values obtained with the model and experimental results.

RESULTS AND DISCUSSION

The main sources of water pollution include industrialization, agricultural activities, municipal wastewater, and other environmental changes. Wastewater treatment provides a source of water supply that is independent of weather conditions such as rainfall and drought and relieves some of the pressure on natural resources [22,23].

Despite the availability of various organic pollutant removal processes, the sorption process is a good choice due to its universality, insensitivity, ease of application, flexibility, insensitivity to toxic pollutants, applicability to both continuous and batch processes, and good removal efficiency and effectiveness [3,23,24]. Moreover, sorp-

tion can also remove soluble and insoluble organic pollutants without generating hazardous byproducts [24].

1. Biosorption Modeling

Adsorption isotherms, which describe the nature of the interaction between sorbate and biosorbent, are important for optimizing the use of biosorbents. Thus, the analysis of equilibrium data is useful for the practical design and operation of adsorption systems [25]. The adsorbent dosage level can be considered as one of the important parameters for cost effective performance in adsorption studies [16]. The biosorption potential of activated sludge indicates a biosorption capacity that depends on the operating conditions, the concentration values of sorbates and sorbents at ambient temperature and the pH. The initial concentrations of the activated sludge in the endogenous respiration phase ranged from 3.18 to 7.02 mg/L. The adsorption equilibrium was described using four different models of adsorption isotherms: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich model.

Biosorption Study E1

In experiment E1, biosorption was carried out under batch conditions with pharmaceutical effluent with an initial concentration S_{01}=1,780±83 mg/L and different initial concentrations of activated sludge. At first contact, prior to metabolism and utilization of organic matter by microbial communities, biological wastewater treatment involves the process of biosorption in the activated sludge [3].

The parameters were estimated from the experimental data by linear regression (Table 1). The values of the linear correlation coefficients of the experimental data from the four models of adsorption isotherms show that the Langmuir isotherm has the best agreement with the experimental data (R^2=0.9983) and is a model that can describe the equilibrium state of biosorption. Since the value of the correlation coefficient is between 0 and 1, a value closer to 1 indicates a strong linear correlation of the data [26]. The values of the parameters of the Langmuir adsorption isotherm, q_m and K_L, indicate the maximum sorption capacity of the activated sludge, i.e., the Langmuir constant associated with the heat of adsorption [27]. In experiment E1, the value of q_m was 131.43 mg/g, and K_L was 0.005 L/mg. The parameter q_m depends on the type of sorbent and is related to the active surface area and porosity of the sorbent, which means that a larger specific surface area and pore volume lead to a higher sorption capacity [19]. The values of K_L for biosorption of pharmaceuticals from wastewater in the literature [28,29] are in a similar range as in exp. E1, from 0.0016 to 0.158 L/mg, depending on the concentration of the sorbent. The affinity between sorbate and sorbent can be predicted by the value of the separation factor R_L (Eq. (5)). For exp. E1, the sorption process can be described as favorable based on the value of R_L=0.091 [19,20].

The Freundlich adsorption isotherm contains the Freundlich constant K_f, whose value indicates the biosorption capacity, and the higher it is, the higher the biosorption capacity, while n indicates the sorption intensity of the sorbate on the activated sludge [30]. The value of 1/n obtained in experiment E1 was 0.34, indicating a favorable process of high-intensity biosorption, since 0<1/n<1 [18]. Based on the value of 1/n<1, it is assumed that there is a strong interaction between sorbents and sorbates, with an increase in the equilibrium concentration leading to a decrease in sorption [31]. Freundlich's isotherm describes well the process of sorption in multicomponent solutions such as wastewater [30,31], but also sorption on heterogeneous multicomponent sorbents such as activated sludge [10]. A value of 1/n can also be considered as a heterogeneity parameter, with a smaller value of 1/n indicating a higher degree of heterogeneity [20].

The values of Temkin's adsorption isotherm parameters A_T and B_T were 1.10 L/g and 29.11, correlating with sorption capacity, i.e., sorption intensity [19]. The D-R model is commonly used to determine the type of adsorption (physical or chemical) based on the free energy (E, kJ/mol), required to remove the sorbate molecule from the active site on the sorbent [21]. The value of the parameter E was 12.24 kJ/mol; therefore, the sorption process in E1 is classified as chemisorption because the free energy value ranges from 8 to 16 kJ/mol. Lim et al. [10] studied the biosorption of organic pollutants (COD) from synthetic wastewater on activated sludge and suggested that the limiting step in the removal of COD may be

Table 1. Parameters obtained from the isotherm models for biosorption in E1

Isotherm	Parameters	Value	Equation (linear regression)
Langmuir	q_m (mg/g)	131.43	$S_e/q_e=(S_e/q_m)+1/(q_m \cdot K_L)$ y=0.0082x+1.5455 R^2=0.9983
	K_L (L/mg)	0.005	
	R_L	0.091	
	F-test	0.978	
Freundlich	n	2.90	$\log q_e=\log K_f+(1/n)\cdot S_e$ y=0.3195x+1.0761 R^2=0.9782
	K_f ((mg/g) (L/mg)$^{1/n}$)	10.91	
	F-test	0.981	
Temkin	B_T	29.11	$q_e=B_T \ln A_T+B_T \ln S_e$ y=25.675x−72.146 R^2=0.9886
	A_T (L/g)	1.10	
	F-test	0.991	
Dubinin-Radushkevich	q_m (mg/g)	103.57	$\ln q_e=\ln q_m-K_{DR}\varepsilon^2$ y=−0.0033x+4.5737 R^2=0.9655
	K_{DR} (mol^2/kJ^2)	0.0033	
	E (kJ/mol)	12.24	
	F-test	0.928	

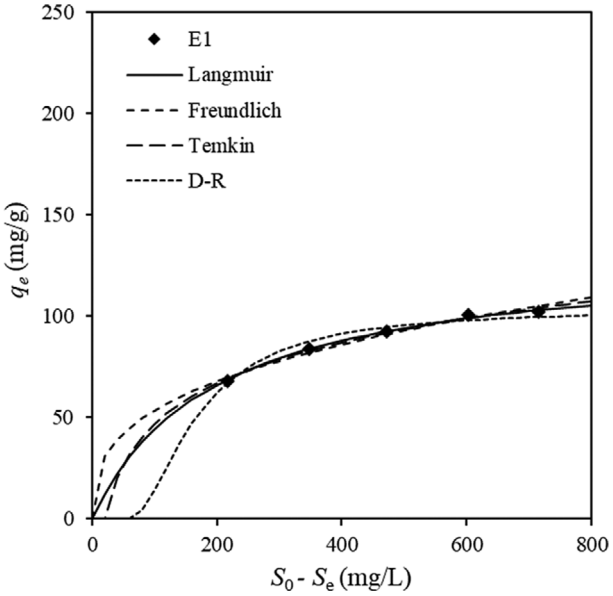

Fig. 1. Comparison of experimental results and simulation results of adsorption isotherms for experiment E1 in the study of biosorption of pollutants from pharmaceutical effluent with activated sludge.

chemisorption due to the structure and electrostatic charge of the activated sludge.

Model acceptance was evaluated by the statistical method using the F-test [26]. In Table 1, high values of the F-test ranging from 0.928 to 0.991 are observed, indicating a good agreement of the model with the experimental results. Comparing the F-test values of the models for the adsorption isotherms, the Temkin isotherm has the highest F-test value of 0.991. The obtained F-test values for all models of adsorption isotherms are above 0.6, which is statistically acceptable and suggests that the selected models describe the process of sorption of pollutants from pharmaceutical effluent in approximately the same way.

Fig. 1 shows a comparison of experimental results and simulation results of adsorption isotherms for experiment E1 in the process of biosorption of pollutants from pharmaceutical effluent with activated sludge. The graph shows that increasing the concentration of sorbate increases the capacity of the activated sludge as the specific surface area of the sludge increases [3,25]. The value of biosorption capacity (Eq. (2)) increased with increasing the initial concentration of the activated sludge and ranged from 68.1 to 101.9 mg/g. The sorption process is based on the concentration of the substance from the solution on the surface of the sorbent, and the active surface area is one of the main factors affecting the sorption capacity of sorbents. The biosorption capacity of sorbents is proportional to their specific surface area, which means that the sorption of the substance increases as the surface area increases [30]. Fig. 1. shows that the simulations of adsorption isotherm models describe the experimental results well. The Freundlich and Temkin models describe well the range of sorbate concentrations between 216.7 and 603.0 mg/L, while the Langmuir adsorption isotherm shows the best fit to the experimental data.

Biosorption Study E2

Biosorption study in experiment E2 was carried out with initial concentration pharmaceutical effluent S_{01}=2,717±102 mg/L and different initial concentrations of activated sludge. As in experiment E1, the Langmuir isotherm (R^2=0.9942) showed the best agreement with the experimental data, and the lowest value of R^2 was obtained using the model D-R (Table 2). The values of Langmuir adsorption isotherm parameters, q_m and K_L, were 209.50 mg/g and 0.003 L/mg, respectively, indicating that at a higher initial concentration of pharmaceutical effluent in E2, there is a higher maximum sorption capacity of activated sludge and a lower value of Langmuir constant associated with the heat of adsorption. The value of R_L increased by 0.017 in E2 compared to E1, indicating that sorption is favorable in both cases [19,20]. The value of Freundlich constant K_f was lower by 10.2% and was 8.17 (mg/g) (L/ mg)$^{1/n}$, while the value of 1/n was 0.43, indicating a favorable process of high-intensity biosorption as in E1 [18]. The parameters of Temkin ad-

Table 2. Parameters obtained from the isotherm models for biosorption in E2

Isotherm	Parameters	Value	Equation (linear regression)
Langmuir	q_m (mg/g)	209.50	$S_e/q_e=(S_e/q_m)+1/(q_m \cdot K_L)$ y=0.0048x+1.7961 R^2=0.9942
	K_L (L/mg)	0.003	
	R_L	0.108	
	F-test	0.962	
Freundlich	n	2.35	$\log q_e=\log K_f+(1/n)\cdot S_e$ y=0.4264x+0.9123 R^2=0.9693
	K_f ((mg/g) (L/mg)$^{1/n}$)	8.17	
	F-test	0.966	
Temkin	B_T	50.11	$q_e=B_T \ln A_T+B_T \ln S_e$ y=50.106x−192.82 R^2=0.9843
	A_T (L/g)	1.35	
	F-test	0.988	
Dubinin-Radushkevich	q_m (mg/g)	153.63	$\ln q_e=\ln q_m-K_{DR}\varepsilon^2$ y=−0.0073x+5.0345 R^2=0.9664
	K_{DR} (mol^2/kJ^2)	0.0073	
	E (kJ/mol)	8.27	
	F-test	0.918	

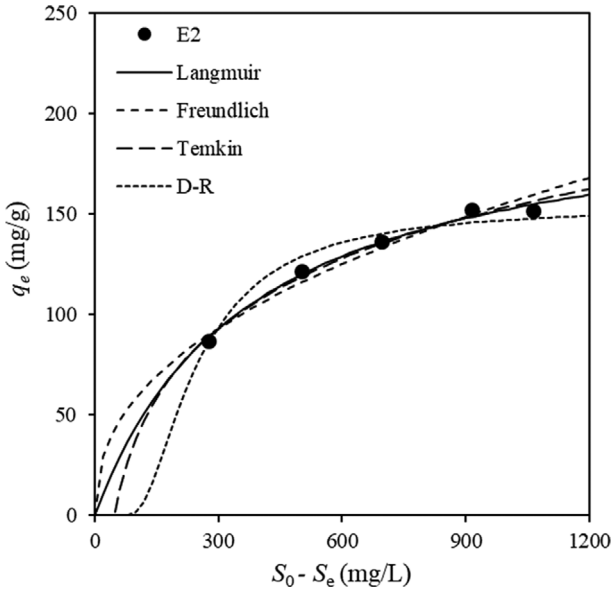

Fig. 2. Comparison of experimental results and simulation results of adsorption isotherms for experiment E2 in the study of biosorption of pollutants from pharmaceutical effluent with activated sludge.

sorption isotherm, A_T and B_T, were 1.35 L/g and 50.11, respectively. The value of the parameter A_T agrees with the value of the same parameter in E1, while the parameter B_T has a significantly higher value in E2 compared to E1. The parameters of the model D-R, q_m and K_{DR}, have higher values in E2 compared to E1, which are 153.63 mg/g and 0.0073 mol^2/kJ^2, respectively. The value of parameter E in experiment E2 was 8.27 kJ/mol, which is very close to the limit where the sorption mechanism is classified as physical sorption (E<8 kJ/mol). Based on the obtained value, it is considered that chemisorption still predominates in the sorption process in E2. From the evaluation of the acceptability of the proposed models, which was performed using the F-test, it can be seen that approximately the same values were obtained as in E1, with the highest value of 0.988 for the Temkin model.

The system in E2 (Fig. 2) shows similar behavior to that in E1 (Fig. 1). Increasing the initial concentration of activated sludge from 3.18 g/L to 7.02 g/L increases the value of the adsorbed sorbate from 275.7 mg/L to 1,064.4 mg/L. The obtained q_e values in E1 were significantly lower, which was influenced by the initial concentration of sorbate, which was 34.5% lower compared to the initial concentration in E2. The value of q_e represents a function of sludge concentration, which is linearly correlated with sludge loading. To reach the saturation state in the sorption of organic material to activated sludge, the biosorption capacity increases to a certain value, after which it does not change and remains stable [3]. This is true for higher activated sludge concentrations, where the sorption capacities had approximately the same value of 152.0±0.46 mg/g. Fig. 2 shows that the Langmuir model best describes the biosorption process over the entire range of sorbate concentrations studied.

Biosorption Study E3

Table 3 shows the results of modelling the biosorption process of the initial concentration of sorbate S_{03}=4,007±111 mg/L using activated sludge in experiment E3. Using the same models of adsorption isotherms as in experiments E1 and E2, biosorption study was performed in exp. E3. In addition to the presented equations linear regression of the adsorption models, high values of the correlation coefficient are visible. The highest value of R^2 of 0.9940 was obtained with the Langmuir model, where the mentioned isotherm shows the best agreement with the experimental data in all conducted experiments. The values of the Langmuir adsorption isotherm parameters, q_m and K_L, were 317.29 mg/g and 0.002 L/mg, respectively, indicating that at a higher initial concentration of pharmaceutical effluent, a higher maximum sorption capacity of the activated sludge and a lower value of the Langmuir constant. This observation indicates that the activated sludge behaves as a better sorbent at higher initial concentrations of pharmaceutical effluent in the studied concentration range, which may be related to the adaptation, i.e., resistance of activated sludge [32] to oscilla-

Table 3. Parameters obtained from the isotherm models for biosorption in E3

Isotherm	Parameters	Value	Equation (linear regression)
Langmuir	q_m (mg/g)	317.29	$S_e/q_e=(S_e/q_m)+1/(q_m \cdot K_L)$ y=0.0032x+2.0231 R^2=0.9940
	K_L (L/mg)	0.002	
	R_L	0.121	
	F-test	0.962	
Freundlich	n	2.19	$\log q_e=\log K_f+(1/n)\cdot S_e$ y=0.4567x+0.9057 R^2=0.9869
	K_f ((mg/g) $(L/mg)^{1/n}$)	8.04	
	F-test	0.979	
Temkin	B_T	76.08	$q_e=B_T \ln A_T+B_T \ln S_e$ y=76.088x−333.36 R^2=0.9895
	A_T (L/g)	1.48	
	F-test	0.992	
Dubinin-Radushkevich	q_m (mg/g)	217.68	$\ln q_e=\ln q_m-K_{DR}\varepsilon^2$ y=−0.0148x+5.383 R^2=0.9216
	K_{DR} (mol^2/kJ^2)	0.0148	
	E (kJ/mol)	5.81	
	F-test	0.848	

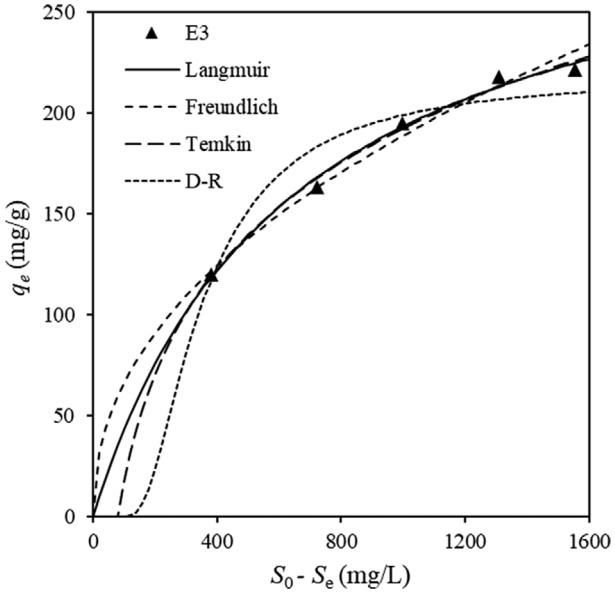

Fig. 3. Comparison of experimental results and simulation results of adsorption isotherms for experiment E3 in the study of biosorption of pollutants from pharmaceutical effluent with activated sludge.

tions in composition pharmaceutical effluent [29,33]. The value of separation factor is related to the value of Langmuir constant K_L. Decreasing the value of K_L increases the value of R_L, (Tables 1-3). In E3, the values of Freundlich isotherm constants K_f and n were 8.04 ((mg/g) (L/mg)$^{1/n}$) and 2.19. The K_f values are approximately the same as in experiment E2. The value of 1/n is the highest in E3 because the initial concentration of sorbates is also the highest. The parameter A_T of Temkin model increases with the increase in the initial concentration of sorbates (Tables 1-3), where the value of B_T increases by 25.97 and 46.97 compared to E2 and E1. The increase in the value of the D-R parameters q_m and K_{DR} also follows the growth trend in experiment E3. The value of parameter E in experiment E3 was 5.81 kJ/mol; therefore, the sorption mechanism is classified as physical sorption as the free energy value is less than 8 kJ/mol [21]. From the above, it can be seen that with an increase in sorbate concentration compared to the initial concentrations of activated sludge, there is a change in the sorption mechanism. At lower sorbate concentrations, chemisorption predominates, while at higher concentrations of sorbate, physical sorption is predominant. Based on the F-test values, it can be observed that the values obtained for the Langmuir (Eq. (3)) and Freundlich (Eq. (6)) models are approximately the same, while a significantly lower value of 0.848 was obtained for the D-R model compared to the other models.

In E3, Fig. 3 shows a similar behavior of the system as in experiment E1 (Fig. 1) and E2 (Fig. 2). The biosorption capacity values increase with increasing initial activated sludge concentration and with increasing sorbate concentration. The q_e values for E3 ranged from 119.8 to 221.5 mg/g.

Furthermore, it can be observed that the Temkin model describes the biosorption process well above the sorbate concentration range of 300 mg/L, while the Freundlich model describes it well at sorbate values below 1,200 mg/L (Fig. 3). The D-R model shows a significant deviation from the experimental results. The Langmuir model describes the entire investigated sorbate concentration range well.

2. Toxicity Assessment and Biosorption Efficiency

Although industrial effluents pose a major risk to humans and the environment [34], according to the most recent evidence published in the literature, there are currently no scientific studies on the ecotoxicological assessment of real pharmaceutical effluents [35]. One of the main roles of toxicity testing is to protect the treatment plant from the shock of incoming polluted toxic effluents [36]. To ensure maximum plant treatment efficiency, it is important to reduce toxicity during treatment. Toxicity studies were conducted with real pharmaceutical effluents before and after the biosorption process to evaluate the dependence of toxicity reduction on the activated sludge concentrations. The toxic responses obtained for the samples were defined by the toxicity impact index, TII_{50}.

The toxicity removed averaged 41.1±7.88% for all experiments (Table 4). Under equilibrium conditions, TII was reduced by 18.6 and 18.2 in E2 and E3, respectively, which is approximately the same. Increasing the initial concentration of sorbate S_0 for E1-E3 increases the value of q_e by 94.1 mg/g, but decreases the efficiency of removal of toxic substances by 15.7%, because there was saturation of active sites on sorbent [3]. All the above factors affected the biosorption efficiency, which was up to 26.5±11.13%. Guided by the goals of the circular economy, the process of biosorption was studied, which in this case reduces the formation of excess sludge. This research has shown that once the optimal concentration of activated sludge is determined, its activity is maintained and that under these equilibrium conditions there is no excess sludge, i.e., waste.

CONCLUSIONS

To reduce pollution of the environment, industrial effluents must be treated. Biosorption is a desirable process for the removal of various pollutants because of its simple and rapid effectiveness. Microorganisms from activated sludge interact with organic substances present in real pharmaceutical effluent. To survive and adapt, they reduce toxicity and organic load by biosorption. By increasing the initial concentrations of the activated sludge, the specific surface

Table 4. Results from toxicity and efficiency in the study of biosorption

Exp. #	$(TII_{50})_0$	$(TII_{50})_e$	% Toxicity removal	S_0, mg/L	q_e, mg/g	% Sorbate removal
E1	22.9±3.31	11.6±1.83	49.4±7.98	1,780±83	89.3±13.86	26.5±11.13
E2	46.2±4.06	27.6±3.70	40.3±8.00	2,717±102	129.6±27.17	25.4±11.60
E3	54.0±5.52	35.8±4.59	33.7±8.50	4,007±111	183.4±42.49	24.8±11.58

area of the sludge increases. Determination of the process parameters is important to achieve optimal operation of the unit. The biosorption process can be well described by the Temkin model for the entire investigated sorbate concentration range, with an F-test value of 0.990±0.002. The overall efficiencies of biosorption and removal of toxic substances averaged 25.6±0.86% and 41.1±7.88%, respectively.

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