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## KINETIC MODELLING OF BIOSORPTION FOR HYDROCARBON REMOVAL FROM WASTEWATER USING A MODIFIED LOGISTIC EQUATION

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**Abstract:** The application of raw and modified biomass to remove hydrocarbons from wastewater by adsorption is a common practice. A mathematical modeling of biosorption kinetics is a crucial step to optimize the remediation process. In the present study, kinetic studies were carried out to describe the sorption process of crude oil on waste sunflower stalk pith. To increase sorption capacity, the pith surface was modified with polydimethylsiloxane (PDMS) and hydrophobic SiO<sub>2</sub> nanoparticles. The maximum loading of sorption for raw and hydrophobized material was 17.76 g/g and 19.62 g/g for crude oil, respectively. The system reached the equilibrium stage after 24 hours. The uptake profiles have been described by the pseudo-first order rate equation and the pseudo-second order rate equation. The calculated results were compared with experimental data and their fit was poor. To predict biosorption kinetics, a new mathematically efficient procedure based on a modified logistic equation was developed. The results indicate that the sunflower pith is an eco-friendly sorbent with significant potential for the removal of crude oil from water phase.

**Keywords:** kinetics, biosorption, oil spills, water treatment

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# 1. Introduction

Natural fibers are useful for removing spills of crude oil and petroleum products from water surfaces. The applied sorbents should have high sorption capacity, selectivity, thermal and chemical stability, low cost of purchase and disposal. Fibers like kapok, barley straw, rice husks and residual leaves are often applied due to their wide availability and biodegradability [1]. Sorption capacity (the amount of adsorbate taken up by 1 g of sorbent) depends on many factors and varies from 1.1 g/g [2] for raw corn cobs up to 55 g/g for populus seed fibers [3]. The disadvantage of natural materials is their low selectivity towards oil. Advances in nanotechnology offer the opportunity to modify sorbents wettability relatively quickly and easily by the immobilization of controlled nanoparticles on the surface. In this way, plant fibers are used as a cheap filler and the introduced nanoparticles serve to improve their sorption properties (enhance the surface affinity to oil, enlarge the specific surface area of the sorbent). Currently, only few such hybrid materials are described in the literature. Wang et al. [4] have developed a super-hydrophobic sorbent based on kapok (*Ceibapentandra*) modified with magnetic nanoparticles of  $\text{Fe}_3\text{O}_4$ . The sorption capacity of the produced material compared to raw fibers increased by 70.8% for n-hexane and 58.5% for toluene. The addition of magnetite not only changed the morphology of the surface of the fibers but also made the sorbent easier to remove from the water surface. Yang et al. [5] produced a sorbent based on coconut dust modified with nanoparticles of  $\text{Fe}_3\text{O}_4$  and octadecylamine. This hybrid material was characterized by good sorption capacity of 8 g of petroleum/g, good selectivity and easy regeneration. A hybrid of nano $\text{Fe}_3\text{O}_4$ - $\text{SiO}_2$ -chitosan showed similar properties [6].

In this study, sunflower stem pith (parenchyma) was selected as a potential oil sorbent. The literature reports confirm good thermal, chemical and mechanical stability of this material. Annual production of sunflower parenchyma is estimated at 30–35 million tons and this plant is the fourth largest globally in terms of growing area [7]. Until now, it has not been considered as a sorbent material for the removal of oil from water bodies.

Studies on sorption kinetics help to understand the mechanism of the process, including the stages limiting the sorption rate. From a practical point of view, these measurements allow the determination of the maximum equilibrium sorption capacity (the amount of sorbent needed to remove a known amount of crude oil or its products). On their basis, it is also possible to determine the optimal time of sorbent contact with hydrocarbons. In the case of sorbents used to eliminate

surface spills, an excessive prolongation of contact time may lead to the secondary release of hydrocarbons from the surface of the material due to the movement of sea waves. Over time, the mechanical stability of the sorbent may deteriorate due to mixing and swelling. In this work, both conventional kinetic models (pseudo-first order rate equation and the pseudo-second order rate equation) and a newly developed modified logistic equation were used to predict sorption kinetics of the tested material.

## 2. Method section

### 2.1. Materials

Raw sunflower stems were harvested from the Tarnów region, Poland, in 2017. The outer woody part of stems were removed in order to obtain the spongy pith. The material was then washed with distilled water and dried in an oven at 30°C until the moisture content decreased to 3% wt. For further experiments a fraction with particle size of 1.5–4.0 mm was used. Hydrophobic nanosilica was purchased from PlasmaChem GmbH. Polydimethylsiloxane from Acros Organics was used as a coupling agent. For sorption experiments a real crude oil from an oilfield in southern Poland was used.

### 2.2. Immobilization of $\text{SiO}_2$ nanoparticles on sunflower fibers by facile one-step spray method

10 g of PDMS was solved in 90 mL of n-pentane and 10 g of hydrophobic  $\text{SiO}_2$  was dispersed in 100 mL of pure ethanol. Both solutions (10 mL of PDMS solution and 25 mL of dispersed  $\text{SiO}_2$ ) were subsequently sprayed over the surface of 10 g of pith using a glass vaporizer from 25 cm distance. The prepared material was dried at 40°C for 6 hours. In further research the raw pith is denoted as material S and the modified pith as nS1.

### 2.3. Kinetics of adsorption

1 g of sorbent was contacted with 50 g of a crude oil in a 250 mL beaker at a specific time of contact (from 1 minute to 48 hours). After the specific time elapsed, the sorbent was removed from the oil using steel sieves (1 mm mesh holes). Dripping for 10 minutes allows for

a complete drainage of the excess of liquid, the remaining sorbent was weighed. Sorption capacity  $q_t$  at time  $t$  was calculated according to equation:

$$q_t = \frac{m_t - m_s}{m_s} \quad (1)$$

where  $m_t$  and  $m_s$  are the mass of the wet and dry sorbent, respectively [g].

## 2.4. Modelling approach

The mathematical description was based on the pseudo-first-order equation and the pseudo-second-order equation. The pseudo-first order (PFO) model is shown by equation:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (2)$$

where  $q_t$  and  $q_e$  are the amount of oil adsorbed by sunflower pith at time  $t$  and at equilibrium, respectively [g/g] and  $K_1$  is the rate constant of the pseudo-first order model [1/min]. For the boundary conditions of  $q_t = 0$  at  $t = 0$  the pseudo-first order model after integrating follows the equation:

$$\ln(q_e - q_t) = \ln q - K_1 t \quad (3)$$

This equation, developed originally by Lagergren, described the kinetics of carboxylic acids sorption on charcoal [9]. Oil sorption on acetylated corn cobs was also well described by this equation [10]. It is assumed that this PFO model well predicts the initial stage of the process before reaching equilibrium [11].

The pseudo-second-order (PSO) kinetic model is expressed as:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (4)$$

where  $K_2$  refers to the adsorption rate constant of PSO kinetic model. This equation can be integrated for initial condition  $q_t = 0$  at  $t = 0$  and described according to:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

In the oil-biosorbent system this kinetic equation was used to model sorption of diesel oil on rice husk [12], crude oil on acetylated pineapple leaves [13], gasoline on carbon nanotubes [14].

Plaźiński and Rudziński [15] showed that both of the abovementioned equations (PSO and PFO) are empirical equations to which no specific physical models correspond. Fitting experimental data to these models does not explain the mechanism of the process. The logistic equation provides more information about interactions in studied systems. Çelekli et al. applied successfully the logistic model to describe kinetic sorption of Reactive Red 120 on *C. contraria* [16] and *Moringaoleifera* seed [17]. The applied equation allowed to explain the physical nature of the sorption and precisely predict the maximum sorption capacity. In this study, the authors used a modified logistic equation in the form:

$$\frac{1}{q_t} \frac{dq_t}{dt} = F(t)(q_e - q_t) \quad (6)$$

where  $F(t)$  is a function of time and can be given in the form:

$$F(t) = \frac{k_{lg}}{t^\alpha} \quad (7)$$

where  $k_{lg}$  is an adsorption rate constant [-] and  $\alpha$  is a constant describing sorbent-sorbate interactions,  $\alpha = 0.5$  was assumed in the work. After integration within the boundaries with the initial condition  $q_{t \rightarrow \infty} = q_e$  the solution of equation (7) can be written as follows:

$$q_t = \frac{q_e}{1 + C \cdot \exp\left(\frac{-q_e \cdot k_{lg}}{1 - \alpha} \cdot t^{1-\alpha}\right)} \quad (8)$$

where  $C$  is the model constant. The parameters  $q_e$ ,  $k_{lg}$ ,  $C$ , and  $\alpha$  were fitted to the experimental values by use of the least squares method.

RMSE (root mean square error) and  $\chi^2$  statistical criteria were applied to compare the measured and calculated results of sorption kinetics for oil sorption onto biomass. These parameters were calculated as follows:

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (q_{e,exp} - q_{e,calc})^2} \quad (9)$$

$$\chi^2 = \sum_{i=1}^N \frac{(q_{e,exp} - q_{e,calc})^2}{q_{e,calc}} \quad (10)$$

where  $N$  is the data numbers,  $q_{e,exp}$  and  $q_{e,calc}$  are the empirical and calculated values, respectively.

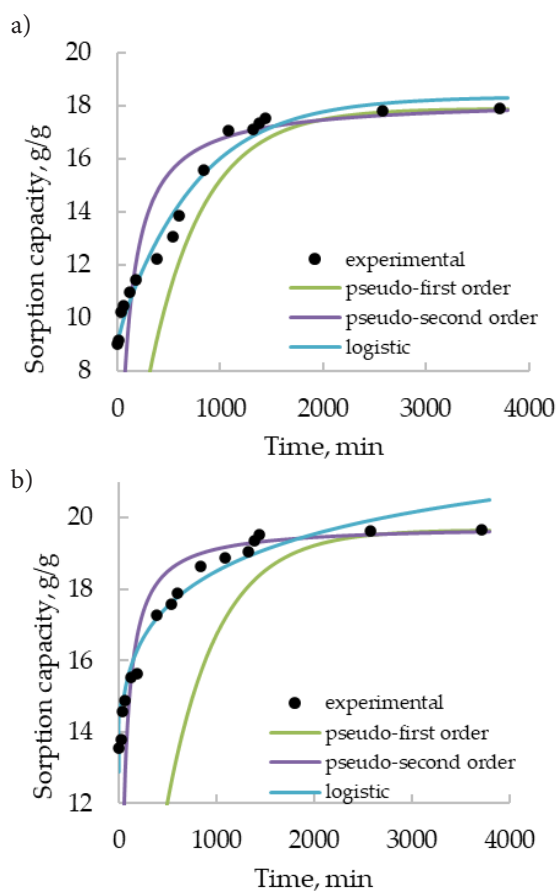
### 3. Results and discussion

The contact time significantly influences oil sorption capacity for both raw and modified pith sorbents as shown in Figure 1. Values of parameters fitted to the kinetic models are given in Table 1.

The sorption capacity increases with time and in the initial stage the relative sorption rate is high. After 24 hours crude oil uptakes attain equilibrium. The specific surface area of the sorbent plays a key role in the first stage of process while the spongy structure of pith determines its high sorption capacity for longer contact times. After 15 minutes of contact, raw sunflower fiber sorbs of 9.03 g of crude oil, while modified material with an increased surface area sorbs 13.79 g/g. Finally, the maximum sorption loading for the tested oil is 17.76 g/g and 19.62 g/g for materials S and nS1, respectively. The structure and composition of the sorbent affect the time after which the maximum sorption capacity is reached. For hydrophobic nanopowders the equilibrium state is attained quickly. The optimum contact time for carbon nanotubes [18] and hydrophobized aluminium nanoparticles is 30 minutes [19]. Plant sorbents (highly fragmented, fibrous and hydrophobized with various chemical additives) are equally effective and achieve maximum absorbency in several minutes. Sugar cane pulp modified with stearic acid [20] and acetylated rice husks [21] reached the equilibrium after 15 minutes. Materials with a complex porous structure such as luffa fruits [22], kapok fibers [22] or polyurethane foams [23] require a longer contact time, up to 24 hours.

The adsorption is faster and more effective for modified material than for raw fibers. Even at very short

contact time, less than 1 minute, the tested materials show rather a high sorption capacity of 8 g/g.



**Fig. 1.** Kinetics of crude oil sorption for: a) unmodified; b) modified pith

**Table 1.** Kinetic parameters for the removal of crude oil by raw and hydrophobized pith

Model	Parameters	Raw pith	Hydrophobized pith
Pseudo-first order	$K_1$ [1/min]	0.0019	0.0019
	$q_e$ [g/g]	17.90	19.67
	$\chi^2$	2678	5521
	RSME	5.164	8.089
Pseudo-second order	$K_2$ [g/(g·min)]	0.0006	0.0014
	$q_e$ [g/g]	18.25	19.80
	$\chi^2$	415.159	321.886
	RSME	3.370	4.108
Modified logistic	$q_e$ [g/g]	18.824	19.932
	$k_{lg}$	0.002	0.002
	$C$	1.336	0.553
	$\alpha A$	0.5	0.5
	$\chi^2$	0.537	0.067
	RSME	0.681	0.262
Maximum sorption capacity determined experimentally	$q_{exp}$ [g/g]	17.757	19.619

**Table 2.** Comparison of kinetic models for adsorption of oil on hydrophobized plant sorbents

Model	Parameters	Adsorbent – adsorbate		
		Enzyme-modified corn stalk – crude oil [24]	Acetylated <i>Dacryodes edulis</i> leaf – crude oil [25]	Kapok modified with PBMA/SiO <sub>2</sub> – oil 150SN [26]
Pseudo-first order	$K_1$ [1/min]	0.840	0.251	3.582
	$q_{e,calc}$ [g/g]	22.744	4.846	75.700
	$\chi^2$	2.574	0.019	0.441
	$RSME$	2.261	0.112	2.166
Pseudo-second order	$K_2$ [g/(g · min)]	0.019	0.102	0.071
	$q_{e,calc}$ [g/g]	25.575	5.064	78.683
	$\chi^2$	6.565	0.004	0.938
	$RSME$	2.419	0.048	2.859
Modified logistic	$k_{lg}$	0.009	0.092	0.012
	$q_{e,calc}$ [g/g]	25.410	4.927	77.246
	$C$	1.023	2.848	0.681
	$\alpha$	0.5	0.5	0.5
	$\chi^2$	0.045	0.003	0.065
	$RSME$	0.313	0.049	0.837
Maximum sorption capacity determined experimentally	$q_{exp}$ [g/g]	24.98	4.990	78.43

The pseudo-first order model is ineffective when describing the sorption of oil on the tested sorbents. The mathematical model should fit the measurement data in their entire range. PSO and PFO models poorly describe the initial stage of sorption (for short contact times) as shown in Figure 1. Based on the  $\chi^2$  and  $RSME$  values it can be seen that the discrepancies between the predictions of both models and the actual data are quite large. A modified logistic model provides the best match to the experimental data.

The developed logistic model was fitted to experimental data reported by other researchers to prove its applicability in kinetics modelling. Table 2 summarizes the kinetic parameters of selected hydrophobized plant sorbents.

In general, in most works, the pseudo-second order model gives a better fit than the pseudo-first order equation, and it predicts well the maximum sorption capacity in particular. The newly developed kinetic model describes well the data over the entire measuring range and can be used for different fibers.

## 4. Conclusions

Mathematical modelling of the adsorption process allows the identification of the process mechanisms

(kinds of interactions between the sorbent and the sorbate) and to predict its course in time. Since the chemical compositions of both crude oil and natural fibers are complex, the most appropriate mathematical model should be fitted separately to each tested system. The sorption capacity is 17.76 and 19.62 g oil/g for raw and modified pith, respectively. The sorption equilibrium time is 24 hours due to the porous structure of the pith. The commonly used kinetics models (pseudo-first order and pseudo-second order equations) do not allow for an accurate prediction of sorption capacity for hydrocarbons in the whole measurement range. Due to the complex structure of the studied sorbents, the typical kinetic description was not sufficient, and a modified logistic equation was proposed. The calculations based on this concept showed that this model closely agreed with the experimental results.

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