

Czech University of Life Sciences Prague
Faculty of Environmental Sciences

DIPLOMA THESIS



Mathematical Modeling of Sorption on Novel Sorbent Materials

Adna Koš

Department of Water Resources and Environmental Modeling

Supervisor of the diploma thesis: doc. Ing. Michal Kuráž, Ph.D.

Study programme: Landscape Engineering

Field of study: Environmental Modeling

Prague, 2021

DIPLOMA THESIS ASSIGNMENT

Adna Koš

Landscape Engineering
Environmental Modelling

Thesis title

Mathematical modeling of sorption on novel sorbent materials

Objectives of thesis

Conducting a study which is representing different sorption approaches for modeling kinetic sorption and equilibrium sorption on sorbent materials. For better representation of hypothesis, synthetic scenarios will be created within this thesis, for different experimental setups.

Methodology

Methodology includes creating a literature review describing different sorption approaches including non-linear Langmuir model and non-linear Freundlich model. Both models will be created using programming language Fortran, and data will be represented and analyzed using different tools (e.g. R). Additionally, in case that sufficient experimental data is available, beside creating and analyzing synthetic scenarios, models will also be tested on conducted experimental data.

The proposed extent of the thesis

60 pages

Keywords

Langmuir model, Freundlich Model, Adsorption Isotherms, Modeling of solute transport, Kinetic Sorption, Equilibrium Sorption

Recommended information sources

- L. Trakal; Environmental Hydrogeology; Czech University of Life Sciences; FES, Prague 2015
M. Kuraz, J.R. Bloecher, Hydrodynamics in porous media, CULS in Prague lecture notes, Prague 2020
Sing, Kenneth S.W. (1998). "Adsorption methods for the characterization of porous materials". Advances in Colloid and Interface Science. 76–77: 3–11. doi:10.1016/S0001-8686(98)00038-4.
Susan L. Brantley, James D. Kubicki, Art F. White; Kinetics of Water – Rock Interaction; Springer, New York, NY
Victor O. Shikuku, Chrispin O. Kowenje and Fredrick O. Kengara; Errors in Parameters Estimation Using Linearized Adsorption Isotherms: Sulfadimethoxine Adsorption onto Kaolinite Clay; Chemical Science International Journal; ISSN: 2456-706X
Xunjun Chen; Modeling of Experimental Adsorption Isotherm Data; Information 2015, ISSN: 2078- 2489

Expected date of thesis defence

2020/21 SS – FES

The Diploma Thesis Supervisor

doc. Ing. Michal Kuráž, Ph.D.

Supervising department

Department of Water Resources and Environmental Modeling

Electronic approval: 19. 1. 2021

prof. Ing. Martin Hanel, Ph.D.

Head of department

Electronic approval: 19. 1. 2021

prof. RNDr. Vladimír Bejček, CSc.

Dean

Prague on 27. 03. 2021

Author acknowledgments

I owe a special thanks to my supervisor doc. Ing. Michal Kuráž, Ph.D., on support, time, knowledge and effort. Thank you for trusting me.

I am grateful to my parents and my family. Although they are kilometers away, at no point did I feel a lack of love and support.

I owe a gratitude to my friends and the family I gained in Prague, for the multitude of advice, for the long conversations, patience and for the immense support. I'm happy to have you.

Many thanks to my partner, Bojan Glavan. Thank you for being with me side by side on this journey. You are my best friend, my pride and my hero. I wouldn't be where I am today if it weren't for you.

Adna Koš

I hereby declare that I carried out the submitted diploma thesis, **Mathematical modeling of sorption on novel sorbent materials** independently, and only sources listed in the Bibliography were used.

In Prague, 27th March 2021

Adna Koš

Abstract

The emission of metal ions in the environment has increased in recent times and since metal ions are not biodegradable, they belong to the cumulative toxins. Contamination of the environment with metal ions poses a serious danger to the entire ecosystem, agricultural production, quality of food and water, as well as to the health of humans and animals. This study investigates sorption as one of the processes which can be used for pollutants removal and efficiency of certain sorbent materials. Specifically, the focus is on the development and validation of non-linear Langmuir model and non-linear Freundlich model. Their application in the sorption experiment is examined by applying different error functions and statistical methods which are employed to calculate the error divergence between the observed and the predicted data of the sorbate-sorbent system. The presented non-linear sorption models are developed by using FORTRAN programming language, and data analysis is performed by using different tools and packages in R programming language. Many authors use linear sorption models in the way that they would linearize non-linear sorption models. It is evident that linear sorption models are used due to their simplicity in parameters estimation. This study shows that both non-linear Langmuir model and non-linear Freundlich model can be used for experimental data representation. The results also denote that the better estimation and better fit are given by Langmuir model due to statistical analysis and graphical representation itself. The choice of sorption model has a great influence on the prediction of solute transfer and great care should be taken in selection of convenient approach.

Keywords: Langmuir model, Freundlich model, Adsorption isotherms, Modeling of solute transport, Kinetic sorption, Equilibrium sorption

Contents

1	Introduction	3
1.1	Objectives	4
1.2	Methodology	5
2	Sorption	6
2.1	Introduction to sorption	6
2.2	Types of sorption	7
2.3	Sorption kinetics models	9
2.3.1	Pseudo-first-order kinetic model	9
2.3.2	Pseudo-second-order kinetic model	10
2.3.3	Intra-particle diffusion model	11
2.4	Sorption isotherms models	13
2.4.1	Langmuir model	13
2.4.2	Freundlich model	14
2.4.3	Comparison of Langmuir and Freundlich model	15
3	Sorbent materials	16
3.1	About sorbent materials	16
3.1.1	Factors influencing the sorption process	17
3.2	Application of sorbent materials	19
3.2.1	Commonly used sorbents	19
3.2.2	Waste materials as sorbents	20
4	Mathematical modeling	24
4.1	Introduction to mathematical modeling	24
4.1.1	Classification of mathematical models	24
4.2	Modeling process	25
4.2.1	Parameter estimation	25
4.2.2	Error functions	26
4.3	Modeling of sorption processes	27
4.3.1	Adsorption isotherms	27
5	Methodology	32
5.1	Objectives	32

5.2	Experiment description	32
5.3	Used tools	33
5.4	Workflow	34
5.4.1	Code development in FORTRAN	34
5.4.2	Parameters estimation in R	35
5.4.3	Obtainment of modeled values	36
5.4.4	Statistical analysis	36
5.4.5	Possible outcomes	38
6	Results and discussion	39
6.1	Results	39
6.1.1	First data set	39
6.1.2	Second data set	42
6.1.3	Third data set	44
6.1.4	Fourth data set	46
6.2	Discussion	48
7	Conclusion	53
	Appendix	63
A.1	Experimental values of concentrations	63
A.2	Adsorption capacities	64

Chapter 1

Introduction

The increase in the number of inhabitants, the huge industrial and agricultural production, the amount of cars, the chemicals that are used every day, and a number of other activities, have significantly influenced the increase in the concentration of pollutants in the environment. The presence of harmful substances in the environment poses a threat to the flora and fauna, as well as ourselves. Although water covers 70% of the world's surface, the amount of fresh water that is available for consumption is decreasing. All of those factors resulted in the need to search for processes and materials that lead to the purification and protection of the environment (C. Chen, 2013; Kajjumba et al., 2019).

One of the processes that play an important role in soil and environmental science, and is the driving force of many technologies, is **sorption**. Sorption is introduced as a process by which a substance accumulates on the boundary of two phases or within another phase. Adsorption and absorption processes can be distinguished based on the location where the substance accumulates. Adsorption is a process where atoms, ions, or molecules are held on the surface of a solid, while absorption implies that they are transferred into, and then distributed throughout the entire substance. (Patiha, Herald, and Hidayat, 2016; Thompson and Goyne, 2012). In order to evaluate the capacity of a sorption system and to provide important information for understanding the interaction between the solute and sorbing substance, the **sorption isotherms** must be established (C. Chen, 2013). They represent an important step towards interpretation and improvement of effective design of sorption system (Ayawei, Ebelegi, and Wankasi, 2017;

El-Khaiary, 2008). In addition to a number of factors influencing the sorption process, the choice of model also has a huge impact on predicting solute transfer (Limousin et al., 2007). Today, many researchers use linear models to describe processes because of their simplicity, however, it should be considered that linearization of a non-linear model can induce deviations that can later significantly change the course of the process. The model is a mathematical description of physical reality, for this reason the model should be presented as accurately as possible in order to get the better result. Within this study, two non-linear models were used: the Langmuir model, which suggests that uptake occurs in homogeneous surface by mono-layer sorption without interaction between sorbed molecules; and Freundlich model, which suggests that uptake occurs in a heterogeneous surface (Hameed, Ahmad, and Latiff, 2007; Benes and Majer, 1980; Attallah, Hassan, and Youssef, 2019).

1.1 Objectives

An increment in the release of phosphate-containing wastewater into natural water bodies have been observed. This has greatly affected water quality, because this pollution encourages the eutrophication process which further leads to depopulation of aquatic living species. Eutrophication is characterized by a supersaturation of water with minerals and nutrients that promote excessive algae growth, which results in oxygen depletion in the water body after bacterial degradation of algae. This study examines how useful the chosen adsorbent is in order to control this process, i.e., to what extent it can participate in reduction of phosphate concentration in wastewater. The chosen data sets are taken from the literature.

The study focuses on mathematical modeling of the sorption process, specifically the adsorption process. It suggests the principle of the mathematical modeling of the process which can be used as a base for developing a discussion of the parameters that contribute to efficient sorption design. Understanding the parameters itself further leads to calculating the deviation of the modeled data from the measured values. The goal is to optimize the process, in other words to

reduce the deviation values in order to get the most effective model.

1.2 Methodology

This thesis is divided into several chapters. The second chapter highlights the basic concepts of sorption and the course of the sorption process. It also gives an insight into kinetic sorption and equilibrium sorption, and a range of assumptions, concepts, and formulations on which they are based. The knowledge acquired in the second chapter is supplemented by information on sorbent materials in the third chapter. In addition to learning about commonly used sorbents such as zeolite, clay, activated carbon and others, the study discusses some other materials that are economically acceptable, the so-called low-cost materials that are readily available in nature. Throughout the fourth chapter, the process of model building is presented through the prism of the concept of mathematical modeling. To better understand the experimental part of the study, this chapter explores concepts such as model types, parameter estimation and the concept of objective function. The chapter is concluded by possible outcomes of modeling the adsorption process. In the fifth chapter of this thesis, together with the thesis objectives, the methodology used in the case study is explained in greater detail, while in the sixth chapter experimental data obtained by batch experiment are presented and analysed. Adsorbent Fe(III)-coordinated amino-functionalized mesoporous MCM-41 with four different amino loads for phosphate removal from solution was examined. For the purpose of analysis, two programming languages were used - FORTRAN and R. Using FORTRAN, the non-linear Langmuir model and the non-linear Freundlich model were developed. Estimation of parameters was performed within the programming language R (R Core Team, 2020). Further analysis included the use of different error functions, coefficient of determination (R-Squared) and graphical representation of data, which can be used to portray a clearer picture of models and the theories behind them. The parameter estimation algorithm is based on non-linear regression, in other words, the data are modeled using a non-linear function. The modeling results provide a certain share of the theoretical base required for the design of the adsorption system.

Chapter 2

Sorption

2.1 Introduction to sorption

Pollution of the environment with metal ions poses a serious danger to the entire ecosystem, agricultural production, quality of food and water, as well as to the health of humans and animals. Metal ions are generally not biodegradable and belong to the cumulative toxins that accumulate in the body in certain organs and tissues, which over time leads to severe damage and disease. Some of the hazardous metals are lead, cadmium, mercury, zinc, copper, chromium, nickel, etc. The emission of metal ions in the environment has increased in recent times due to industrial, agricultural and domestic activities. From the atmosphere, soil surface, and groundwater, metals are introduced and accumulated in plants, and further through the food chain they reach the human body. Apart from food, they can reach the human body through the skin or respiratory tract. Metals can be inhaled in the form of aerosols or vapors into the lungs where they are absorbed into the bloodstream (El-Naas and Alhaija, 2013; Mihajlović-Kostić, 2016).

One of the processes that can be used for removal of pollutants is **sorption**. We define the process of removal of a compound from solution to a solid phase as sorption. Opposite to that, the release of atoms, ions or molecules from solids into solutions is defined as **desorption**, it refers to the loss of matter from the interface. The term sorption, in many cases, encompasses adsorption and absorption phenomena. **Adsorption** is a surface based process in which atoms, ions

or molecules attach to the surface of a substance without entering it. In other words, it represents an adhesion of particles on surfaces. **Absorption** involves the whole volume of the material where atoms, ions or molecules of one phase enter the substance of another phase, and are incorporated by it.

The term sorption is sometimes used for borderline cases, when it is impossible to distinguish between adsorption and absorption. What is common in the cases of sorption and adsorption is that both of the phenomena are based on the colonization of a solid solvent by a solute. When discussing sorption processes, we call the adsorbing/absorbing solid phase the *sorbent*; solutes in the liquid phase that could potentially sorb are known as *sorptives*, and constituents that accumulate on or within a solid are termed as *sorbates* (Thompson and Goyne, 2012; Chorover and Brusseau, 2008; Enciklopedija, 2018; Schaetzel, Thomas, and Louahlia-Gualous, 2017).

2.2 Types of sorption

Sorption is considered to be performed through several consecutive phases. The first stage is the transfer of sorbates (toxic metals) to the outer surface of the sorbent. The second stage is usually a much slower diffusion of sorbates into the internal porous structure of the sorbent, which mainly takes place in mesopores, micropores or capillaries, and only a small amount of sorbates binds to the outer surface of the sorbent. The third stage is the binding of sorbates to the inner or outer surface of the sorbent (Marinić Pajc et al., 2012; El-Naas and Alhaija, 2013). Interactions between sorbent and sorbate can be divided into *physical* (inter-molecular) and *chemical* (inter-atomic). Based on this division, two basic types of sorption are distinguished:

- physical sorption (physisorption),
- chemical sorption (chemisorption).

The sharp line distinguishing chemisorption from physisorption cannot always be drawn. There are cases where it is difficult to define the type of sorption.

One of the most important criteria is *the enthalpy* of sorption, which is significantly higher for chemical than for physical sorption. Significantly lower enthalpy of physisorption compared to chemisorption is a consequence of the type of bond between sorbent and sorbate. Physical sorption is based on Coulomb's electrostatics attractive interactions, an impact of weak van der Waals forces, and the construction of hydrogen bonds between sorbate and sorbent. Van der Waals forces are weak forces, so the energy released during physisorption is small (from 1 kJ/mol to 40 kJ/mol). The hydrogen bond is also a weak bond and is based on electrostatic attraction between a hydrogen atom and a nucleophilic atom containing free electron pairs. Unlike van der Waals bonds, the hydrogen bond has a certain orientation. Hydrogen bond energies range from 20 kJ/mol to 40 kJ/mol. The energy released during physical sorption is small and is released through the vibrations of the sorbent lattice and is dissipated as heat accepted by the sorbate particles. Thanks to this energy, sorbate particles move on the surface of the sorbent, gradually lose energy and eventually sorb in a stage called accommodation. Physisorbed particles retain their chemical identity, in other words, the initial chemical structure, so that they can be returned to their original state in solution by desorption (reversible process). In contrast, chemisorption involves the transfer of electrons that lead to the formation of chemical bonds between sorbent particles and sorbates on the surface layer, meaning that chemisorbed particles have undergone a chemical change (chemical reaction or dissociation) thus losing their chemical identity and cannot return to solution by simple desorption, so these processes are often irreversible processes.

High activation energy (from 40 kJ/mol to 800 kJ/mol) indicates chemical sorption, while *low activation energy* (from 5 kJ/mol to 40 kJ/mol) is a characteristic of physical sorption. Since chemisorption requires higher activation energy, it takes place at lower temperatures at a limited rate, which increases with increasing temperature. In contrast, the rate of physical sorption is high at lower temperatures and decreases with increasing temperature. Thus, the sorption rate is also an important criterion for distinguishing between physical and chemical sorption.

Another criterion, based on which it can be concluded whether it is physisorption or chemisorption, is the *thickness of the sorbed layer*: multi-layer adsorption definitely indicates physical sorption (Mihajlović-Kostić, 2016).

2.3 Sorption kinetics models

The sorption kinetics is very important for describing the rate of removal of the pollutant, which is needed from the aspect of determining the possibility of sorbent application. Experimental determination of the dependence of the amount of sorbed matter on time is the basis of kinetic analysis of sorption (Marinić Pajc et al., 2012).

The sorption process takes place until a dynamic equilibrium is established between the residual amount of sorbate in solution and its amount on the surface of the solid phase. If the sorption process is represented as a function of time, then it is most often described by **kinetic equations**. By determining the parameters of different kinetic models, based on experimentally determined sorption capacities at different contact times of sorbate and sorbent solution, it is possible to determine which model is most suitable for describing sorption kinetics. In that way, information is obtained about the sorption mechanism. The most commonly used are *pseudo-first-order* and *pseudo-second-order kinetic model*, and as well, *intra-particle diffusion model* (Mihajlović-Kostić, 2016).

2.3.1 Pseudo-first-order kinetic model

Lagergren, 1898, proposed a pseudo-first-order equation for sorption in a system liquid-solid, based on solid phase capacity. The expression for the reaction rate can be represented by the equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \quad (2.1)$$

and it represents the Lagergren equation of the pseudo-first-order, where q_t (mg g⁻¹) represents the sorption capacity at time t (min), q_e (mg g⁻¹) is the sorption

capacity at equilibrium conditions, and k_1 (min^{-1}) is the pseudo-first-order rate constant. By integrating the expression for the boundary conditions $t = 0$ to $t = t$, and $q_t = 0$ to $q_t = q_t$, we obtain a linearized form of the Lagergren equation:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t. \quad (2.2)$$

The model is applicable to describe the kinetics of a given sorption process if the dependence of $\log(q_e - q_t)$ on time t is linear, and in that case q_e and k_1 can be calculated from the slope and intersection of line with y axis (see Figure 2.1). In many cases, the pseudo-first-order kinetic model cannot be applied during the entire sorption, but only in the case when the sorption process takes place at high speed, i.e., only for the first phase of the process (Sandić et al., n.d.; Mihajlović-Kostić, 2016). Most commonly, this model is used to describe the adsorption of solute from a liquid solution (El-Naas and Alhaija, 2013).

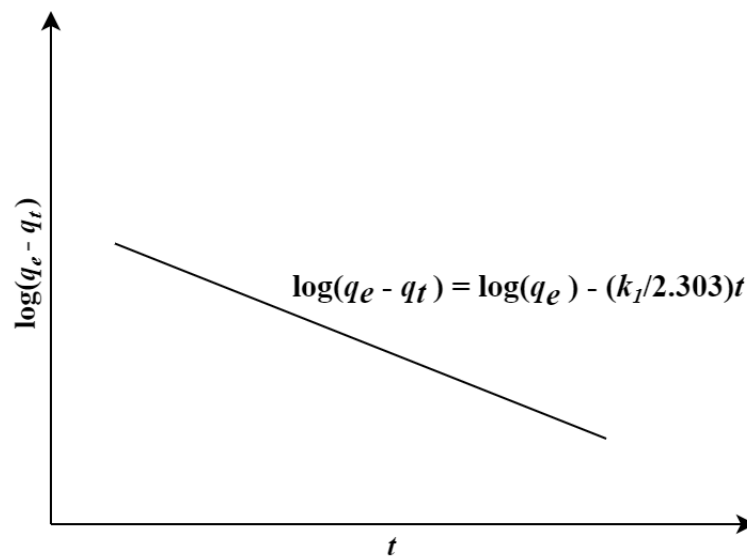


Figure 2.1: Pseudo-first-order kinetic model

2.3.2 Pseudo-second-order kinetic model

The pseudo-second-order equation was first performed by Blanchard, Maunaye, and Martin, 1984. Later, Ho and McKay, 1999, bearing in mind that the kinetic model of the pseudo-first-order can be applied only to the first phase of

the process, developed a model of the pseudo-second-order, which can describe the entire period of the sorption process. The expression for the sorption rate is:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2, \quad (2.3)$$

where q_e (mg g⁻¹) and q_t (mg g⁻¹) are the quantities of sorbates sorbed at equilibrium and at time t (min), and k_2 (g mg⁻¹ min⁻¹) is a pseudo-second-order rate constant. By integrating the expression for the boundary conditions $t = 0$ to $t = t$, and $q_t = 0$ to $q_t = q_t$, we obtain the integral form of equation of pseudo-second-order:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}. \quad (2.4)$$

Simple kinetic models, such as pseudo-first and pseudo-second-order models, do not describe the true rate and mechanism of the sorption process, especially if the surface is in-homogeneous and/or if multiple processes occur simultaneously (e.g., diffusion, hydrolysis, ion exchange, hemisorption, etc.), but a good correlation between experimental data and simple kinetic models is important in predicting and comparing results (Mihajlović-Kostić, 2016). The pseudo-second-order kinetic model is applicable if the dependence of ratio t/q_t on time t is linear (Sandić et al., n.d.).

2.3.3 Intra-particle diffusion model

To examine the role of diffusion in the sorption process, the data are analyzed using the intra-particle diffusion model proposed by Weber and Morris, 1963. By applying this model to the results of sorption kinetics testing, it is possible to predict the influence of individual stages of the sorption process on the total sorption rate. The intra-particle diffusion model is represented by the expression:

$$q_t = k_d t^{1/2} + I, \quad (2.5)$$

where section I (mg g⁻¹) refers to the thickness of the boundary layer along the surface of the sorbent, and k_d (mg g⁻¹ min^{-0.5}) is the velocity constant of the intra-particle diffusion model. If a straight line is obtained by drawing the dependence of q_t on $t^{1/2}$, then intra-particle diffusion is part of the sorption process.

The value of the constant k_d can be determined from the slope of the specified rectilinear dependence (see Figure 2.2). The model further predicts the influence of intra-particle diffusion, i.e., diffusion in the pores, on the speed of the sorption process according to the position of the rectilinear dependence in relation to the coordinate origin:

1. if a straight line passes through the coordinate origin then intra-particle diffusion is the degree that determines the rate of the sorption process, and
2. if the straight line does not pass through the coordinate origin, then the rate of sorption is determined by the rate of diffusion through the boundary layer, where the influence of diffusion through the boundary layer is greater the greater the segment I (Mihajlović-Kostić, 2016).

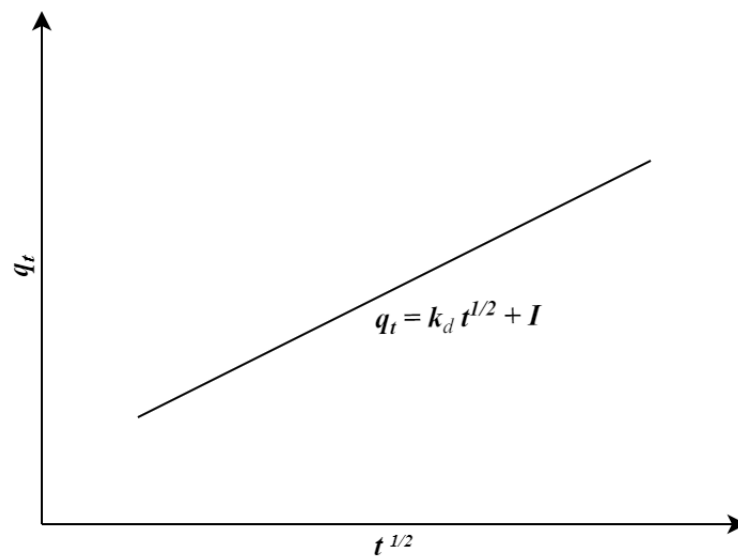


Figure 2.2: Intra-particle diffusion model

2.4 Sorption isotherms models

If the sorption rate (see Equations (2.1) and (2.3)) is equal to zero, it means that the system has reached the equilibrium state, and that we are dealing with an **equilibrium sorption process** (Fetter, Boving, and Kreamer, 2018). **The sorption isotherm** represents the dependence between the amount of sorbate on the sorbent at equilibrium, q_e , and the equilibrium concentration of sorbate in solution in contact with the sorbent, C_e , at a constant and specified temperature. This dependence can be applied only if there is a sorption equilibrium of the sorbent/sorbate system and if all other physicochemical parameters of the system are constant (Limousin et al., 2007).

For the description and analysis of equilibrium sorption processes, models that are most commonly used are: *Langmuir model* and *Freundlich model*. From these models, important data for understanding the mechanism of sorption processes is obtained (Mihajlović-Kostić, 2016).

2.4.1 Langmuir model

The original Langmuir model of the adsorption isotherm from 1918, refers to the mono-molecular adsorption of gases on homogeneous solid surfaces. The gas molecules are adsorbed in uniform places on a solid surface and the adsorbed molecules are not interconnected, in other words, the binding sites have the same affinity for the adsorption and no interaction occurs between adsorbates. According to this model, the adsorbent has a final capacity for adsorbate, i.e., the adsorbed molecules can cover the surface until a complete mono-molecular layer is formed. Therefore, the Langmuir model of the adsorption isotherm was chosen for the process of maximum adsorption capacity corresponding to the formation of a complete mono-layer on the surface adsorbent. As well the enthalpy of adsorption is the same for all molecules (El-Naas and Alhajja, 2013; Mihajlović-Kostić, 2016).

The q_e (mg g^{-1}) adsorption capacity at equilibrium, can be calculated using

the mass balance equation:

$$q_e = \frac{(C_0 - C_e)V}{m}, \quad (2.6)$$

where C_0 (mg L⁻¹) is the initial concentration of the adsorbate, C_e (mg L⁻¹) is the equilibrium concentration of the adsorbate, V (L) is the volume of solution to be treated, and m (g) represents the mass of sorbent. In this way, experimental value of adsorption capacity can be obtained. Now, the non-linear Langmuir model is expressed as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}, \quad (2.7)$$

where q_m (mg g⁻¹) is the maximum adsorption capacity of the adsorbent and K_L (L mg⁻¹) is the Langmuir adsorption constant related to the energy of adsorption. Coefficient K_L defines the strength of the bond between the adsorbent and the adsorbate (Shikuku, Chrispin, and Kengara, 2018; Marinić Pajc et al., 2012; Langmuir, 1916).

2.4.2 Freundlich model

The Freundlich isotherm occurs very often in systems where sorption takes place by physical forces and is not limited to the formation of a mono-molecular layer on the sorbent surface, but the molecules can still bind to the previously formed layer (Marinić Pajc et al., 2012). The model is represented by an empirical equation predicting that the adsorption occurs on an energetically heterogeneous surface, on which the adsorbed molecules are interactive and adsorption capacity is related to the concentration of the adsorbate at equilibrium. The non-linear Freundlich model is expressed as:

$$q_e = K_F C_e^{\frac{1}{n}}, \quad (2.8)$$

where K_F ((mg g⁻¹)(mg L⁻¹)ⁿ) is the Freundlich coefficient that represents adsorption capacity equivalent, n (-) is the constant related to adsorption intensity, q_e (mg g⁻¹) and C_e (mg L⁻¹) are the adsorption capacity at equilibrium and the equilibrium concentration of adsorbate in liquid phases, respectively. The large

value of the Freundlich constant K_F indicates a large adsorption capacity, meaning high affinity of the adsorbent for the adsorbate (Mihajlović-Kostić, 2016). The value of the constant n denotes the favorability of the adsorption process. If the value of n is less than 1 then adsorptive potential is considered as poor; in the case that value is in the range from 1 to 2, adsorptive potential is moderately difficult; value from 2 to 10 depicts good adsorptive potential (Shikuku, Chrispin, and Kengara, 2018).

2.4.3 Comparison of Langmuir and Freundlich model

If we compare the Langmuir and Freundlich isotherms, the Freundlich constant K_F is analogous to the maximum adsorption capacity q_m for the Langmuir isotherm. Unlike the Langmuir isotherm, which implies energetically identical places on the surface and saturation during mono-layer formation, the Freundlich isotherm does not predict the saturation of the solid surface with adsorbate, so the constant K_F represents a relative indicator of adsorption capacity (Mihajlović-Kostić, 2016).

The Freundlich equation requires that adsorption increases with increasing pressure, but in many cases it can be found that this amount increases only up to a certain value and then remains constant despite the increase in pressure. Langmuir explained this by assuming that in these cases the adsorption stops when the surface is completely covered by the mono-molecular layer of the adsorptive. Assuming further, that at any moment the rate of adsorption is proportional to the surface still uncovered, and the rate of desorption to the surface already covered by the mono-molecular layer. Langmuir obtains equilibrium when the rate of adsorption is equal to the rate of desorption (Enciklopedija, 2018).

Chapter 3

Sorbent materials

3.1 About sorbent materials

Examination of the sorption process, including sorbent materials, in order to prevent the interaction of heavy metals and radionuclides with living matter and their accumulation, as well as monitoring migration in the environment and finding innovations for their immobilization is currently expanding (Kampa and Castanas, 2008). The European Union (EU) produces 2.3 billion tons of waste per year, of which 10% is household waste, while 90% includes industrial, commercial, agricultural and other types of waste generated during some economic activity (Ruggiero, 2013).

Lately, we are facing with high costs of immobilization, temporary storage and final disposal of liquid radioactive waste (RAW) and wastewater treatment of heavy metals, but also with the reduction of raw materials and increasing costs of synthesis of new materials. Therefore, this encourages the development of research in the direction of searching economically appropriate, so-called low-cost materials and locally easily accessible which can be used for purpose of compound removal (Mihajlović-Kostić, 2016; Dimović, Šljivić-Ivanović, and Jelić, 2019; Fu and Qi Wang, 2011; Grace, Clifford, and Healy, 2016).

3.1.1 Factors influencing the sorption process

Many factors influence the sorption process in the solid-liquid system, for example: nature of sorbent, nature of sorptives, nature of sorbate, pH value, temperature, etc.

Nature of sorbent

The most important properties of a solid sorbent are chemical and phase composition, structure, specific surface area and porosity. Sorbents can be organic and inorganic, and by origin natural or synthetic. The structure of the sorbent can be crystalline, amorphous or combined (Mihajlović-Kostić, 2016).

Nature of sorptives

There are three so-called sorptive categories according to relevant chemicals: anionic sorptives, cationic sorptives and uncharged organic sorptives. Anionic sorptives are negatively charged, cationic sorptives are positively charged, and uncharged organic sorptives are neutrally charged according to the number of electrons and protons. The number of ions that system is able to sorb is expressed by parameter named sorption efficiency and it is expressed by cation exchange capacity. It should be denoted that for ionic sorptives, the sign and magnitude of electrical charge are important, meaning that anionic sorptives will be attracted by long-range electrostatic forces to positively charged sorbents, and vice versa (Thompson and Goyne, 2012; Trakal, 2015).

Nature of sorbate

The solubility of adsorbates is of great importance for sorption. The degree of sorption is inversely porportional to the solubility of the sorbate in the liquid phase from which the sorption takes place. The influence of the polarity of sorbate molecules on the sorption process is based on a general rule: polar sorbate gives preference to the polar phase, which means that the polar sorbate is more strongly sorbed on the polar sorbent. Regardless of the composition of the solid phase, multivalent ions are better sorbed then monovalent ones, and ions of the same

charge are sorbed differently depending on the ionic radius. Ions of larger radius are sorbed better since they are less solvated (hydrated), because the solvation (hydration) layer around the ions causes the weakening of electrostatic attractive forces. Also, the ion will sorb better if the surface has the opposite charge. The sorption of metal ions on the surface of the solid phase is also affected by the electronegativity of the metal. The higher the electronegativity, the stronger the bond (Mihajlović-Kostić, 2016).

pH value

The pH value of an aqueous solution is an important parameter for controlling the sorption process. Its influence is important because the pH value of the solution affects both the degree of ionization and surface charge of the sorbent, as well as the ionic species present in the solution (Mihajlović-Kostić, 2016).

Temperature

Change of temperature affects the kinetics rate and sorption capacity of the sorbent. When it comes to sorption of ions, which are hydrated in aqueous solution, it is necessary to remove the hydration layer so that the ion can be sorbed on a solid surface, which requires a certain amount of energy, so the total thermal effect of sorption process depends on the thermal effect, which can be either endothermic or exothermic (Mihajlović-Kostić, 2016). If the adsorption capacity is increasing with the temperature increment, the process is endothermic. In other scenario, if the sorption capacity is decreasing with the temperature, then the process is identified as exothermic (Senthilkumar and Reddy Prasad, 2020; Vijayaraghavan and Yun, 2008).

Dosage

The dosage of the sorbent is related to the percentage of removal of harmful substances. As the dose of the sorbent increases, the total number of bound groups which are present on the surface of the sorbent, also increases. This results in an increase in the total concentration of bounded toxins, in other words a higher percentage of toxins removal. On the other hand, the sorption capacity

decreases with increasing sorbent dose, due to the nature of the interactions between sorbent and sorbate (Senthilkumar and Reddy Prasad, 2020).

3.2 Application of sorbent materials

Sorbent materials should be environmentally friendly, not expensive and effective for a wide range of different concentrations of polluting metals. Except the commonly used sorbents, scientist are researching the use of waste materials as sorbents. This is considered to reduce the use of natural non-renewable resources and/or the use of various types of energy for the synthesis or modification of natural raw materials and artificial materials (Mihajlović-Kostić, 2016; Dimović, Šljivić-Ivanović, and Jelić, 2019).

Throughout couple of next sections, examples of sorbents which are commonly used and some of the waste materials which have also been shown as good sorbents, will be given.

3.2.1 Commonly used sorbents

Zeolite

Although there are many sources of metal ions, the metal processing industry (primarily the galvanizing process) contributes greatly to the pollution of the environment with toxic metals. One of the main ways of contamination from this industry is the emission of liquid effluents containing chromium, nickel, zinc, copper and cadmium. Successful application of zeolite for the purpose of wastewater treatment from galvanization process has been proven. Zeolite represents important microporous, selective adsorbent that occurs naturally and is being prepared synthetically (El-Naas and Alhaija, 2013). It has a number of advantages such as: low cost, availability in large quantities in many parts of the world, good mechanical and thermal properties and large sorption capacity that can adjust soil pH. The removal of radioactive isotopes of cesium by zeolite was also investigated and it was concluded that it can be successfully applied for wastewater treatment at the Fukushima nuclear power plant in Japan (Mihajlović-Kostić, 2016).

Activated carbon

Activated carbon is one of the oldest and most commonly used adsorbents. It is usually prepared from wood, coconut shells, lignite, coal, etc., using different processes which include physical and chemical activation. Activated carbon for water treatment can be found in two forms: granular activated carbon (GAC) and powdered activated carbon (PAC). GAC is more adaptable to continuous contact in regards to PAC, and there is no need to separate the carbon from the bulk fluid, where on the other hand, when using PAC some practical problems can occur because of the requirement to separate the adsorbent from the fluid after use (El-Naas and Alhajja, 2013). The market value of this adsorbent is growing due to the reduction of natural raw materials and due to the increase of production costs by thermal treatment from waste bio-materials (Dimović, Šljivić-Ivanović, and Jelić, 2019).

Clay minerals

Clay minerals belong to the diverse group of hydrous aluminium phyllosilicates minerals. They are the major constituent of fine-grained sediments and rocks and are an important constituent of soils, lake, estuarine, delta, and the ocean sediments (Huggett, 2005). They are used for removal of toxic pollutants, pigments and in the re-refining of edible and mineral oils. One of the great advantages is that they are inexpensive (El-Naas and Alhajja, 2013).

3.2.2 Waste materials as sorbents

Blast furnace slag

In one of the studies, blast furnace slag was examined as a multifunctional sorbent since it was found to contain mainly silicates and a smaller amount of carbonates. Cationic and anionic sorbates were used in the experiments. Based on the results, it was concluded that blast furnace slag can be used for wastewater treatment containing metals in both cationic and anionic form (Blahova et al., 2015). Cd^{2+} (cadmium), Pb^{2+} (lead) and Cu^{2+} (copper) ions were sorbed on blast furnace slag and the results showed relatively high sorption capacities of

all tested ions. The maximum sorption capacities for Cu^{2+} , Cd^{2+} and Pb^{2+} ions are 0.101 mmol/g; 0.058 mmol/g and 0.120 mmol/g, respectively (X. Chen, Hou, and Q. Wang, 2009).

Sorption of metal ions on this material showed satisfactory efficiency, with the fact that this sorbent is generated in large quantities and represents the final waste (Dimović, Šljivić-Ivanović, and Jelić, 2019).

Biomass

Research on the sorption of heavy metals is also focused on the use of waste materials such as various types of biomass, agro-waste, waste from the food industry and households. For example, algal biomass has a great ability to bind metal ions due to the fact that the cell wall of algae, as well as polymers that are part of algae, contain various negatively charged functional groups. Since metal ions in solutions are usually in cationic form, they easily bound to this biomass. This type of sorption has great potential and can be used for a wide range of cations and for commercial purposes (Kumara, Pandey, and Gaur, 2016).

Biosorption of Pb^{2+} , Cu^{2+} and Cd^{2+} ions was also investigated on waste biomass from the brewing industry. The results showed high sorption capacities for all three cations (0.465 mmol/g for Pb^{2+} , 0.769 mmol/g for Cu^{2+} and 0.127 mmol/g for Cd^{2+} ion at 35 °C) (Kim et al., 2005).

Pomegranate peel was used as biomass for sorption of Pb^{2+} and Cu^{2+} ions. The sorption process depending on pH value, contact time, initial cation concentration and sorbent amount was investigated. The maximum sorption for both cations was observed in the pH range from 5 to 8. The obtained results indicated that the sorption capacities increase with increasing contact time, decreasing the initial cation concentration and increasing the amount of sorbent (Dimović, Šljivić-Ivanović, and Jelić, 2019).

Fishing waste

Research on the sorption of shellfish waste has included the immobilization of heavy metals, e.g., lead, cadmium, copper, zinc, nickel, cobalt on oyster and mussel waste due to large amounts of waste originating from fisheries. Since the shellfish waste contains large amounts of biogenic calcium carbonate, it can be used instead of geological sources for sorption of heavy metals and radionuclides. The use of shellfish waste would also mitigate the environmental problems of accumulation of this type of waste in coastal areas. Some of the tests on this waste material included determining the sorption efficiency of Cu^{2+} , Zn^{2+} , Pb^{2+} and Sr^{2+} (strontium). The maximum sorption capacity during the sorption of Zn^{2+} ions is about three times higher (4.77 mmol/g) than for Pb^{2+} and Sr^{2+} (1.55 mmol/g and 1.53 mmol/g, respectively), and far higher than the value obtained for the Cu^{2+} ion (0.21 mmol/g) (Dimović, Šljivić-Ivanović, and Jelić, 2019; Bozbas and Boz, 2016; Smiciklas et al., 2018).

Construction waste

Construction waste and its components as sorbents haven't been so much investigated so far. However, due to the great availability, abundance, economic profitability and similarity of the chemical composition with known conventional sorbents, these materials represent great potential, especially given the wide range of construction waste composition. Generation and further crushing of construction and demolition (C&D) waste leads to the formation of a coarse fraction consisting of primary aggregates such as gravel, stone, crushed brick, etc. However, in these processes a large amount of fine particles with dimensions less than 5 mm is generated (Oikonomou, 2015).

Construction waste contains valuable amounts of various minerals such as quartz, calcite, dolomite, etc., as well as the other compounds, for example chloride and calcium aluminum iron hydroxide. Most of these minerals in research have been shown to be good sorbents for various pollutants, such as nickel, copper, lead, cadmium, caesium, europium, thorium, chromium, cobalt, zinc, strontium, mercury or uranium (VI), which indicates that C&D waste can have a very good potential for sorption of inorganic pollutants.

Also, the removal of anionic pollutants on these waste materials, such as phosphate sorption from aqueous media using cement-based materials, was investigated, and these studies showed that construction waste materials can be very effective as sorbents of anionic pollutants (Dimović, Šljivić-Ivanović, and Jelić, 2019).

Chapter 4

Mathematical modeling

4.1 Introduction to mathematical modeling

For better understanding the concept of sorption process modeling, it is necessary to get more familiar with the term of mathematical modeling itself. Model represents a simplified description of a system or a certain process. In mathematical modeling, this system or a process is translated to the precise, concise and well-defined language of mathematics (Lawson and Marion, 2008; Fox and Bolton, 2002). Mathematical modeling can be used in almost any sphere of our lives, it gives us a chance for thorough understanding of the model that we are observing. It connects the world we live in with an engineering disciplines.

Mathematical modeling among all of its applications, is used for transport of contaminants. One of the goals of the modeling of this type is studying the movement of a pollutants in order to evaluate ecological risks and/or to give us a solution for removal of pollutants from the environment (Kuráž and Bloecher, 2017).

4.1.1 Classification of mathematical models

Classification of models can be done based on the amount of information that is used for model description and that is: theoretical (black box) models and empirical (white box) models.

Theoretical models are using big amount of information in order to describe

the processes which are happening, and as well they consider the mechanisms through which changes occur. On the other side, **empirical models** do not take into account mechanisms through which changes occur. Empirical models attempt to quantitatively explain the changes associated with different conditions (Lawson and Marion, 2008).

4.2 Modeling process

When starting with modeling, it is important to divide the process to several stages, meaning stage of building-up the model, studying, testing and then using it.

Building-up the model requires to collect as much as possible information in order to understand the problem that is being modeled and to set-up the amount of details on which model will depend. Definition of the model goal and determining the objectives of the model is from great importance. Model can be described as qualitative and quantitative. Qualitative description answers to question about "how", while quantitative description gives an answer to "how much". Third stage is known as the validation step. Data used for validation should differ from those used in parameter estimation. And the fourth, last stage, considers the methods of model presentation to its user (Neumaier, 2004; Lawson and Marion, 2008).

4.2.1 Parameter estimation

Before the validation of the model, parameter estimation is required and these problems are in general an **inverse analysis**. The inverse analysis includes a search for the unknown inputs from the known outputs, usually the ones obtained from the experiment. There are two main approaches for parameters estimation: mathematical based methods and stochastic methods. Mathematical based methods are also known as gradient methods and they are using gradient information (and/or curvature in case of Newton's method) to minimize the objective function. Stochastic methods are based on artificial intelligence (Kuráž, 2011).

Mathematical model, or in other words approximation of a system, is parameter dependent system. It means that we have a set of data that describes the observed system which is dependent on some parameters. These parameters need to be estimated in that way that they minimize the error value of such an approximation. This will provide a best fit set of parameters. The error function which depends on this set of parameters is called **the objective function**. It can be said that the parameter estimation process is a search for global minimum of the objective function (Kuráž, 2011; Lawson and Marion, 2008).

The Langmuir model and Freundlich model are two-parameter models (Xunjun Chen, 2015).

4.2.2 Error functions

Error functions are used to estimate the divergence between the experimental (observed) and the modeled (predicted) values in order to determine the best fit (Subramanyam and Das, 2014; Riahi, Chaabane, and Thayer, 2017). There can be many reasons why certain error has occurred, but we can organize them in three groups:

- measurement error while performing the experiment,
- effect of ignored factors which depends on amount of used information,
- mis-specification of the model which can be due to errors in functional form or to parameter estimates (Lawson and Marion, 2008).

It should be noted that there are two types of model analysis, which are: linear regression analysis and non-linear regression analysis. Term regression analysis is used in order to determine the set of statistical process used. Non-linear regression analysis means that the data are modeled by a non-linear function, while in linear regression analysis linear function is used. Researchers found out that it is easier to estimate the parameters using the linear analysis due to the mathematical simplicity, but what is done is linearization of non-linear equation, and this will induce errors that may lead to unreliable conclusions. It is recommended to estimate the parameters by non-linear method, because when using the non-linear

function it means that error is being distributed on the entire curve; and in case if linear function is used, then the results must be accepted as approximate and not exact (Kajjumba et al., 2019; Subramanyam and Das, 2014; Subramanyam and Das, 2009; Xunjun Chen, 2015; Shikuku, Chrispin, and Kengara, 2018; Hinz, 2001).

4.3 Modeling of sorption processes

4.3.1 Adsorption isotherms

Modeling the adsorption data is from great importance for optimization of the adsorption mechanisms, expression of the adsorbent capacities and effective design of the adsorption systems (Xunjun Chen, 2015).

There are several possible outcomes of adsorption modeling. We can classify resulting adsorption curves as following:

- the "C" isotherm,
- the "L" isotherm,
- the "H" isotherm, and
- the "S" isotherm.

The "C" isotherm

As mentioned, an adsorption isotherm is a graphical representation of the adsorption capacity, meaning the amount of solute adsorbed by an adsorbent, as the function of the equilibrium concentration of the solute (Roy, 1993). The "C" isotherm is represented in that way that the ratio between the concentration of the compound remaining in solution and adsorbed on the solid is the same at any concentration. Because of its simplicity, it is preferably used as an approximation than an accurate description (Limousin et al., 2007).

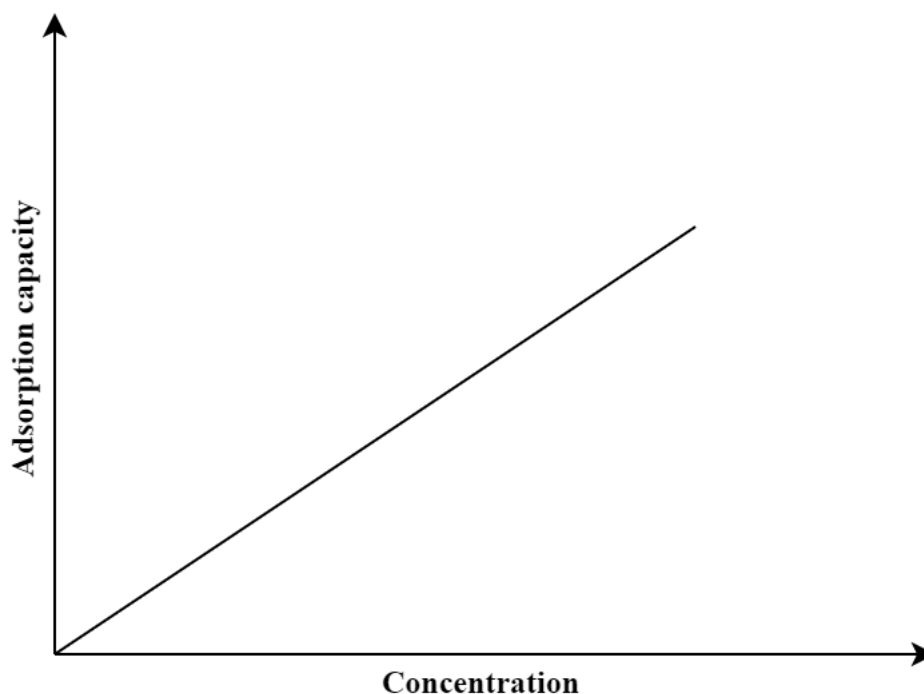


Figure 4.1: The "C" type of isotherm

The "L" isotherm

The "L" isotherm can be described by the ratio between the concentration of the compound remaining in solution and adsorbed on the solid, which decreases when to solute concentration increases. This process is providing a concave curve and it proposes progressive saturation of solids. Two sub-groups are present:

- with strict plateau, i.e., solid has a limited sorption capacity;
- without strict plateau, i.e., solid doesn't have a limited sorption capacity (Limousin et al., 2007).

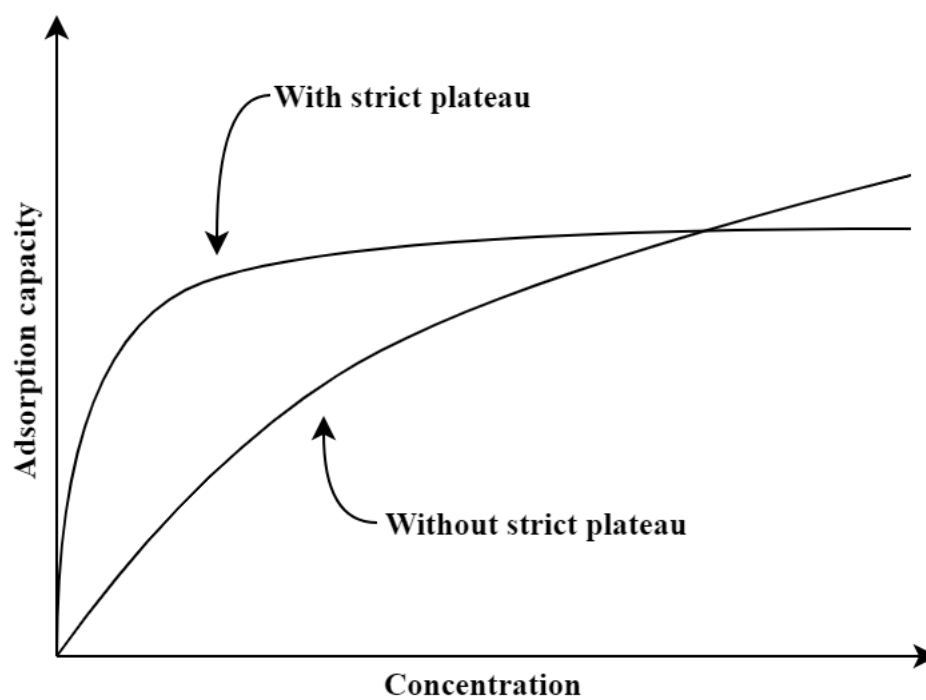


Figure 4.2: The "L" type of isotherm

The "H" isotherm

The "H" type of isotherm can be considered as particular case of the "L" isotherm with high initial slope. The compound sometimes exhibits a high affinity for the solid that the initial slope cannot be distinguished from the infinity (Limousin et al., 2007; Toth, 1995).

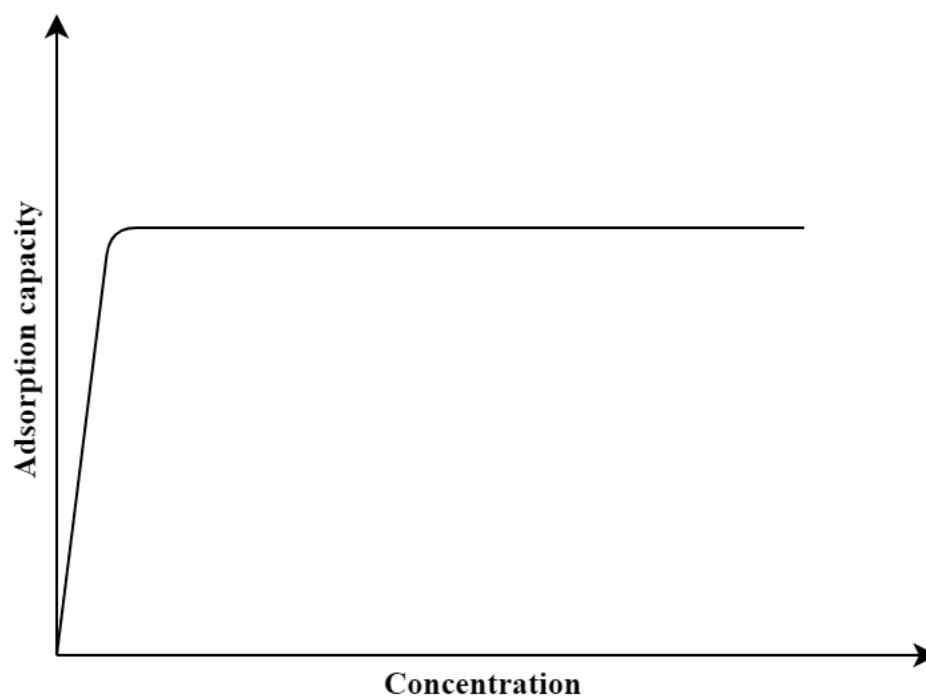


Figure 4.3: The "H" type of isotherm

The "S" isotherm

The "S" isotherm is the result of minimum two opposite mechanisms and non-organic compounds are a typical case. It is described by phenomenon called "cooperative adsorption". As an example, we can take non-polar organic compounds that have a low affinity with clays, but as soon as a clay surface is covered by non-organic compounds, other organic molecules are adsorbed easily (Limousin et al., 2007; Pignatello, 2000; Karimi-Lotfabad, Pickard, and Gray, 1996).

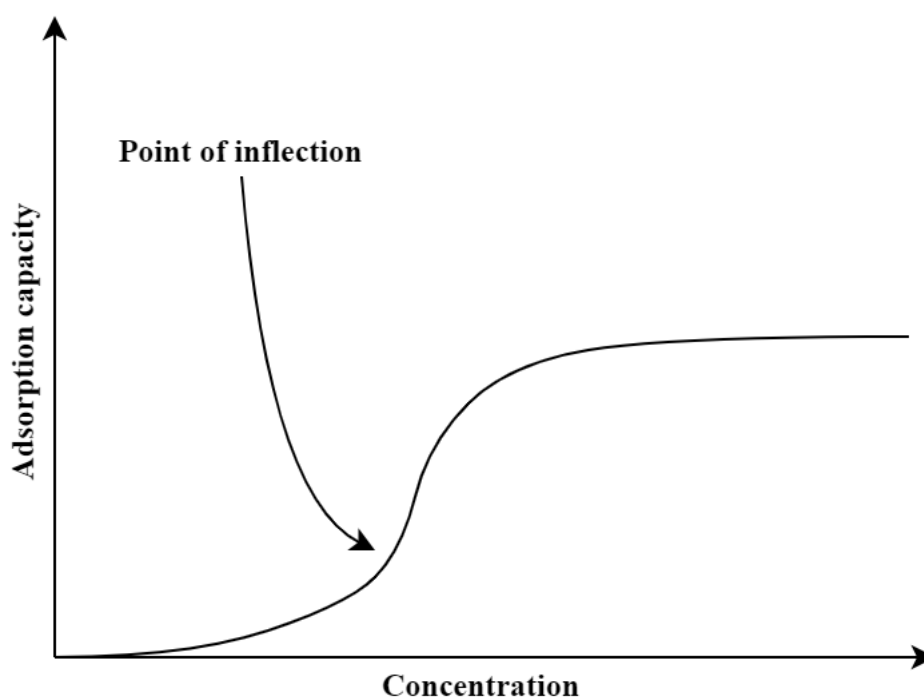


Figure 4.4: The "S" type of isotherm

Chapter 5

Methodology

In order to examine the sorption process, specifically the adsorption, as one of the most important processes in nature for environmental protection, data from the literature "*Modeling of Experimental Adsorption Isotherm Data*" by Xunjun Chen, 2015, were taken.

5.1 Objectives

This research focuses on creating an efficient system for describing the adsorption process. Throughout theory, it can be seen that there are a number of things to know before creating a model. It is a worrying fact to what extent the world around us is polluted, and this is exactly what encourages scientists around the world to study adsorbents and their efficiency day by day. The aim of this study is to present a model that adequately describes the experimental values and analyze in more detail the parameters that affect the adsorption process by conducting a thorough examination of its main principles. Based on the analysis, the study further discusses how effective a given adsorbent is in order to remove harmful pollutant (phosphate) from wastewater.

5.2 Experiment description

Four data sets that were experimentally obtained from a series of batch experiments, are presented. The experiments are based on the removal of phos-

phate in solutions with different initial concentrations using synthesized adsorbent Fe(III)-coordinated amino-functionalized mesoporous MCM-41 with different amino loads of 0%, 10%, 20% and 30%. The experimental values of the initial concentrations and the equilibrium concentrations are given in Appendix A.1. The duration of the experiment was 2 h, at the temperature of 35°C. Upon completion, the solutions were removed by filtering thru syringe nylon-membrane filters, and the equilibrium phosphate concentrations in the filtrates were analyzed (Xunjun Chen, 2015).

This type of sorbent has high-surface area and large pore volume which contributes to the adsorption capacity. It has controllable pore size (between 2 nm and 50 nm), thermal stability, chemical stability and it can have different porous structures (Nakanishi, Tomita, and Kato, 2015).

5.3 Used tools

In order to analyze given data sets within case study, two programming languages were used - FORTRAN and R. Primarily, FORTRAN programming language was used to develop models based on the definitions and formulas given in the theoretical part of this thesis, while R programming language was used for further data analysis (R Core Team, 2020). By further data analysis is considered: estimation of parameters, determination of the deviation between modeled (predicted) data and experimental (observed) data, and finally graphical representation of data.

For parameter estimation, an algorithm was used within the PUPAIM package, which is available in R programming language (Saroyda et al., 2020). The parameter estimation algorithm in this case is based on non-linear regression, specifically non-linear regression with brute force (grid-search). Grid-search is the brute-force method used for performing hyperparameter tuning. This approach tries all of the combinations of hyperparameters from a grid of parameter values.

5.4 Workflow

Figure 5.1 schematically shows the workflow of the case study.

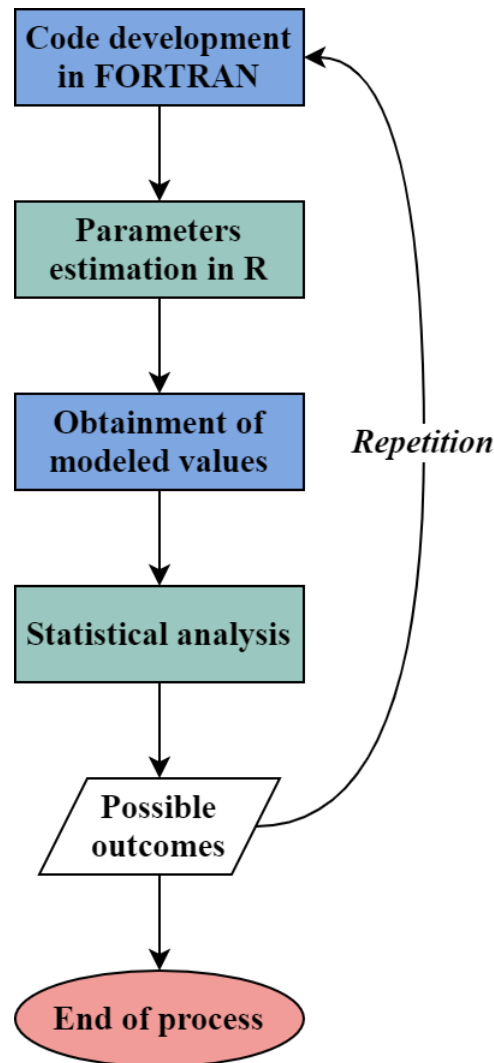


Figure 5.1: Workflow of the case study

5.4.1 Code development in FORTRAN

Model formulations

As the first step, I developed the code in the FORTRAN programming language based on the formulation of models. Langmuir model implementation was developed using the Equation (2.7) and implementation of Freundlich model was

developed using Equation (2.8).

- **Input.** The estimated parameters and the equilibrium concentrations (C_e) for each model are used as input. The Langmuir model and the Freundlich model belong to a group of models called two-parameter models, in other words two parameter estimates are needed for each model. Accordingly, the Langmuir isotherm depends on the maximum adsorption capacity (q_{max}) and the Langmuir coefficient (K_L); while the Freundlich isotherm depends on the Freundlich coefficient (K_F) and the constant that denotes the favorability of the adsorption process (n).
- **Output.** As an output, this part of the code obtains modeled values of the adsorption capacities for each model, which later on will be used for presenting sorption isotherms and further data analysis.

Mass balance equation

In addition to the code corresponding to the formulations of the above mentioned non-linear models, part of the code is dedicated to calculating the adsorption capacity values based on the experimentally measured concentrations, using the mass balance equation (see Equation (2.6)). The initial concentrations and the equilibrium concentrations obtained from the experiments are given in Table A.1.

- **Input.** As input, this part of code takes the volume of solution to be treated (V), the mass of adsorbent (m), the initial concentration of the adsorbate (C_0) and the equilibrium concentration of the adsorbate (C_e).
- **Output.** As output, this part of code gives the adsorption capacity (q_e).

5.4.2 Parameters estimation in R

Using the principle of inverse analysis, in R programming language, I performed parameters estimation by non-linear regression with brute force, using the package PUPAIM.

- **Input.** As input, the experimental values of the equilibrium concentration (C_e) and the previously obtained the adsorption capacity (q_e) based on mass balance equation, were used.
- **Output.** As parameters estimation output, four parameters were obtained - two for each model, as earlier mentioned; for Langmuir model: the maximum adsorption capacity (q_{max}) and the Langmuir coefficient (K_L); for Freundlich model: the Freundlich coefficient (K_F) and the constant (n).

5.4.3 Obtainment of modeled values

The parameters estimated in the previous procedure are then used as an input to the code developed in FORTRAN. The output of this step results in modeled values, in addition to the experimental data. Those data sets are used for further analysis.

5.4.4 Statistical analysis

The next step involves statistical analysis of the deviation of the modeled values from the experimentally determined values. For this purpose, four error functions and a coefficient of determination (R-Squared) were used. The statistical analysis was performed in programming language R, based on the following formulations.

Mean Squared Error (MSE)

The aim of the Mean Squared Error function (MSE) is to find the average of a set of errors by calculating the distances (errors) from the points to the regression line. These distances are then squared in order to remove possible negative values. The formulation of MSE is given by:

$$MSE = \frac{1}{N} \sum_{i=1}^N (y_i - \hat{y}_i)^2, \quad (5.1)$$

where N denotes the number of variables (measurements), y are the observed (measured) values, while \hat{y} denotes the predicted (modeled) values. A lower

value of the MSE indicates the line of a better fit (Glen, 2013; Binieli, 2018).

Root Mean Square Error (RMSE)

In order to calculate the Root Mean Square Error (RMSE), determination of the differences between observed values and predicted values is needed. RMSE can be defined as a measure of the spread of the observed values, around the predicted values. The formulation of RMSE is given as:

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (\hat{y}_i - y_i)^2}, \quad (5.2)$$

where N denotes the number of variables (measurements), y are the observed values, while \hat{y} denotes the predicted values (Holmes, 2000).

Mean Absolute Error (MAE)

Mean Absolute Error (MAE) gives an average value of the absolute differences between the observed values and the predicted values. It is formulated as:

$$MAE = \frac{1}{N} \sum_{i=1}^N |y_i - \hat{y}_i|, \quad (5.3)$$

where N denotes the number of variables (measurements), y are the observed values, while \hat{y} denotes the predicted values (Wesner, 2016).

Relative Absolute Error (RAE)

Relative Absolute Error (RAE) compares a mean error to errors produced by a trivial or naive model. It is given by:

$$RAE = \frac{\sqrt{\sum_{i=1}^N (\hat{y}_i - y_i)^2}}{\sqrt{\sum_{i=1}^N y_i^2}}, \quad (5.4)$$

where N denotes the number of variables (measurements), y are the observed values, while \hat{y} denotes the predicted values. A smaller value of RAE indicates a

better fit (Glen, 2019).

R-Squared (R^2)

R^2 determines how well the regression model fits the observed data. It denotes the share of variance in the dependent variable that can be explained by the independent variable. R^2 is represented by the following formula:

$$R^2 = 1 - \frac{\text{Residual sum of squares}}{\text{Total sum of squares}} \quad (5.5)$$

The values of R^2 are in the range of 0 to 1. A value of R^2 that is closer to 1, indicates a better fit (Fernando, 2020).

5.4.5 Possible outcomes

After calculating the deviation of the modeled values from the observed ones, there are two possible outcomes:

- High deviation value.
- Low deviation value.

In the case of high deviation value, I would continue with the process of code adjustment for parameter estimation in R by setting different minimum and/or maximum value for parameter search, and/or changing the value of *set.seed()* function which sets the starting number used to generate a sequence of random numbers. After adjustment, as shown on Figure 5.1, I would repeat the procedure. If the low deviation value occurs, I would end the process by presenting the results and developing the discussion.

It is difficult to say how low or how high a value need to be in order to consider it as adequate. However, there is also a part of subjectivity in this process.

Chapter 6

Results and discussion

6.1 Results

6.1.1 First data set

As the first set of data, synthesized adsorbent Fe(III)-coordinated amino-functionalized mesoporous MCM-41 with amino loading of 0% for removal of phosphate from solution is presented. The estimated parameters for the models are given in Table 6.1.

Adsorption model	Estimated parameters
Freundlich model	$K_F = 1.1994 \text{ (mg/g)(mg/L)}^n$; $n = 2.5504$
Langmuir model	$q_{\max} = 5.90889 \text{ mg/g}$; $K_L = 0.15562 \text{ L/mg}$

Table 6.1: Estimated parameters for adsorption isotherm, amino loading 0%

The graph of the adsorption capacity as a function of the equilibrium concentration is shown in Figure 6.1. The graph shows three curves. One of the curves is obtained on the basis of experimental data, the second curve represents the modeled data by the Langmuir model, and the third curve determines the modeled data by the Freundlich model (see Equations 2.7 and 2.8).

Figure 6.2 shows the Langmuir model in more detail in relation to experimentally determined values. The graph also shows the maximum adsorption capacity.

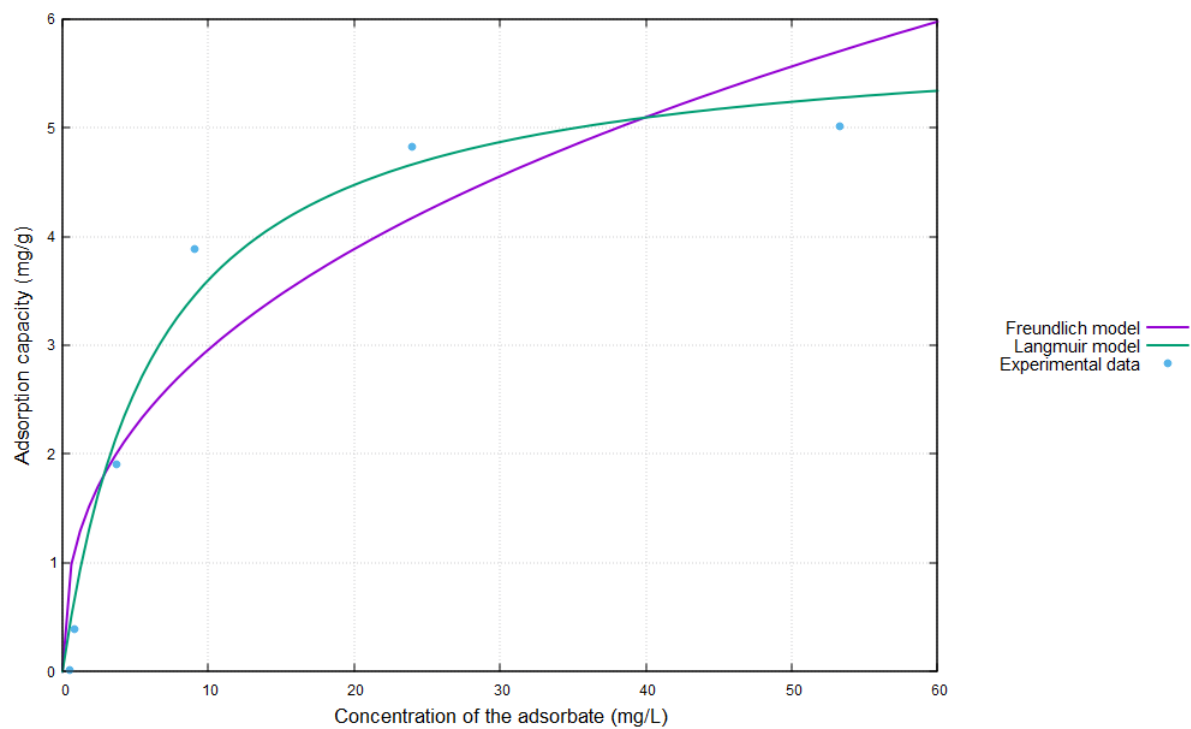


Figure 6.1: Modeling adsorption isotherm data for phosphate removal, amino loading 0%

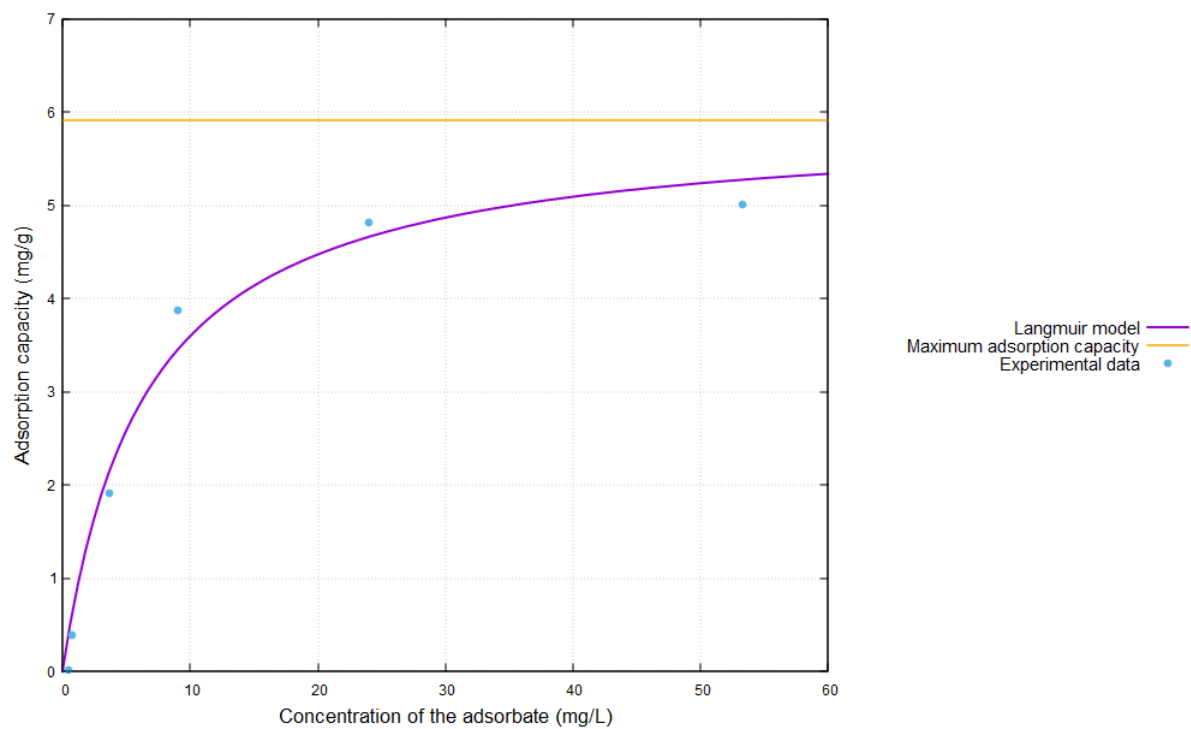


Figure 6.2: Langmuir model for amino loading 0%

The deviation of the predicted values from the observed ones is calculated using the error functions and R-Squared, which values are shown in Table 6.2.

Error function	Langmuir model	Freundlich model
Mean Squared Error	0.092	0.543
Root Mean Square Error	0.304	0.737
Mean Absolute Error	0.289	0.675
Relative Absolute Error	0.152	0.356
R-Squared	0.977	0.866

Table 6.2: Values of different error functions and R-Squared for Langmuir model and Freundlich model, amino loading 0%

It can be seen that the values of the error functions for the Langmuir model are lower compared to the Freundlich model. The value of R-Squared for the Langmuir model is higher than for the Freundlich model.

6.1.2 Second data set

In the second set of data, synthesized adsorbent Fe(III)-coordinated amino-functionalized mesoporous MCM-41 with amino loading of 10% for removal of phosphate from solution is examined.

As in the previous case, the Figure 6.3 shows three adsorption isotherms obtained - based on experimental data, data modeled by the Langmuir model and data modeled by the Freundlich model. Estimates of the parameters necessary to obtain modeled curves are presented in Table 6.3.

Adsorption model	Estimated parameters
Freundlich model	$K_F = 9.901 \text{ (mg/g)(mg/L)}^n$; $n = 4.434$
Langmuir model	$q_{\max} = 20.8242 \text{ mg/g}$; $K_L = 1.8815 \text{ L/mg}$

Table 6.3: Estimated parameters for adsorption isotherm, amino loading 10%

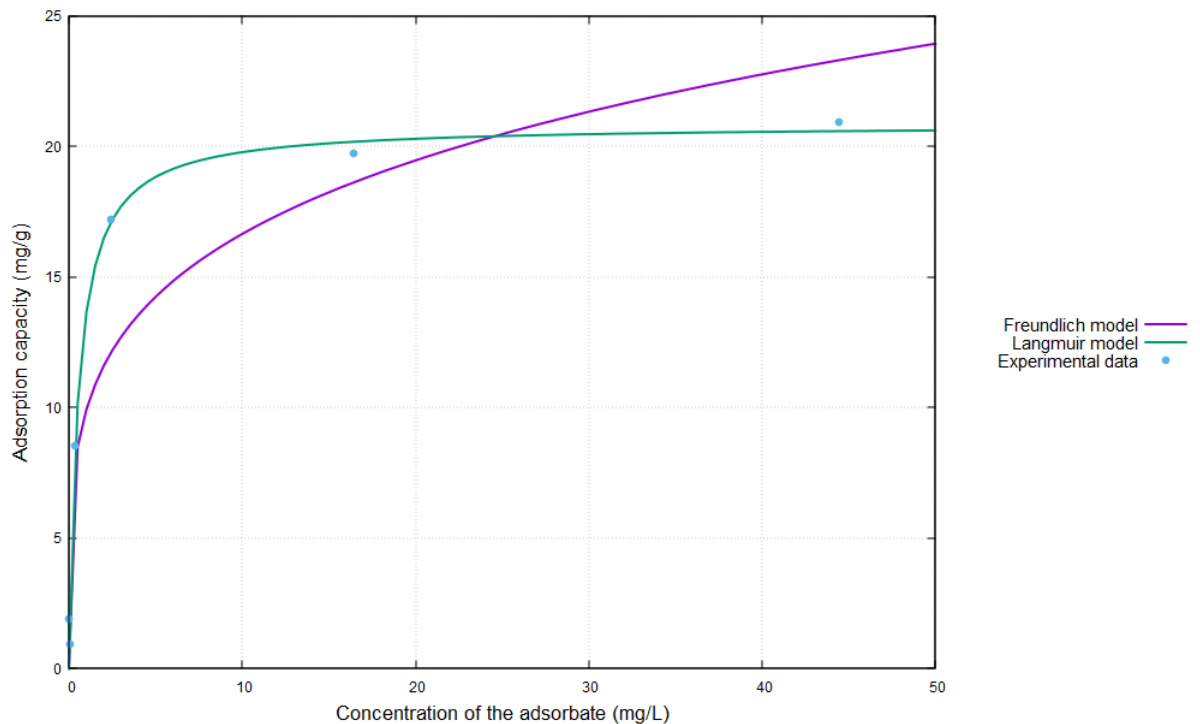


Figure 6.3: Modeling adsorption isotherm data for phosphate removal, amino loading 10%

Data predicted by Langmuir model, including the maximum adsorption capacity and experimentally obtained data are shown in Figure 6.4.

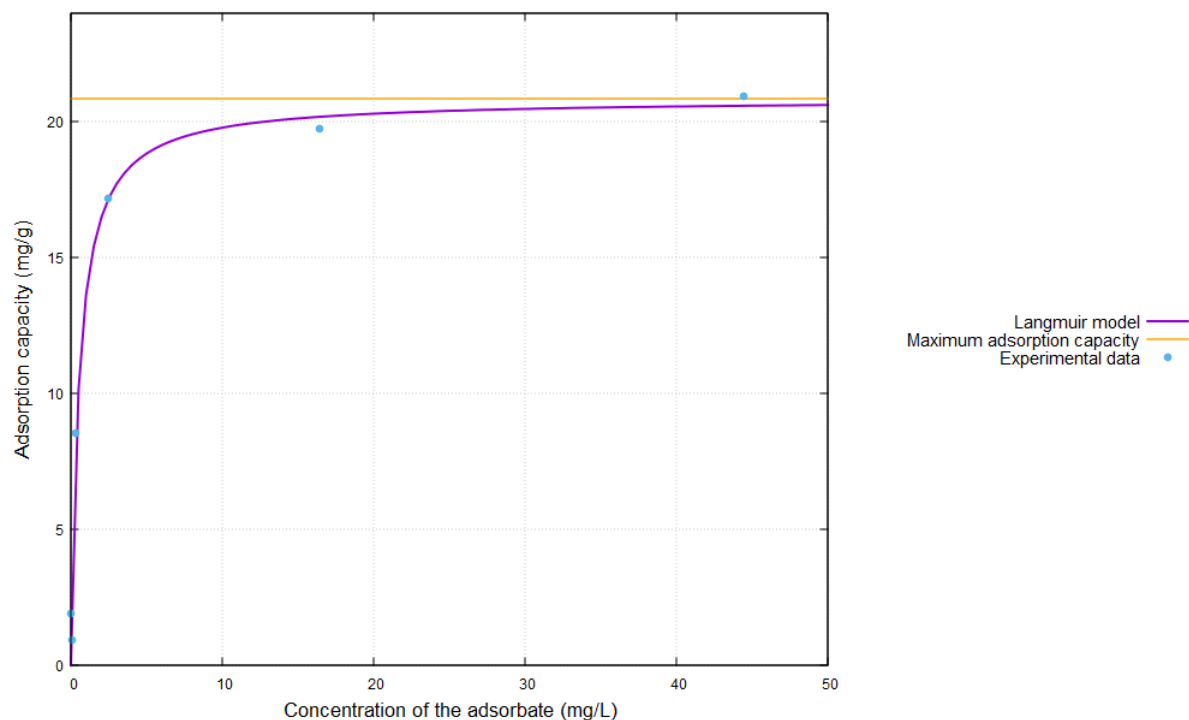


Figure 6.4: Langmuir model for amino loading 10%

In Table 6.4, the divergence between observed and predicted data is presented. As it can be seen, values of error functions are smaller in the case of Langmuir model, while R-Squared value is higher for Langmuir model with regards to Freundlich model.

Error function	Langmuir model	Freundlich model
Mean Squared Error	4.92	9.554
Root Mean Square Error	0.702	3.091
Mean Absolute Error	0.564	2.662
Relative Absolute Error	0.073	0.344
R-Squared	0.993	0.857

Table 6.4: Values of different error functions and R-Squared for Langmuir model and Freundlich model, amino loading 10%

6.1.3 Third data set

In the third set of data, synthesized adsorbent Fe(III)-coordinated amino-functionalized mesoporous MCM-41 with amino loading of 20% for removal of phosphate from solution is investigated.

Estimated parameters for both models are given in Table 6.5. In Figure 6.5, required isotherms are shown, while in Figure 6.6 the Langmuir model can be examined more closely.

Adsorption model	Estimated parameters
Freundlich model	$K_F = 21.489 \text{ (mg/g)(mg/L)}^n$; $n = 4.068$
Langmuir model	$q_{\max} = 44.388 \text{ mg/g}$; $K_L = 4.443 \text{ L/mg}$

Table 6.5: Estimated parameters for adsorption isotherm, amino loading 20%

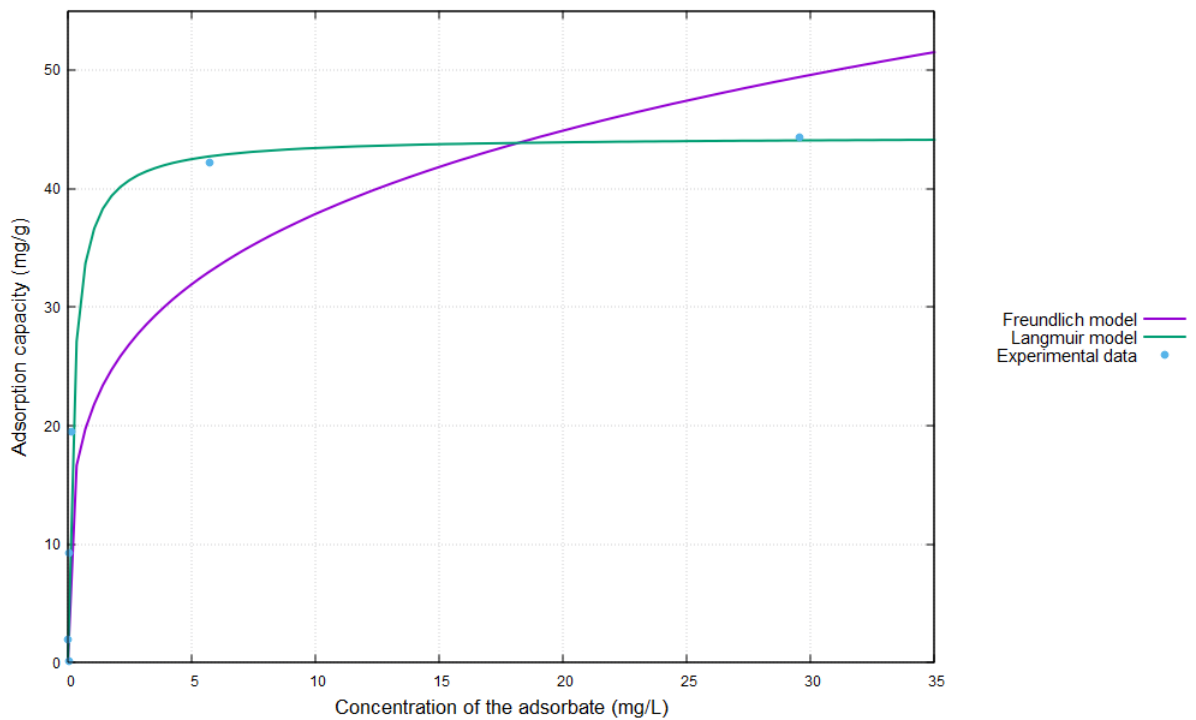


Figure 6.5: Modeling adsorption isotherm data for phosphate removal, amino loading 20%

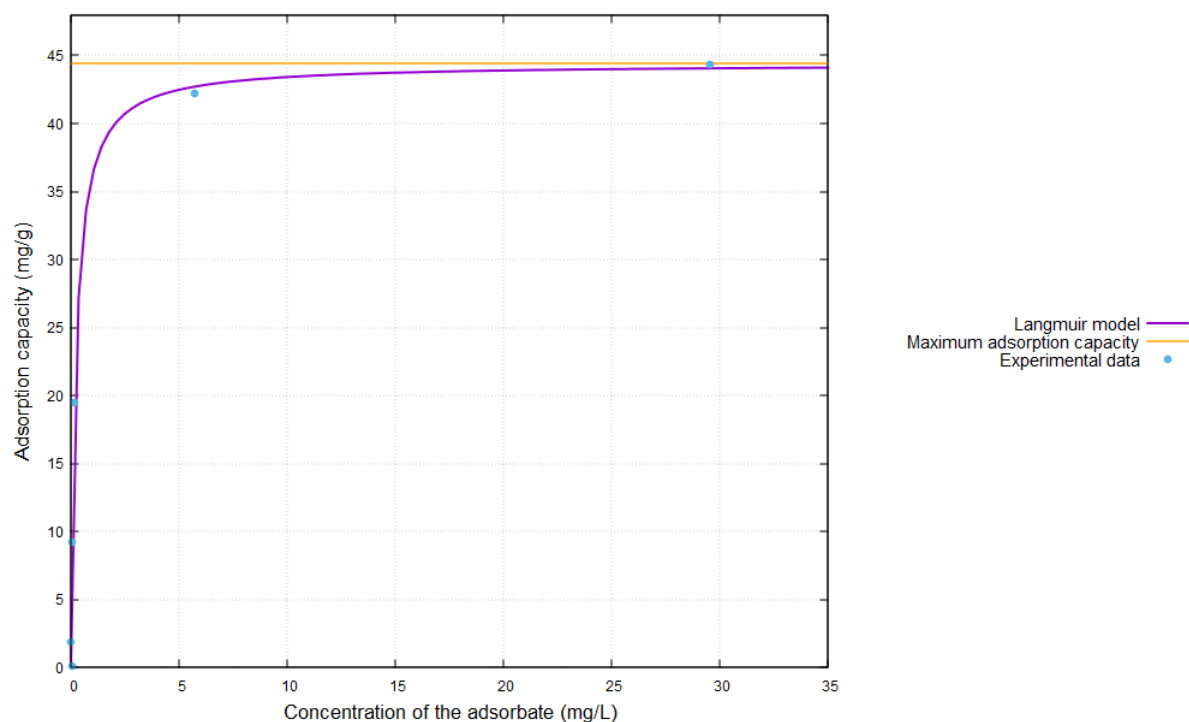


Figure 6.6: Langmuir model for amino loading 20%

Values of error functions and R-Squared are given within Table 6.6. Deviation is smaller in the case of Langmuir model according to presented values, while value of R-Squared is higher for Langmuir model.

Error function	Langmuir model	Freundlich model
Mean Squared Error	8.581	44.354
Root Mean Square Error	2.929	6.66
Mean Absolute Error	2.048	5.910
Relative Absolute Error	0.130	0.374
R-Squared	0.973	0.862

Table 6.6: Values of different error functions and R-Squared for Langmuir model and Freundlich model, amino loading 20%

6.1.4 Fourth data set

The fourth set of data studies synthesized adsorbent Fe(III)-coordinated amino-functionalized mesoporous MCM-41 with amino loading of 30% for removal of phosphate from solution.

Table 6.7 shows evaluated parameters for Langmuir model and Freundlich model. Using the estimated values of the parameters, the values of the adsorption capacities were determined in accordance with the definitions of the given models.

Adsorption model	Estimated parameters
Freundlich model	$K_F = 22.9490 \text{ (mg/g)(mg/L)}^n$; $n = 3.5839$
Langmuir model	$q_{\max} = 52.4688 \text{ mg/g}$; $K_L = 1.7157 \text{ L/mg}$

Table 6.7: Estimated parameters for adsorption isotherm, amino loading 30%

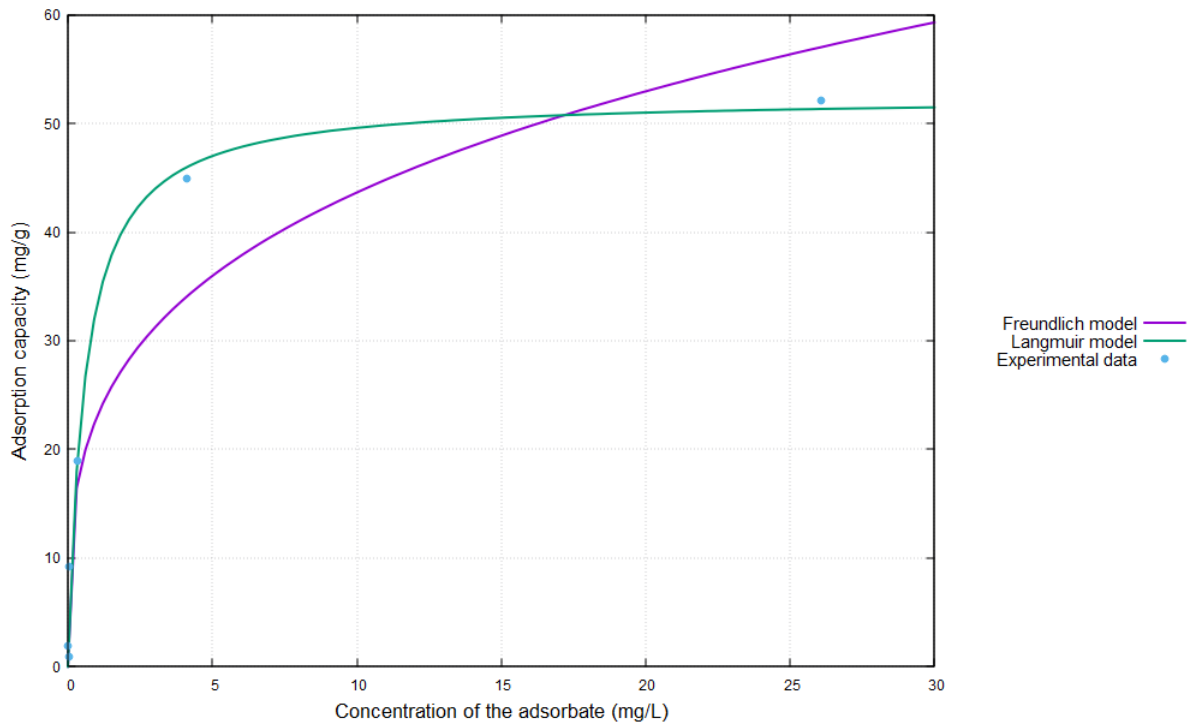


Figure 6.7: Modeling adsorption isotherm data for phosphate removal, amino loading 30%

A graph of the dependence of the adsorption capacities on the equilibrium concentration is shown in Figure 6.7, from which we can observe isotherms. Also,

as in the previous cases, the Langmuir isotherm together with the experimental values and the maximum adsorption capacity are shown in the Figure 6.8.

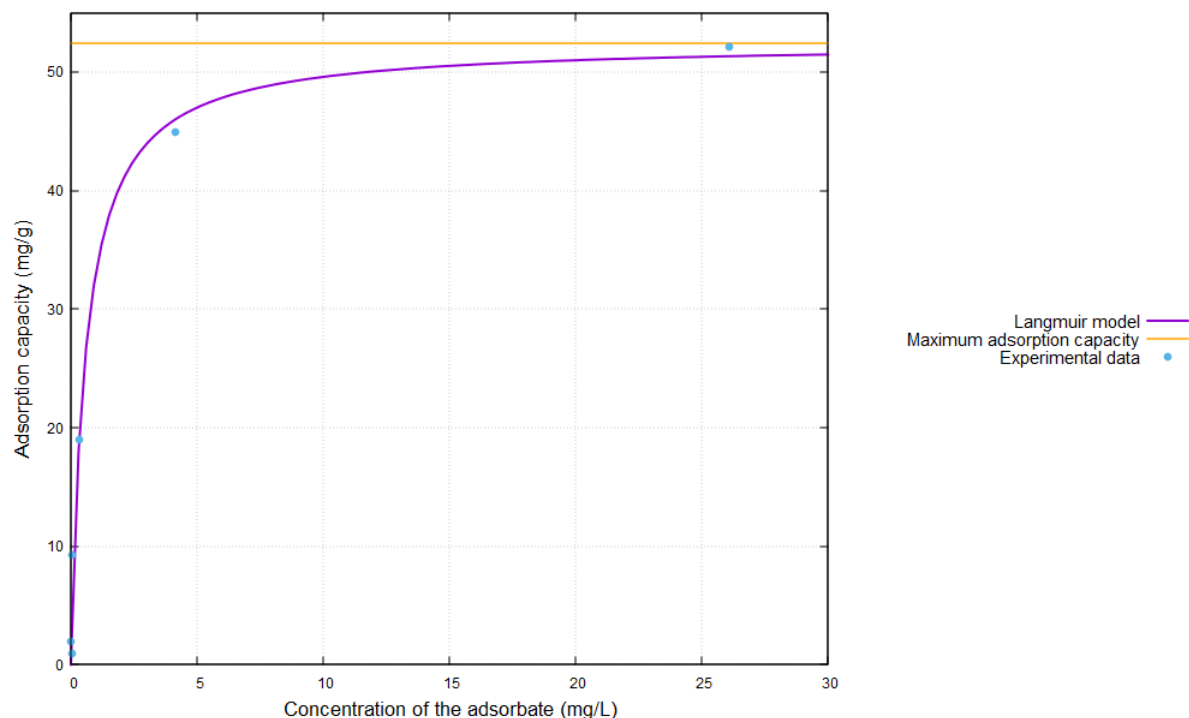


Figure 6.8: Langmuir model for amino loading 30%

Table 6.8 denotes the extent of deviation of the predicted values from the observed ones. It can be seen that the deviation is smaller for Langmuir model than for Freundlich model. The value of R-Squared registers a higher number in the case of Langmuir model.

Error function	Langmuir model	Freundlich model
Mean Squared Error	8.944	43.199
Root Mean Square Error	2.991	6.573
Mean Absolute Error	2.001	5.457
Relative Absolute Error	0.110	0.301
R-Squared	0.978	0.894

Table 6.8: Values of different error functions and R-Squared for Langmuir model and Freundlich model, amino loading 30%

6.2 Discussion

As mentioned in Section 6.1, four different data sets were analyzed depicting the chosen adsorbent. The estimated parameters which were obtained are: the Langmuir maximum adsorption capacity (q_{max}), the Langmuir coefficient (K_L), the Freundlich coefficient (K_F) and the Freundlich constant (n). Each of these parameters has a certain share in a given adsorption process, which ultimately gives a unique picture of the system we are describing.

Maximum adsorption capacity (q_{max})

The maximum adsorption capacity increases with amino loading increment. Accordingly, the value is the lowest for the adsorbent with amino loading of 0% (5.90889 mg/g); and the highest when it comes to amino loading of 30% (52.4688 mg/g), as shown in the Table 6.9. Based on this, the adsorbent with amino loading of 30% is then superior to the others.

Amino loading	q_{max} (mg/g)
0%	5.90889
10%	20.8242
20%	44.388
30%	52.4688

Table 6.9: Estimated parameters for the maximum adsorption capacity

In order to better understand the concept of the maximum adsorption capacity, experimentally obtained data and data predicted by the Langmuir model in relation to the maximum adsorption capacity are presented in Figures 6.2, 6.4, 6.6 and 6.8. The maximum adsorption capacity represents the highest value of the adsorption capacity. On the graph, it is expressed by a constant line which corresponds to the formation of a complete mono-layer on the surface of the adsorbent.

Langmuir coefficient (K_L)

The coefficient K_L defines the strength of the bond between the adsorbent and the adsorbate. Results suggest that the bond between the adsorbent and the adsorbate is the strongest in the case of amino loading of 20% (4.442 L/mg), and the weakest for amino loading of 0% (0.15562 L/mg), as it is represented in Table 6.10.

Amino loading	K_L (L/mg)
0%	0.15562
10%	1.8815
20%	4.443
30%	1.7157

Table 6.10: Estimated parameters for the Langmuir coefficient

Freundlich coefficient (K_F)

The Freundlich coefficient indicates the affinity of the adsorbent for the adsorbate, or in other words the adsorption capacity. Results shown in Table 6.11 suggest that the lowest adsorption capacity is in the case of the adsorbent with amino loading of 0% (1.1994 (mg/g)(mg/L)ⁿ), while the highest adsorption capacity is expressed in the case of amino loading of 30% (22.9490 (mg/g)(mg/L)ⁿ). The value of the coefficient increases with increasing amino loads of the adsorbent. This result matches with the fact that the Freundlich coefficient is equivalent to the Langmuir maximum adsorption capacity.

Amino loading	K_F (mg/g)(mg/L) ⁿ
0%	1.1994
10%	9.901
20%	21.489
30%	22.9490

Table 6.11: Estimated parameters for the Freundlich coefficient

Freundlich constant (n)

The Freundlich constant is indicator of adsorption process favorability. Since the values vary from 2.5504 to 4.434 as presented in Table 6.12, they belong to the group of adsorbents that have a good adsorptive potential.

Amino loading	n (dimensionless)
0%	2.5504
10%	4.434
20%	4.068
30%	3.5839

Table 6.12: Estimated parameters for the Freundlich constant

Type of isotherm

One of the many ways to analyze the data is graphically. In the previous section, all four data sets are graphically presented with the corresponding observed values and predicted values in the form of adsorption isotherms (see Figures 6.1, 6.3, 6.5 and 6.7). It has been shown that in all four cases the curve obtained by modeling the data based on the formulation given by the Langmuir model represents a better fit compared to the data predicted by the Freundlich formulation. The isotherms obtained by these models in all of the given figures correspond to the "L" isotherm type (see Section 4.3.1). But, it should be pointed out that there is a difference between the curves obtained by Langmuir model and the curves obtained by Freundlich model.

Isotherms obtained by the Langmuir model belong to the group of "L" isotherms with strict plateau, which means that solid has a limited sorption capacity (see Figure 6.9); while isotherms obtained by the Freundlich model for most common values of n , belong to the group of "L" isotherms without strict plateau, in other words solid does not have a limited sorption capacity (see Figure 6.10). Which also confirms the theory by which these models are presented.

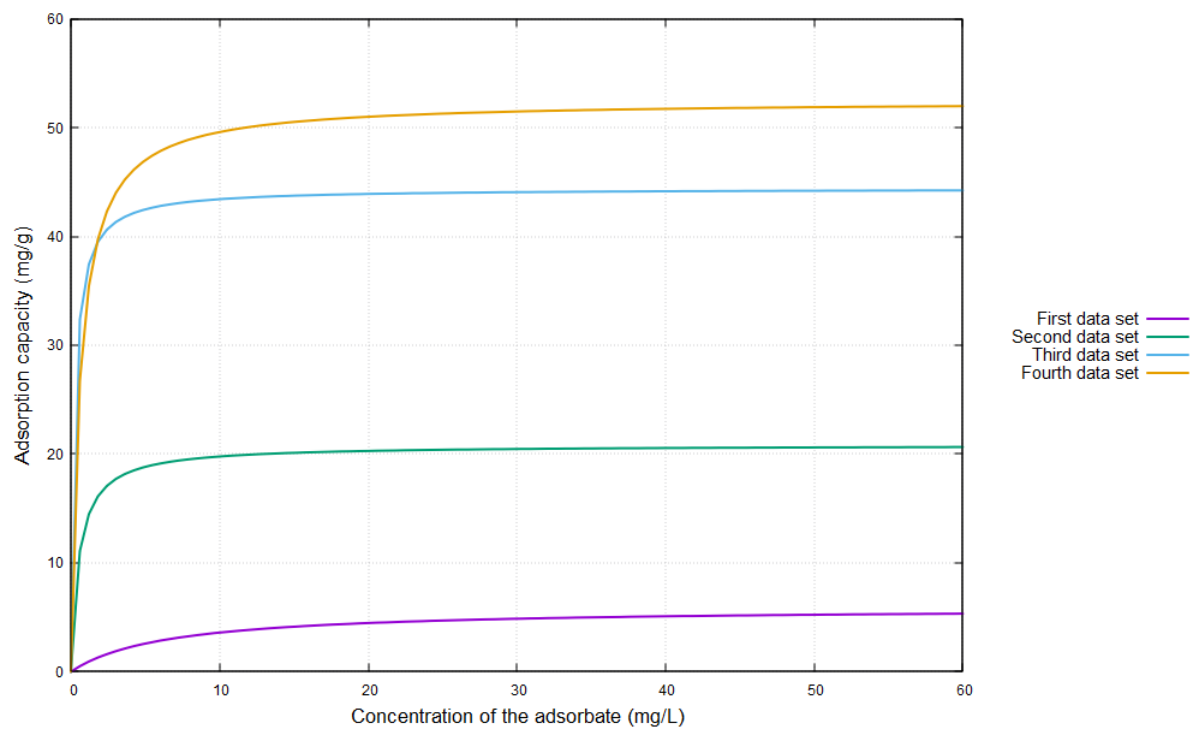


Figure 6.9: Langmuir isotherms

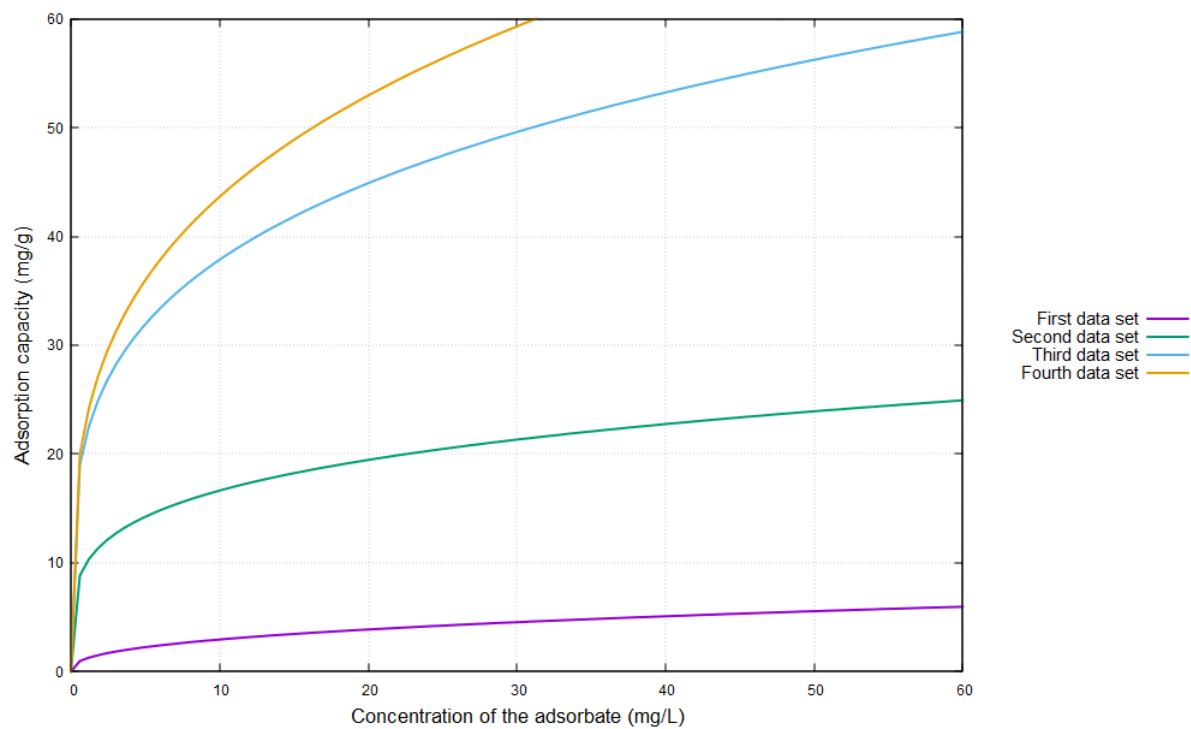


Figure 6.10: Freundlich isotherms

Error functions

The model whose value of the error function is smaller represents a better fit. As already mentioned, the goal is to optimize the function. The Tables 6.2, 6.4, 6.6 and 6.8 show the values of the error functions from which it can be concluded that in all four cases, the Langmuir model has a smaller deviation from the observed data, which makes it a more adequate model for describing experimental data.

R-Squared

The R-Squared factor aims to show how close the data are to fitted regression line. Better fit represents the value of R-Squared which is closer to value 1. The data given in Tables 6.2, 6.4, 6.6 and 6.8, point out to the already mentioned. Although the values do not differ much, both models are good in the data modeling process, but for a certain percentage the Langmuir model explains and predicts future outcome better.

Therefore, comparing these two non-linear models, the above suggests that the Langmuir model has an advantage when it comes to describing experimental data, over the Freundlich model. Moreover, the adsorption characteristics of the observed systems can be caused by mono-layer adsorption.

Chapter 7

Conclusion

The aim of this research was to present a certain share of the theoretical foundation that is necessary for the efficient design of the adsorption system. Great care is required in the construction of the model itself. Experimental data should be studied well before making a decision on model selection, and then applying the model to experimental data. When opting for a model, it is important to further explore the significance of individual parameters that have a huge impact on the possible outcome of modeling. Based on the analysis performed on the adsorbent Fe(III)-coordinated amino-functionalized mesoporous MCM-41, which was examined in the case of phosphate removal, I came to the following conclusions:

- The investigated adsorbent showed good adsorption capacity, which makes it adequate in the process of removing phosphates from wastewater.
- Non-linear models are a great tool in data modeling.

If two models are used to describe a system, it is necessary to compare these two models and define what their similarities are and what their differences are. Differences must exist, otherwise the models would be the same. There are many elements on which a decision can be based but it is certain that in one such decision, the greatest support is provided by error statistics. The results from this study point out that the Langmuir model represents a better fit compared to the Freundlich model. This conclusion indicates that the given adsorbent has

a limited sorption capacity and that the characteristics of the system correspond to the mono-layer adsorption that takes place on a homogeneous surface.

Phosphates are a natural form of the element phosphorus that is a very important element in our ecosystem, but the excessive presence of phosphorus promotes the growth of bacteria. Not only phosphorus, there are other elements whose presence in quantities that are above the permitted damage the ecosystem; such as thallium, manganese, zinc, cobalt, copper, nickel and others. Some of the consequences of their excessive presence are oxygen depletion, damage to the nervous system, causing various diseases that can be fatal and many more. Because of all the above mentioned, it is extremely important to research and study processes such as sorption in order to protect the environment, because the ecosystem needs our help.

Bibliography

- Attallah, M.F., H.S. Hassan, and M.A. Youssef (2019). “Synthesis and sorption potential study of $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-CeO}_2$ composite material for removal of some radionuclides from radioactive waste effluent”. In: *Applied Radiation and Isotopes* 147, pp. 40–47. DOI: <https://doi.org/10.1016/j.apradiso.2019.01.015>.
- Ayawei, Nimibofa, Augustus N. Ebelegi, and Donbebe Wankasi (2017). “Modelling and Interpretation of Adsorption Isotherms”. In: *Journal of chemistry*. DOI: <https://doi.org/10.1155/2017/3039817>.
- Benes, P. and V. Majer (1980). *Trace Chemistry of Aqueous Solutions*.
- Binieli, Moshe (2018). *Machine learning: An introduction to mean squared error and regression lines*. URL: <https://www.freecodecamp.org/news/machine-learning-mean-squared-error-regression-line-c7dde9a26b93/>.
- Blahova, L. et al. (2015). “Sorption Properties of Slags”. In: *Journal of the Polish Mineral Engineering Society*, pp. 89–94.
- Blanchard, G., M. Maunaye, and G. Martin (1984). “Removal of heavy metals from waters by means of natural zeolites”. In: *Water Research* 18(2), pp. 1501–1507.
- Bozbas, S. K. and Y. Boz (2016). “Low-cost biosorbent: Anadara inaequalis shells for removal of Pb(II) and Cu(II) from aqueous solution”. In: *Process Safety and Environmental Protection* 103, pp. 144–152.
- Chen, Chiachung (2013). “Evaluation of Equilibrium Sorption Isotherm Equations”. In: *The Open Chemical Engineering Journal* 7, pp. 24–44.
- Chen, X., W. Hou, and Q. Wang (2009). “Removal of metal ions Cu^{2+} , Cd^{2+} and Pb^{2+} from solutions by sorption on slag”. In: *Medline* 30(10), pp. 2940–2945.

- Chen, Xunjun (2015). “Modeling of Experimental Adsorption Isotherm Data”. In: *Information* 6, pp. 14–22.
- Chorover, Jon and Mark L. Brusseau (2008). *Kinetics of Sorption-Desorption. Kinetics of Water-Rock Interaction*. New York, NY: Springer. ISBN: 978-0-387-73563-4.
- Dimović, Slavko D., Marija Z. Šljivić-Ivanović, and Ivana V. Jelić (2019). “Primenjena otpadnih materijala u imobilizaciji teških metala i radionuklida sorpcijom”. In: *Tehnika - Novi Materijali* 28.
- Enciklopedija, Hrvatska Tehnička (2018). *Adsorpcija*. Tehnička enciklopedija 1963-97. Zagreb, Croatia: Leksikografski zavod Miroslav Krleža.
- Fernando, Jason (2020). *R-Squared Definition*. URL: <https://www.investopedia.com/terms/r/r-squared.asp>.
- Fetter, C.W., Thomas B. Boving, and David Kreamer (2018). *Contaminant Hydrogeology*. 3-rd Edition. Waveland Press. ISBN: 978-1478632795.
- Fox, Huw and Bill Bolton (2002). *Mathematics for Engineers and Technologists*. IIE Core Textbooks Series. Butterworth-Heinemann. ISBN: 978-0-7506-5544-6.
- Fu, Fenglian and Qi Wang (2011). “Removal of heavy metal ions from wastewaters: A review”. In: *Journal of Environmental Management* 92, pp. 407–418.
- Glen, Stephanie (2013). *Mean Squared Error: Definition and Example*. URL: <https://www.statisticshowto.com/mean-squared-error/>.
- (2019). *Relative Absolute Error*. URL: <https://www.statisticshowto.com/relative-absolute-error/>.
- Grace, M., E. Clifford, and M. Healy (2016). “The potential for the use of waste products from a variety of sectors in water treatment processes”. In: *Journal of Cleaner Production* 137, pp. 788–802.
- Hameed, B., A. Ahmad, and K. Latiff (2007). “Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust”. In: *Dyes pigments* 75, pp. 143–149.
- Hinz, Christoph (2001). “Description of sorption data with isotherm equations”. In: *Geoderma* 99, pp. 225–243.
- Ho, Y.S. and G. McKay (1999). “Pseudo-second order model for sorption processes”. In: *Process Biochemistry* 34, pp. 451–465.

- Holmes, Susan (2000). *RMS Error*. URL: <https://statweb.stanford.edu/~susan/courses/s60/split/node60.html>.
- Huggett, J.M. (2005). “Clay Minerals”. In: *Encyclopedia of Geology*, pp. 358–365.
- Kajjumba, George William et al. (2019). *Modelling of Adsorption Kinetic Processes—Errors, Theory and Application*. Advanced Sorption Process Applications. IntechOpen. Chap. 10.
- Kampa, Marilena and Elias Castanas (2008). “Human health effects of air pollution”. In: *Environmental Pollution* 151, pp. 362–367.
- Karimi-Lotfabad, S., M.A. Pickard, and M.R. Gray (1996). “Reactions of polynuclear aromatic hydrocarbons on soil”. In: *Environmental Science & Technology* 30, pp. 1145–1151.
- El-Khaiary, M.I. (2008). “Least-squares regression of adsorption equilibrium data: comparing the options”. In: *Journal of Hazardous Materials* 158, pp. 73–87.
- Kim, T. et al. (2005). “Adsorption of heavy metals by brewery biomass”. In: *Korean Journal of Chemical Engineering* 22(1), pp. 91–98.
- Kumara, D., L. Pandey, and J. Gaur (2016). “Metal sorption by algal biomass: From batch to continuous system”. In: *Algal Research* 18, pp. 95–109.
- Kurář, Michal (2011). *Numerical Solution of the Flow and Transport Equations in Porous Media with the Dual Permeability Conceptual Approach*. Doctoral Dissertation. Prague, Czech Republic: Faculty of Environmental Sciences, Czech University of Life Sciences Prague.
- Kurář, Michal and Johanna R. Bloecher (2017). *Hydrodynamic of porous media*. Teaching notes. Prague, Czech Republic: Faculty of Environmental Sciences, Czech University of Life Sciences Prague.
- Lagergren, S. (1898). “About the theory of so-called adsorption of soluble substances”. In: *Kungl. Svenska vetenskapsakademiens handlingar* 24, pp. 1–39.
- Langmuir, Irving (1916). “The constitution and fundamental properties of solids and liquids. Part I: Solids”. In: *Journal of the American Chemical Society* 38(11), pp. 2221–2295. DOI: 10.1021/ja02268a002.
- Lawson, Daniel and Glenn Marion (2008). *An Introduction to Mathematical Modelling*.

- Limousin, G. et al. (2007). "Sorption isotherms: A review on physical bases, modeling and measurement". In: *Applied Geochemistry* 22, pp. 249–275.
- Marinić Pajc, Ljiljana et al. (2012). "Ravnotežna i kinetička analiza sorpcijskog vezanja bakra na dijatomejsku zemlju". In: *GOMABN* 51, 2, pp. 97–122.
- Mihajlović-Kostić, Marija T. (2016). *Sorpcija jona olova, kadmijuma i cinka iz vodenih rastvora na priridonom i modifikovanom zeolitu*. Doctoral Dissertation. Belgrade, Serbia: University in Belgrade.
- El-Naas, Muftah and M.A. Alhaija (2013). *Modelling of adsorption processes*. Mathematical Modelling. United Arab Emirates University, UAE: Nova Publishers, Inc.
- Nakanishi, Kazuma, Masahiro Tomita, and Katsuya Kato (2015). "Synthesis of amino-functionalized mesoporous silica sheets and their application for metal ion capture". In: *Journal of Asian Ceramic Societies* 3, pp. 70–76.
- Neumaier, Arnold (2004). *Mathematical Model Building*. Modeling Languages in Mathematical Optimization. Boston, MA: Kluwer Academic Publishers.
- Oikonomou, D. (2015). "Recycled concrete aggregates". In: *Cement and Concrete Composites* 27, pp. 315–318.
- Patiha, E., Y. Heraldly, and M. Firdaus Hidayat (2016). "The Langmuir isotherm adsorption equation: The monolayer approach". In: *IOP Conference Series: Materials Science and Engineering* 107. DOI: doi:10.1088/1757-899X/107/1/012067.
- Pignatello, J.J. (2000). "The measurement and interpretation of sorption and desorption rates for organic compounds in soil media." In: *Advances in Agronomy* 69, pp. 1–73.
- R Core Team (2020). *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing. Vienna, Austria. URL: <https://www.R-project.org/>.
- Riahi, Khalifa, Safa Chaabane, and Béchir Ben Thayer (2017). "A kinetic modeling study of phosphate adsorption onto Phoenix dactylifera L. date palm fibers in batch mode". In: *Journal of Saudi Chemical Society* 21, pp. 143–152.

- Roy, W.R. (1993). “Adsorption-Desorption methodologies and selected estimation techniques for transport-modeling parameters”. In: *Migration and Fate of Pollutants in Soils and Subsoils* 32, p. 169.188.
- Ruggiero, D. (2013). *Waste in Europe: Production and Treatment of Waste in the European Union’s Countries*. URL: <http://www.lteconomy.it/%20en/articlesen-%20/articoli/waste-in-europe-production-&-treatment-%20of-waste-in-european-union-s-countries>.
- Sandić, Z. et al. (n.d.). “Brzina sorpcije jona metala na modifikovanim makroporoznim kopolimerima na bazi glicidilmetakrilata”. In: *Glasnik hemičara, tehnologa i ekologa Republike Srpske* ().
- Saroyda, John Ray V. et al. (2020). *PUPAIM: A Collection of Physical and Chemical Adsorption Isotherm Models*. R package version 0.2.0. URL: <https://CRAN.R-project.org/package=PUPAIM>.
- Schaetzel, Pierre, Sébastien Thomas, and Hasna Louahlia-Gualous (2017). “Analogy between adsorption and sorption: An elementary mechanistic approach. I. Monolayer adsorption and sorption without solvent cluster formation”. In: *Chinese Journal of Chemical Engineering* 25, pp. 1740–1749.
- Senthilkumar, Ramalingham and Donipathi Mogili Reddy Prasad (2020). *Sorption of Heavy Metals onto Biochar*. Applications of Biochar for Environmental Safety. Rijeka: IntechOpen. Chap. 13.
- Shikuku, Victor, Kowenje Chrispin, and Fredrick Orori Kengara (2018). “Errors in Parameters Estimation Using Linearized Adsorption Isotherms: Sulfadimethoxine Adsorption onto Kaolinite Clay”. In: *Chemical Science International Journal* 23(4), pp. 1–6.
- Smiciklas, Egeric M.I. et al. (2018). “Experimental and theoretical consideration of the factors influencing cationic pollutants retention by seashell waste”. In: *Journal of Chemical Technology & Biotechnology* 93, pp. 1477–1487.
- Subramanyam, Busetty and Ashutosh Das (2009). “Linearized and non-linearized isotherm models comparative study on adsorption of aqueous phenol solution in soil”. In: *International Journal of Environmental Science & Technology* 6, pp. 633–640.

- Subramanyam, Busetty and Ashutosh Das (2014). “Linearised and non-linearised isotherm models optimization analysis by error functions and statistical means”. In: *Journal of Environmental Health Science & Engineering*.
- Thompson, Aaron and Keith W. Goynes (2012). “Introduction to the Sorption of Chemical Constituents in Soils”. In: *Nature Education* 4(4):7.
- Toth, J. (1995). “Thermodynamical correctness of gas/solid adsorption isotherm equations”. In: *Journal of Colloid and Interface Science* 163, pp. 299–302.
- Trakal, Lukáš (2015). *Environmental Hydrogeology*. Teaching notes. Prague, Czech Republic: Faculty of Environmental Sciences, Czech University of Life Sciences Prague.
- Vijayaraghavan, K. and Y.S. Yun (2008). “Bacterial biosorbents and biosorption”. In: *Biotechnology Advances* 26, pp. 266–291.
- Weber, W. and J. Morris (1963). “Kinetics of adsorption on carbon from solutions”. In: *Journal of the Sanitary Engineering Division*. 89, pp. 31–60.
- Wesner, Janet (2016). *Mean Absolute Error versus Root Mean Squared Error*. URL: <https://medium.com/human-in-a-machine-world/mae-and-rmse-which-metric-is-better-e60ac3bde13d>.

List of Tables

6.1	Estimated parameters for adsorption isotherm, amino loading 0%	39
6.2	Values of different error functions and R-Squared for Langmuir model and Freundlich model, amino loading 0%	41
6.3	Estimated parameters for adsorption isotherm, amino loading 10%	42
6.4	Values of different error functions and R-Squared for Langmuir model and Freundlich model, amino loading 10%	43
6.5	Estimated parameters for adsorption isotherm, amino loading 20%	44
6.6	Values of different error functions and R-Squared for Langmuir model and Freundlich model, amino loading 20%	45
6.7	Estimated parameters for adsorption isotherm, amino loading 30%	46
6.8	Values of different error functions and R-Squared for Langmuir model and Freundlich model, amino loading 30%	47
6.9	Estimated parameters for the maximum adsorption capacity	48
6.10	Estimated parameters for the Langmuir coefficient	49
6.11	Estimated parameters for the Freundlich coefficient	49
6.12	Estimated parameters for the Freundlich constant	50
A.1	Experimental values of the initial concentrations and the equilibrium concentrations for different amino loads	63
A.2	Values of the adsorption capacities for amino loading 0%	64
A.3	Values of the adsorption capacities for amino loading 10%	64
A.4	Values of the adsorption capacities for amino loading 20%	65
A.5	Values of the adsorption capacities for amino loading 30%	65

List of Figures

2.1	Pseudo-first-order kinetic model	10
2.2	Intra-particle diffusion model	12
4.1	The "C" type of isotherm	28
4.2	The "L" type of isotherm	29
4.3	The "H" type of isotherm	30
4.4	The "S" type of isotherm	31
5.1	Workflow of the case study	34
6.1	Modeling adsorption isotherm data for phosphate removal, amino loading 0%	40
6.2	Langmuir model for amino loading 0%	40
6.3	Modeling adsorption isotherm data for phosphate removal, amino loading 10%	42
6.4	Langmuir model for amino loading 10%	43
6.5	Modeling adsorption isotherm data for phosphate removal, amino loading 20%	44
6.6	Langmuir model for amino loading 20%	45
6.7	Modeling adsorption isotherm data for phosphate removal, amino loading 30%	46
6.8	Langmuir model for amino loading 30%	47
6.9	Langmuir isotherms	51
6.10	Freundlich isotherms	51

Appendix

A.1 Experimental values of concentrations

Experimental data of the initial concentrations and the equilibrium concentrations for adsorbent Fe(III)-coordinated amino-functionalized mesoporous MCM-41 with four different amino loads for phosphate removal from solution, that were carried out by series of batch experiments, are given in Table A.1.

0%		10%		20%		30%	
C_0 (mg/L)	C_e (mg/L)	C_0 (mg/L)	C_e (mg/L)	C_0 (mg/L)	C_e (mg/L)	C_0 (mg/L)	C_e (mg/L)
0.5005	0.49	0.526	0.061	0.086	0.037	0.527	0.052
0.975	0.78	0.978	0.023	0.973	0.013	0.987	0.017
4.625	3.67	4.63	0.35	4.666	0.036	4.664	0.034
10.97	9.03	11.04	2.45	9.895	0.15	9.815	0.33
26.39	23.98	26.3	16.43	26.85	5.74	26.595	4.12
55.755	53.25	54.855	44.4	51.69	29.54	52.16	26.09

Table A.1: Experimental values of the initial concentrations and the equilibrium concentrations for different amino loads

A.2 Adsorption capacities

The Tables A.2, A.3, A.4 and A.5 contain observed values of the adsorption capacities and predicted values of the adsorption capacities for each data set. According to these data, a data analysis was performed.

0%		
Experiment	Langmuir model	Freundlich model
$Q_{e,\text{experiment}}$ (mg/g)	$Q_{e,\text{model}}$ (mg/g)	$Q_{e,\text{model}}$ (mg/g)
0.021	0.419	0.907
0.39	0.640	1.088
1.91	2.148	1.997
3.88	3.452	2.842
4.82	4.660	4.169
5.01	5.273	5.700

Table A.2: Values of the adsorption capacities for amino loading 0%

10%		
Experiment	Langmuir model	Freundlich model
$Q_{e,\text{experiment}}$ (mg/g)	$Q_{e,\text{model}}$ (mg/g)	$Q_{e,\text{model}}$ (mg/g)
0.93	2.144	5.269
1.91	0.864	4.229
8.56	8.268	7.814
17.18	17.122	12.118
19.74	20.172	18.614
20.91	20.578	23.292

Table A.3: Values of the adsorption capacities for amino loading 10%

20%		
Experiment	Langmuir model	Freundlich model
$Q_{e,experiment}$ (mg/g)	$Q_{e,model}$ (mg/g)	$Q_{e,model}$ (mg/g)
0.098	6.267	9.555
1.92	2.424	7.389
9.26	6.121	9.491
19.49	17.752	13.480
42.22	42.713	33.020
44.3	44.052	49.394

Table A.4: Values of the adsorption capacities for amino loading 20%

30%		
Experiment	Langmuir model	Freundlich model
$Q_{e,experiment}$ (mg/g)	$Q_{e,model}$ (mg/g)	$Q_{e,model}$ (mg/g)
0.95	4.298	10.058
1.94	1.487	7.362
9.26	2.892	8.933
18.97	18.968	16.843
44.95	45.966	34.067
52.14	51.322	57.016

Table A.5: Values of the adsorption capacities for amino loading 30%