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YAPAY ZEKA KULLANARAK AĞIR METAL
GİDERİMİ İÇİN HİDROJEL VE METAL
ORGANİK ÇERÇEVELERİN
KOMPOZİTLERİNİN KULLANIMININ
İNCELENMESİ

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**INVESTIGATING THE USE OF
COMPOSITES OF HYDROGELS AND
METALORGANIC FRAMEWORKS FOR
HEAVY METAL REMOVAL USING
ARTIFICIAL INTELLIGENCE**

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ÖZET

YAPAY ZEKA KULLANARAK AĞIR METAL GİDERİMİ İÇİN HİDROJEL VE METAL ORGANİK ÇERÇEVELERİN KOMPOZİTLERİNİN KULLANIMININ İNCELENMESİ

Teknolojinin gelişmesi ve sanayileşme ile birlikte ağır metaller, toksik etkileri ve kalıcı yapılarıyla insan sağlığı ve ekosistem için büyük tehditler oluşturmaya başlamıştır. Özellikle yüksek toksisiteye sahip olan kurşun (Pb), bu ağır metaller içerisinde sudan uzaklaştırılması gereken öncelikli kirleticiler arasında yer almaktadır. Bu nedenle, son yıllarda, ağır metal iyonlarının uzaklaştırılmasında yüksek yüzey alanına ve mekanik dayanıma sahip kompozit adsorbanların geliştirilmesi araştırmacılar arasında ön plana çıkmaya başlamıştır. Özellikle metal-organik çerçeveler (MOF) ve biyopolimer bazlı hidrojellerin kombinasyonu içeren kompozit malzemeler araştırmacıların en çok ilgisini çeken yapıların başında gelemeye başlamıştır.

Bu tez çalışmasında, sodyum aljinat (SA) temelli hidrojel ile metal-organik çerçeve olan Zeolitik İmidazolat Çerçevesi-8 (ZIF-8) kullanılarak sentezlenen kompozit adsorbanın sulardaki Pb(II) iyonlarını uzaklaştırma kapasitesi araştırılmıştır. Tez çalışması beş temel aşamada gerçekleştirilmiştir. İlk aşamada, ZIF-8 sentezlenmiştir. İkinci aşamada, belirli oranlarda SA ve ZIF-8 birleştirilerek yüksek adsorpsiyon kapasitesi ve mekanik stabiliteye sahip SA@ZIF-8 kompozitleri elde edilmiştir. Üçüncü aşamada kompozitlerin kurşun giderim performansı sıcaklık (23-50 °C), başlangıç Pb(II) iyonu derişimi (400-500 mg/L) ve temas süresi (10-240 dakika) gibi parametrelerin etkisi altında incelenmiştir. Dördüncü aşamada, elde edilen deneysel veriler kinetik (yalancı birinci derece, yalancı ikinci derece, Dumwald-Wagner), izoterm (Langmuir, Freundlich, Jovanović) ve termodinamik (Van't Hoff) modeller kullanılarak analiz edilmiştir. Yapılan analizler sonucunda, adsorpsiyon sürecinin büyük oranda kimyasal adsorpsiyon mekanizmasına uyduğu, ayrıca intrapartikül difüzyonun da belirli koşullarda etkili olduğu belirlenmiştir. İzoterm analizi tek tabakalı ve adsorpsiyonun heterojen bir yüzeyde gerçekleştiğini göstermiştir. Termodinamik analizlerle, adsorpsiyonun endotermik ve kendiliğinden gerçekleşen bir süreç olduğu saptanmıştır.

Beşinci ve son aşamada ise, optimize edilen veriler ANFIS modeli için istatistiksel olarak derlendi. Bu veriler, daha sonra Uyarlamalı Ağ Tabanlı Bulanık Çıkarım Sistemi (ANFIS) ile optimize edilerek yapay zeka yaklaşımını içeren modelleme gerçekleştirilmiş ve modelin yüksek tahmin başarısına sahip olduğu ($R^2=0,98$) tespit edilmiştir. Ayrıca, optimum çalışma koşullarının 40 °C sıcaklık, %6 ZIF-8 yükleme oranı, 450 mg/L Pb(II) başlangıç derişimi ve 60 dakika temas süresi olduğu tespit edilmiştir. Sonuç olarak, SA@ZIF-8 kompozit adsorbanının yüksek adsorpsiyon kapasitesi (~260 mg/g) ve tekrar kullanılabilirliği ile ağır metal gideriminde oldukça etkili olduğu ve ANFIS modellemesinin süreç optimizasyonu için güçlü bir araç olduğu ortaya konmuştur.



ABSTRACT

INVESTIGATING THE USE OF COMPOSITES OF HYDROGELS AND METAL ORGANIC FRAMEWORKS FOR HEAVY METAL REMOVAL USING ARTIFICIAL INTELLIGENCE

The advancement of technology and industrialization has rendered heavy metals a significant hazard to human health and the ecology because to their poisonous properties and enduring structures. Lead (Pb), which has a high toxicity, is one of these heavy metals that must be removed from water as a priority. For this reason, the development of composite adsorbents with a large surface area and mechanical strength for the removal of heavy metal ions has become the focus of researchers in recent years. Composite materials, especially those containing a combination of metal-organic frameworks (MOF) and biopolymer-based hydrogels, are now among the structures attracting the most attention from researchers.

In this thesis, the capacity of the adsorbent synthesized from sodium alginate (SA)-based hydrogel and the metal-organic framework Zeolitic Imidazolate Framework-8 (ZIF-8) to remove Pb(II) ions from water was investigated. The study was conducted in five main phases. In the first phase, ZIF-8 was synthesized. In the second phase, SA@ZIF-8 composites with high adsorption capacity and mechanical stability were prepared by combining SA and ZIF-8 in specific ratios. In the third stage, the lead removal performance of the composites was investigated under the influence of parameters such as temperature (23-50 °C), initial Pb(II) ion concentration (400-500 mg/L) and contact time (10-240 minutes). In the fourth step, the obtained experimental data were analyzed using kinetic (pseudo-first order, pseudo-second order, Dumwald-Wagner), isothermal (Langmuir, Freundlich, Jovanović) and thermodynamic (Van't Hoff) models. As a result of the analyzes, it was found that the adsorption process largely corresponds to the chemical adsorption mechanism and that intraparticle diffusion is also effective under certain conditions. Isotherm analysis showed that adsorption took place on a single-layered and heterogeneous surface. Thermodynamic analysis showed that adsorption was an endothermic and spontaneous process.

In the fifth and final phase, the optimized data was statistically compiled for the ANFIS model. This data was then optimized using the Adaptive Network-Based Fuzzy Inference System (ANFIS) and modeling was performed using the artificial intelligence approach. It was found that the model had a high predictive success ($R^2=0.98$). It was also found that the optimum operating conditions were 40 °C temperature, 6% ZIF-8 loading rate, 450 mg/L initial Pb(II) concentration and 60 min contact time. As a result, it was found that the SA@ZIF-8 composite adsorbent with its high adsorption capacity (~260 mg/g) and reusability was very effective in removing heavy metals and ANFIS modeling was a powerful tool for process optimization.



SYMBOLS

Pb²⁺: Lead ion

CaCl₂: Calcium Chloride

Ca²⁺: Calcium ion

ΔG°: Change in Gibbs free energy at standard conditions

ΔH°: Change in enthalpy at standard conditions

ΔS°: Change in entropy at standard conditions

T: Temperature

μl: Microliter

ml: Milliliter

rpm: revolution per minute

M: molarity

ppm: parts per million

q_t: adsorption capacity at time t

C₀: composition at t=0

C_t: composition at time t

V: volume

m: mass

k₁: pseudo-first-order rate constant

k₂: pseudo-second-order rate constant

q_e : adsorption capacity at equilibrium

K_L : Langmuir constant

q_e : the amount of substance adsorbed at equilibrium

C_e : the equilibrium concentration in the solution

q_m : the maximum adsorption capacity

K_F : Freundlich constant

$1/n$: the Freundlich exponent

K_J : Jovanović constant

K_D : the adsorption equilibrium constant

R : the universal gas constant (8.314 J/mol K)

T : the absolute temperature (in Kelvin)

$Pb(NO_3)_2$: lead(II)nitrate

NO_3^- : nitrate ion

ABBREVIATIONS

AL: Sodium Alginate

MOF: Metal-Organic Framework

ZIF-8: Zeolitic Imidazolate Framework-8

ANFIS: Adaptive Neuro-Fuzzy Inference System

ANN: Artificial Neural Network

MOF-5: Metal-Organic Framework-5

PNaSS: Poly(sodium p-styrenesulfonate)

SA: Sodium Alginate

IPN: Interpenetrating Network

PFO: Pseudo-First-Order

PSO: Pseudo-Second-Order

MO: Mixed-Order

AI: Artificial Intelligence

SWM: Solid Waste Management

MLP: Multi-Layer Perception

EDTA: Ethylenediaminetetraacetic acid

EBT: Eriochrome Black T

SOD: Sodalite

FIS: Fuzzy Inference System

IQR: Interquartile Range

RMSE: Root Mean Square Error



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1. INTRODUCTION

In the 21st century, increasing pollution has become one of the biggest challenges, with aquatic ecosystems bearing the brunt of this crisis. Industrial activities have primarily contributed to this degradation by discharging a plethora of organic and inorganic pollutants into water bodies. Among these pollutants, heavy metals have proven to be particularly dangerous due to their inherent toxicity and a variety of adverse effects on the environment and human health. Among the heavy metals leaching into these ecosystems are mercury [1] [2] [3], lead [4] [5], cadmium [6] [7], cobalt [8] [9], and nickel [10] [11]. Lead is particularly notorious for its high toxicity, which is alarmingly high in industries such as paint manufacturing, battery production and the fishing industry.

The insidious nature of lead lies in its cumulative effect on biological organisms, including humans. Unlike some other elements, the human body does not have an effective mechanism to excrete lead ions, so they gradually accumulate in body tissues. This accumulation can lead to a variety of health complications, ranging from acute poisoning to long-term effects such as neurological disorders, kidney damage and cardiovascular disease. The severity of this problem is underscored by the fact that lead contamination primarily affects water sources, posing a direct threat to both aquatic life and the people who rely on these water sources. Therefore, the need to develop effective strategies to remove toxic lead ions from industrial effluents and contaminated waters cannot be overstated. Given the far-reaching effects of lead contamination on ecological and human health, this task must be given urgent attention and priority.

In recent decades, the increasing challenge of remediating Pb (II) contaminated water has catalyzed the development of various treatment methods. Among these, adsorption is characterized by its simplicity, cost-effectiveness and high efficiency, especially in complicated aqueous matrices. This affinity for adsorption stems from its inherent properties: low energy consumption, operational stability and versatility in practical applications. The focus is now on improving this technology for the selective removal of Pb (II) ions, taking advantage of its ease of use, long-term effectiveness and high removal efficiency.

The development of new adsorbents is an important step towards overcoming the inherent disadvantages of classical materials such as metal oxides, silica gels, zeolites and carbon-based compounds. Although these classical adsorbents are widely used, they often have limitations in

adsorption capacity, structural tunability and selectivity. In this context, the revolutionary AL@ZIF-8 adsorbent has proven to be a breakthrough. This composite material combines the properties of alginate, and zeolite imidazolate framework-8 (ZIF-8), each contributing to the overall effect.

Because of their biodegradability, affordability, and abundance of carboxyl groups that efficiently chelate with metal ions, sodium alginate hydrogels have been thoroughly researched for heavy metal adsorption; yet, when utilized alone, they have a number of intrinsic drawbacks. These restrictions include limited selectivity for particular heavy metals in complex wastewater matrices, a tendency to swell excessively, which can cause structural collapse after extended use, poor mechanical stability in aqueous environments, and a relatively low adsorption capacity when compared to inorganic adsorbents. According to Wang et al. (2021) [12], the sodium alginate hydrogel demonstrated inadequate mechanical characteristics, when it is used alone.

Furthermore, because of the restricted number of available binding sites and diffusion constraints within the gel matrix, pure alginate hydrogels frequently show delayed adsorption kinetics, especially in the later stages of the adsorption process.

Similar difficulties arise when ZIF-8 is utilized alone as an adsorbent, even if it has remarkable qualities like large surface area, adjustable pore structure, and heat stability. Using pure ZIF-8 has several drawbacks, including limited binding sites for heavy metal ions in comparison to polymeric materials rich in functional groups, poor dispersibility in aqueous solutions because of its hydrophobic nature, difficulty in separation and recovery following the adsorption process, and potential metal leaching in acidic conditions that could result in secondary pollution. Liu et al. (2013) [13] state that although ZIF-8's remarkable adsorption selectivity, flexible pore apertures, and superhydrophobic pore surface allow it to effectively adsorb least polar organic molecules, two major challenges must be addressed before a practical implementation of ZIF-8 is feasible: the poor dispersion of ZIF-8 nanoparticles at high particle loading and the degradation of membrane performance over extended operation due to significant swelling.

Additionally, high temperatures and organic solvents are frequently used in the synthesis of ZIF-8, which raises questions regarding the sustainability of the environment and cost-

effectiveness in large-scale applications. According to El Ouardi et al. (2022) [14], several groups have employed methanol as a reaction medium for ZIF-8 synthesis since it is one of the most widely used solvents in organic synthesis. Nevertheless, these organic solvents are highly costly and may pose health and environmental hazards due to their flammability and toxicity.

The necessity to overcome these individual constraints while combining the beneficial qualities of both components in a synergistic manner is the driving force behind the development of the AL@ZIF-8 composite structure. After synthesizing this composite material, CaCl₂ solution was used as a crosslinker. Feng et al. (2024) [15] argue that, the findings showed that adding Ca²⁺ as a cross-linker improved the AL@AZIF-8 composite hydrogel's adsorption capacity and swelling characteristics. ZIF-8's incorporation into the alginate matrix solves a number of important problems, including improving the hydrogel's mechanical stability by serving as a reinforcing agent, adding more porosity and greatly increasing the specific surface area available for adsorption, improving the selectivity towards Pb(II) ions by coordinating with imidazolate ligands in ZIF-8, and offering a more effective diffusion pathway for metal ions to reach internal binding sites, which improves the adsorption process's kinetics. On the other hand, the alginate component makes it easier for ZIF-8 particles to disperse and immobilize, stops them from clumping together, adds more binding sites with its carboxyl groups, and makes it possible to create stable hydrogel beads that are simple to remove from the treated water. Garg and Sabouni (2023) [16] claim that by inhibiting particle aggregation and enhancing the mechanical strength of the adsorbent material, the coating of ZIF-8 with sodium alginate can improve the stability and reusability of ZIF-8 beads. When compared to each component employed alone, this clever combination produces a composite material with better performance parameters, such as increased adsorption capacity, enhanced mechanical stability, improved selectivity, and more favorable kinetics.

Alginate, a biopolymer derived from algae, has a high affinity for metal ions due to its anionic nature and carboxylate groups. These groups promote efficient chelation with Pb(II) ions. The second component, ZIF-8, is a type of metal-organic framework that forms a microporous structure with a large surface area and increases the capacity and selectivity of the adsorbent. The porosity of ZIF-8 makes it ideal for trapping Pb(II) ions as it provides an abundance of active adsorption sites.

The AL@ZIF-8 composite, which combines alginate, and ZIF-8, results in a multifunctional

adsorbent. It has excellent mechanical and chemical stability, high adsorption capacity and outstanding selectivity for Pb (II) ions. However, composite materials that incorporate multiple components, such as AL@ZIF-8, exhibit a synergy of characteristics derived from each constituent. This synergistic effect is pivotal in material science, as it significantly enhances the performance of the composite beyond what single-component materials can achieve. In the case of AL@ZIF-8, the integration of metal-organic frameworks (MOFs) and hydrogels (derived from alginate) demonstrates this principle. The design of such composites necessitates a careful balance of components tailored to the specific application. For instance, in MOF-inclusive composite structures, the proportion and interaction of MOFs with hydrogel constituents are critical for optimizing the composite's functionality. This meticulous design process ensures that the composite material exhibits the desired properties, such as high adsorption capacity and selectivity for specific heavy metals like Pb (II).

In the advanced domain of multi-component composite systems like AL@ZIF-8, particularly in the context of heavy metal Pb (II) removal from aqueous solutions, the operational intricacies present significant scientific and engineering challenges. The efficacy of multi-component composite hinges critically on the fine-tuning of several operational parameters - pH, temperature, adsorbent dosage, and contact time - each of which plays a pivotal role in the adsorption kinetics and equilibrium.

The pH of the wastewater is a paramount factor, as it directly influences the ionization state of the heavy metal ions and the functional groups on the adsorbent's surface. This ionization governs the electrostatic interactions between the adsorbent and the metal ions, thereby affecting the adsorption capacity. Moreover, the temperature of the system is another critical parameter, impacting both the adsorption kinetics and thermodynamics. Variations in temperature can alter the mobility of metal ions and the dynamic behavior of the adsorbent, thereby influencing the adsorption rate and equilibrium capacity. Additionally, the amount of adsorbent used in the system - the adsorbent dosage - dictates the total surface area available for adsorption, determining the system's maximum adsorption capacity. The contact time, or the duration over which the adsorbent is in contact with the contaminated solution, directly affects the time it takes to reach adsorption equilibrium.

In view of these complex relationships, the optimization of these parameters is difficult and requires a thorough understanding of the adsorption mechanism. Mathematical and computer-

based modeling is proving to be an important tool in this context. These models allow the adsorption process to be modeled under a variety of hypothetical conditions so that it can be investigated how changes in one parameter may affect the overall performance. They serve as a platform for predictive analytics, allowing researchers to anticipate adsorption behavior under different operating situations and thus optimize the system's design and operating parameters in advance.

These models serve a dual purpose. Firstly, they facilitate a deeper understanding of the physicochemical interactions at play, offering insights into the adsorption process at a molecular level. This understanding is crucial for tweaking the system to achieve maximum efficiency. Secondly, modeling offers a cost-effective and expedient pathway to explore a wide range of operational conditions, circumventing the time and resource-intensive nature of empirical experimentation. This aspect is particularly salient for AL@ZIF-8, where the specific interaction of its constituents under different conditions determines its effectiveness in removing Pb (II) ions.

Several strong arguments that address the inherent drawbacks of traditional modeling approaches led to the choice of ANFIS (Adaptive Neuro-Fuzzy Inference System) as the modeling strategy in this work. The intricate, non-linear interactions between several operating factors and adsorption performance are frequently difficult for traditional statistical models to represent, especially in heterogeneous systems like the AL@ZIF-8 composite. In a similar vein, although artificial neural networks (ANNs) are highly effective at identifying patterns, they function as "black boxes" that offer little information on the fundamental principles guiding the adsorption process. In contrast, ANFIS offers a potent hybrid solution that gets over these drawbacks by combining the interpretability of fuzzy logic systems with the learning capabilities of neural networks. According to Al-Mahasneh et al. (2016) [17], compared to other learning methods, ANFIS has the benefit of simple learning algorithms with faster training speeds and faster convergence outcomes. Despite being a strong modeling platform, ANFIS is typically employed when more traditional mechanistic modeling techniques are just not appropriate, too complex, ineffective, or insufficient.

The fuzzy inference system of the ANFIS approach makes it possible to convert human knowledge and linguistic variables (such "high pH" or "low temperature") into exact mathematical frameworks in a unique way. In adsorption investigations, where expert

knowledge frequently directs initial parameter selection but need quantitative refining, this skill is very beneficial. Furthermore, because of the complexity of actual wastewater systems and measurement constraints, ANFIS exhibits a higher capacity to manage noisy or missing experimental data, a major difficulty in adsorption research. The model is incredibly well-suited for optimizing the AL@ZIF-8 adsorption system under a variety of operating situations because of its adaptive nature, which enables it to continuously improve its predictions as fresh data becomes available. Dolatabadi et al. (2018) [18] claim that its ubiquitous ability to simulate nonlinear variation, its use in predicting the performance of several processes, and its extrapolation based on historical data in a range of fields have led to its widespread acceptance as a technology.

Most notably, ANFIS offers clear and understandable guidelines that clarify the connections between adsorption performance and input parameters, providing important mechanistic insights that are not possible with only data-driven methods. Finding the best operating conditions and creating useful instructions for large-scale applications are made easier by this interpretability. According to Karaboga and Kaya (2019) [19], ANFIS combines fuzzy logic's decision-making mechanism with the relational structure and learning capabilities of artificial neural networks. Similar to artificial neural networks, ANFIS uses train data sets to achieve learning with samples. The best ANFIS structure for resolving the associated issue is thus found. ANFIS was chosen for this study due to its higher predictive accuracy than traditional models, especially when it comes to extrapolating performance outside of the tested experimental range. This allows for more effective design and operation of Pb(II) removal systems based on the AL@ZIF-8 composite.

The adsorption behavior of Pb(II) ions onto AL@ZIF-8 composite hydrogel has been thoroughly predicted in the present study using sophisticated adaptive neuro-fuzzy inference system (ANFIS) modeling methodologies. ANFIS offers a strong framework for simulating intricate nonlinear interactions between operational parameters and adsorption efficiency by fusing the reasoning structure of fuzzy logic with the learning capabilities of artificial neural networks. Karaboga and Kaya (2019) [19] claim that the inability to provide an explanation for the weight values obtained is one of the biggest drawbacks of artificial neural networks. The fuzzy inference system, which is part of the ANFIS framework, removes this drawback. This structure makes it useful for resolving a wide range of real-world issues. The complex

relationships between temperature, adsorbent dosage, contact time, and the resulting Pb(II) removal effectiveness are precisely captured by the ANFIS model created in this study, allowing for accurate prediction of adsorption performance under a range of circumstances. This prediction capability represents a significant improvement in the field of water treatment technologies by greatly improving our ability to tune the adsorption process without requiring costly experimental trials.

This study's use of kinetic and thermodynamic studies was crucial for several important reasons that go beyond scholarly curiosity. The rate-limiting components of the adsorption process are fundamentally understood through kinetic studies, and these insights have a direct impact on the design parameters of realistic water treatment systems. In large-scale applications, engineering decisions about contact time requirements, reactor configurations, and mixing conditions are guided by an understanding of whether the adsorption process is controlled by diffusion limitations (as shown by intraparticle diffusion models) or chemical reactions (as indicated by pseudo-second-order kinetics). Ebelegi et al. (2020) [20] state that the rate of adsorption is related to the number of unoccupied binding sites on adsorbents, according to the pseudo-first-order kinetic model. On the other hand, the pseudo-second-order kinetic model helps with the assessment of sorption capacity and predicts the order of the sorption process. These kinetic experiments demonstrated intricate multi-stage adsorption mechanisms in the case of AL@ZIF-8 that would not be discernible from equilibrium studies alone, underscoring the significance of optimizing the structure and operational parameters of the composite in order to increase adsorption rates.

Conversely, thermodynamic evaluations offer vital insights into the intrinsic characteristics of the adsorption process, including its spontaneous, endothermic, or exothermic nature, as well as the level of affinity between the adsorbent and adsorbate. Doke and Khan (2013) [21] argue that whether the adsorption process is spontaneous or not is predicted using adsorption thermodynamics. Additionally, it forecasts the characteristics of the adsorbent and adsorbate at equilibrium, identifies certain ideal conditions for the viability of the adsorption process, and explores the temperature range at which the adsorption process is advantageous or disadvantageous. These factors have a direct impact on operational choices like the need for temperature control, energy inputs, and the adsorption system's viability. The thermodynamic calculations for AL@ZIF-8 demonstrated that Pb(II) adsorption is endothermic, which explains

the improved performance at high temperatures and offers helpful advice for maximizing thermal conditions in real-world applications. Additionally, the positive ΔS° value indicated a higher degree of randomness at the solid-solution interface during adsorption, which might be explained by Pb(II) ions dislodging water molecules that were previously attached to adsorption sites, raising the system's total entropy. According to Doke and Khan (2013) [21], the adsorption process is spontaneous ($\Delta G^\circ < 0$) if it is endothermic (ΔH° is positive) and happens when the disorder at the solid-liquid interface increases (ΔS° is positive), as long as $\Delta H^\circ < T \Delta S^\circ$. Our research offers significant insights into the mechanisms driving Pb(II) adsorption onto AL@ZIF-8 composite hydrogel by the use of a rigorous scientific methodology that includes sophisticated modeling approaches, in-depth kinetic and isotherm studies, and thorough thermodynamic analysis. In addition to improving our basic knowledge of the adsorption process, these results offer helpful recommendations for the development and widespread use of this potential adsorbent in environmental cleanup. The comprehensive strategy used in this work marks a major breakthrough in the creation of composite materials that satisfy the particular needs of heavy metal remediation and significantly improve environmental protection.

2. LITERATURE REVIEW

2.1. Heavy Metal Pollution

In today's world, because of the increase in industrialization activities, pollution that negatively affects natural life occurs. One of the most significant of these is heavy metal pollution, which over time has detrimental effects on both human health and the environment.

Heavy metals are typically defined as elements with high atomic weights or densities, though classification may vary depending on context. Briffa et al. (2020) [22] claims that nowadays, metallic elements and metalloids that have negative effects on human health and the environment, in other words, have high toxicity, are also considered heavy metals. Metalloid is a toxic structure, the toxicity of some light metals such as selenium and arsenic are also high, even though they are not heavy metals. Additionally, some heavy metals are non-toxic, gold being an important example.

Zhang et al. (2023) [23] synthesized a novel MOF-5/PNaSS/SA composite material to remove Pb(II). In addition, the effects of temperature, concentration, pH, contact time, other ions, and material reusability were investigated. A variety of models, including adsorption kinetics, adsorption isotherm, and thermodynamics, were also used to assess the adsorption data. Their results indicated that metal organic framework included composite materials are highly efficient in removing Pb(II).

2.1.1. The Origins and Impact of Heavy Metals

The pollution caused by heavy metals for the environment is becoming a serious problem and it gives an apprehension for the life because of its negative impacts on the world. There are lots of sources for heavy metals such as agriculture and metal industries that are growing very fast, inconvenient annihilation of the wastes, the pesticides and the fertilizers. To ease this issue, all these are discarded to our soils, atmosphere and water sources. While these metals affect some biological functions in the body, such as growth functions, they can also cause serious health problems like cancer in some organs.

There may be various ways for pollutants to enter the ecosystem and atmosphere. This may be due to some volcanic activities or erosion of rocks, as well as anthropogenic activities. Some

events such as mining activities, ship accidents and oil spills can result releasing heavy metals to the environment. Additionally, industrial wastewater and sewage waste can also be considered as sources of heavy metals.

As highlighted by Briffa et al. (2020) [22], there are some factors that enable heavy metals to move in nature. Wind speed, temperature, flow direction of surface waters and air mass circulation can be counted as these factors. Except these, some of the other factors that can be considered are distribution coefficient, molecular balance, vapor pressure and polarity.

Additionally, according to Mitra et al. (2022) [24], nine distinct toxicity categories for human health can be brought on by heavy metal pollution: genotoxicity, immunological toxicity, skin toxicity, cardiovascular toxicity, hepatotoxicity, nephrotoxicity, neurotoxicity, and carcinogenesis.

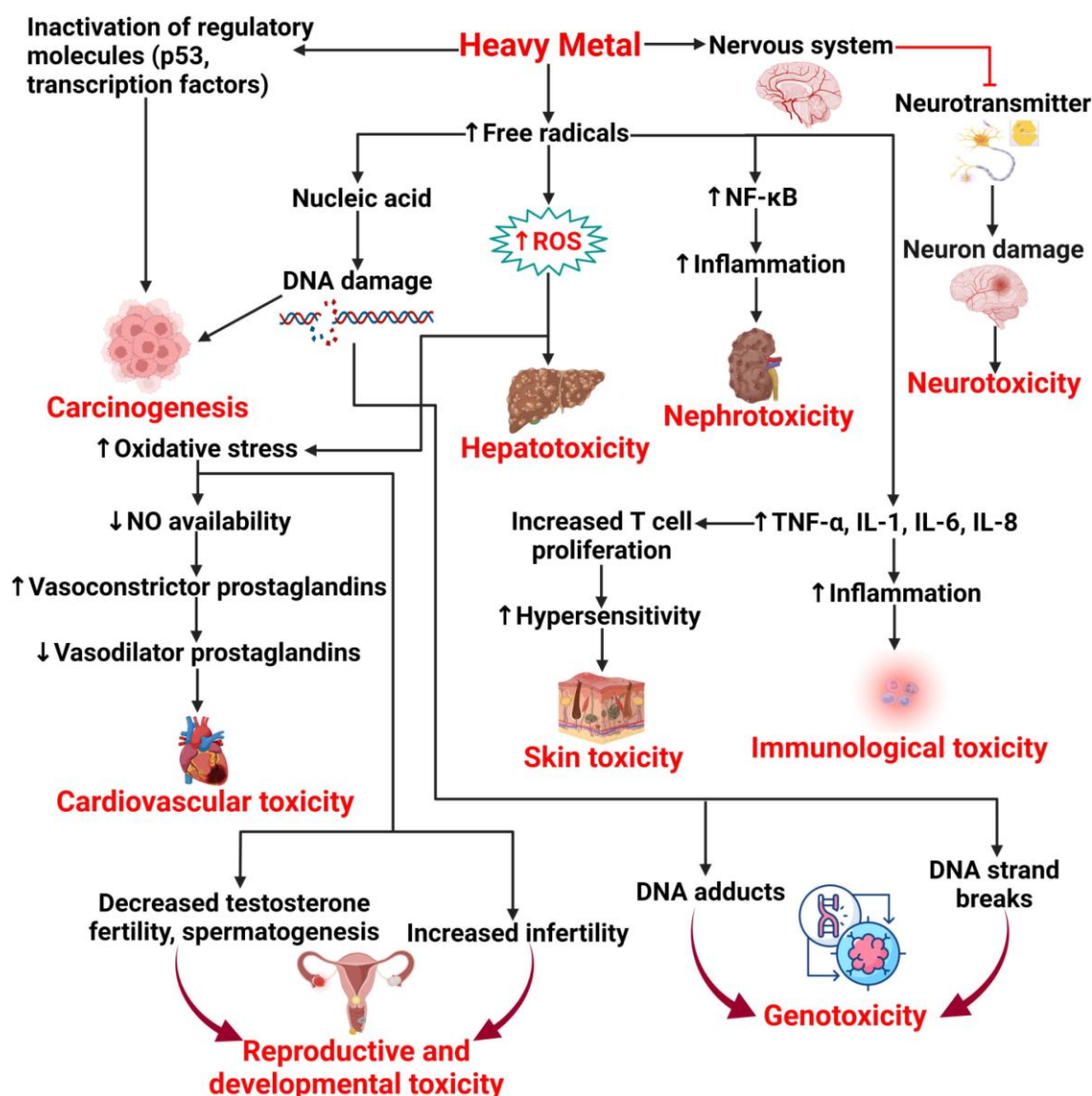


Figure 2.1:The human body's response to heavy metal poisoning [24]

2.2. Hydrogels in Heavy Metal Removal

One of the biggest known facts about heavy metals is undoubtedly that these materials are difficult to clean. Therefore, water pollution caused by heavy metals is not an issue that can be solved in the short term. Heavy metals have a high toxicity and since they do not biodegrade in nature, they constantly migrate, accumulate and grow in the natural ecosystem, posing serious threats to human and environmental health. Zhang et al. (2021) [25] claimed that some of the heavy metals can be carcinogenic even at the low concentrations. Therefore, research has been conducted on various methods for the removal of these materials. Among the possible methods, adsorption is considered extremely advantageous due to its low cost and wide applicability.

However, at this stage, the types and properties of adsorbents are very important for a tremendous adsorption. For this reason, the discovery and development of new adsorbents is the biggest goal of research at this point.

According to Sutirman (2021) [26], because of the dispersion of large hydroxyl and carbonyl groups along the polymer chains, researchers are now particularly interested in using alginate in the removal of heavy metals. These functional groups are perfect components for heavy metal immobilization, according to recent research. Alginate is a structure that not only shows swelling and dissolving in alkaline solutions, but it also demonstrates these behaviors in water. The necessary remedy to this issue is turning alginate into a gel.

2.2.1. Hydrogels Made from Alginate

Alginate is a type of polyuronic saccharide and linear anionic polymer that is produced from brown seaweed. Significant hydrophilicity, good mechanical strength, high viscosity, biocompatibility, biodegradability, and nontoxicity are only a few of its promising qualities. Furthermore, it can be easily and inexpensively produced from bacteria (such as a mutant strain of *Azotobacter vinelandii*) or seaweeds (such as *Saccharina japonica*, *Laminaria hyperborea*, *Macrocystis pyrifera*, *Ascophyllum nodosum*, etc.). According to Nagaraja et al. (2021) [27], alginate's potential physicochemical qualities have led to its widespread application in a variety of industries, including the food, pharmaceutical, and chemical sectors. Sutirman et al. (2021) [26] state that, as a crosslinker, alginate is a material that can gel inotropically when divalent cations are present.

It has been widely documented that sodium alginate, a naturally occurring polysaccharide with a high concentration of hydroxyl and carboxyl groups, is where heavy metals are first adsorbed from aqueous solutions. According to Gao (2020) [28], adsorbents made from sodium alginate have demonstrated significant adsorption capabilities and high rates of heavy metal ion removal through surface grafting and cross-linking.

There are several ways to create alginate-based hydrogels using chemical or physical crosslinking methods. The most widely used method is physical crosslinking, which is based on ionic interactions between alginate's carboxyl groups and divalent cations. As

highlighted by Tan et al. (2023) [29], studies have shown that, despite the low cost and straightforward nature of this crosslinking technique, the resulting hydrogel typically has poor mechanical and thermal durability and is easily degraded in physiological settings. As a result, a growing number of researchers began focusing on alternative crosslinking techniques, namely chemical crosslinking and interpenetrating network (IPN) technologies.

2.3. Metal-Organic Frameworks (MOFs)

Because of their exceptional qualities, metal-organic frameworks (MOFs) are a family of highly organized porous crystalline materials that have garnered a lot of interest. These materials are characterized by their impressive adsorption capabilities, customizable multifunctionality, structured pore organization, and large specific surface areas. The interaction between MOFs and different contaminants is greatly improved by the addition of active species and unsaturated coordination sites. This interaction is of key importance for environmental remediation, especially in the adsorption of hazardous substances from aqueous solutions. According to Abdollahi et al. (2022) [30], these properties make MOFs particularly effective in the uptake and removal of a wide range of environmental pollutants. Their tunable nature enables the precise tailoring of their chemical and physical properties to specific pollutants, making them extremely versatile in the field of environmental remediation.

Despite the promising properties of MOFs, there are still problems with their practical application, especially in the retrieval of MOFs. This issue is crucial because, when employing MOF-based adsorbents, it causes secondary contaminations and makes the separation process for solid-liquid more difficult during the adsorption phase. These challenges emphasize the need for advanced methods and strategies to refine the synthesis and application processes of MOFs. Addressing these issues is critical to improving the efficiency and environmental safety of MOF-based technologies in pollution abatement. Developing innovative approaches to mitigate these drawbacks could significantly expand the applicability and effectiveness of MOFs in environmental remediation.

Because of its distinct composition, which consists of imidazole rings and tetrahedral zinc ions, zeolitic imidazolate framework-8 (ZIF-8) has become a material of note among the different MOFs. This composition gives ZIF-8 remarkable abilities to remove a broad spectrum of

impurities, including dyes [31], phthalic acid, arsenic and benzotriazole from water. As highlighted by Wang et al. (2021a) [32], the structural and chemical properties of ZIF-8 make it a powerful adsorbent for removing certain dangerous chemicals from water. The ability of ZIF-8 to selectively eliminate such a wide range of pollutants emphasizes its potential as a versatile and powerful tool in water treatment technology.

Further advances in the synthesis of ZIF-8 have been reported that enhance its porosity and adsorption capacity. By reacting zinc with 2-methylimidazole, Ahmad et al. (2021) [33] were able to create ZIF-8 with improved porosity and showed how well it absorbed lead (Pb^{2+}) and mercury (Hg^{2+}) ions from water. This development represents a significant milestone in the optimization of ZIF-8 for the removal of heavy metals and provides an effective solution to mitigate the harmful effects of these toxic substances on human health and the environment. The increased porosity of ZIF-8 not only increases adsorption capacity but also improves selectivity for certain pollutants, highlighting the importance of material design in environmental applications.

2.3.1. Zeolitic Imidazolate Framework-8 (ZIF-8)

Zeolitic Imidazolate Framework-8 (ZIF-8) is the metal-organic framework structure that will be used in this study. According to Lee (2015) [34], zeolitic imidazolate frameworks (ZIFs), which are porous hybrid materials with structures resembling zeolites, are constructed upon 4-connected nets of tetrahedral units. In ZIFs, metal ions (such as Zn^{2+} or Co^{2+}) are connected by N atoms in ditopic imidazolate anions. A promising material for applications like CO_2 adsorption, H_2 storage, alkane/alkene separation, and heterogeneous catalysis, ZIFs have drawn interest because of their flexible structure, which allows for the reasonable conception of the sizes of their pores and the activity of their surfaces, as well as their comparatively high chemical and thermal stability.

Chu et al. (2019) [35] stated that imidazolate or its derivatives usually serve as linkers between tetrahedrally-coordinated transition metal ions (such as Fe, Co, Cu, and Zn) to form ZIFs. ZIFs have a stronger thermal and chemical stability than the other MOFs, although having a comparable structure, which enables them to function at a wider temperature range. They have also claimed that the hydrophobic qualities and water stability of ZIFs set them apart from the other MOFs and contribute to their virtually equal

performance in both dry and humid environments. These features make ZIFs highly promising for use in energy storage, gas separation, carbon dioxide capture, catalysis, drug delivery, and biosensing.

2.4. Kinetic and Thermodynamic Studies of Adsorption

2.4.1. Adsorption Kinetics

Pollutants are transferred by mass from the liquid phase to the solid adsorbent through the process of adsorption. One of the most popular technologies for treating water and wastewater is adsorption, which has several benefits including an easy-to-maintain design, cheap cost, and high efficiency. The mass transfer processes, adsorption rate, and adsorbent performance are all revealed by the adsorption kinetic analysis. The design of the adsorption systems depends on the understanding of the adsorption kinetic. As highlighted by Wang et al. (2020) [36], there are three steps in the adsorption mass transfer kinetic, as shown in the figure below. The outward diffusion is the initial stage. The liquid layer surrounding the adsorbent is broken down in this step by the adsorbate. What drives the external diffusion are the concentration differences between the adsorbent surface and the bulk solution. It is referred to this second phase as internal diffusion. The adsorbate's diffusion inside the adsorbent's pores is referred to as internal diffusion. In the third stage, the adsorbate is adsorbed onto the adsorbent's active regions.

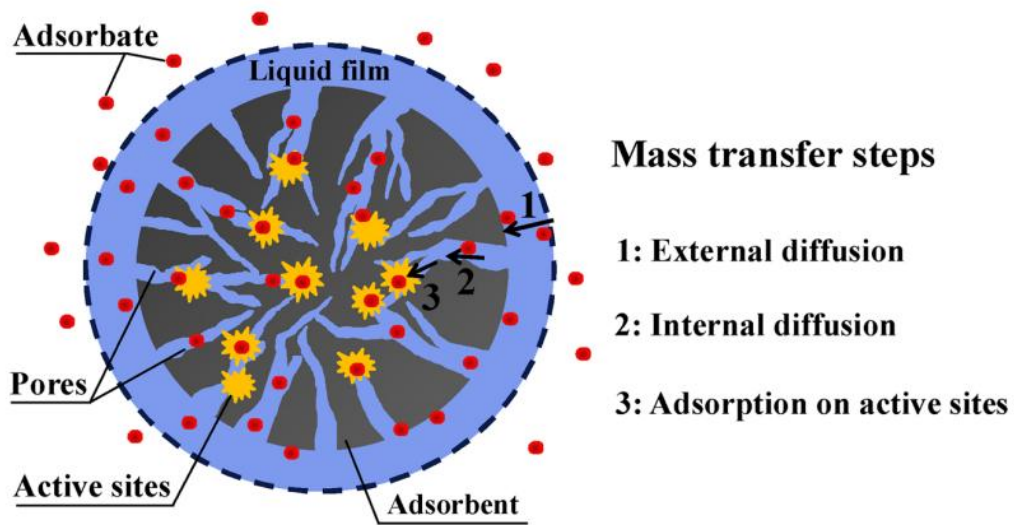


Figure 2.2:The mass transfer steps of adsorption. [36]

According to Revellame et al. (2020) [37], the adsorption kinetic process has been described by a number of adsorption kinetic models, including the pseudo-first-order (PFO) model, the pseudo-second-order (PSO) model, the mixed-order (MO) model, Ritchie's equation, the Elovich model, and the phenomenological mass transfer models. Nevertheless, there were a few issues with these kinetic models' applicability. First off, the PFO and PSO models that are most frequently used are empirical models with no clear physical interpretation. We are unable to use these empirical kinetic models to study the mass transfer pathways. Consequently, it is necessary to define the empirical kinetic models' physical meanings. Differential kinetic models, like the phenomenological external/internal and adsorption in active sites models, have complex solving techniques even though they have clear physical meanings. The mechanisms by which these models transfer mass have not been thoroughly studied. These models' usefulness is limited by their complex solutions. The third is the incorrect application or solution of kinetic models in some published works. The Frusawa and Smith (F&S) model, for instance, can only simulate adsorption processes with a linear isotherm. In the adsorption process, the Langmuir-type isotherm has been used, though.

2.4.2. Adsorption Thermodynamics

It is amazing how well thermodynamics can relate seemingly unconnected properties. For instance, the heat of the solid adsorbent's immersion in the gas directly relates to the temperature coefficient of adsorption. Phase equilibrium between a gaseous mixture and a solid adsorbent is calculated, and this is the most significant use of thermodynamics in adsorption. Myers (2004) [38] claimed that the adsorption isotherm, which provides the amount of gas adsorbed in the nanopores as a function of the external pressure, serves as the foundation for thermodynamic calculations. Adsorption isotherms can be determined theoretically by molecular simulations or through experimental measurement. Potential functions are utilized to construct a thorough molecular model for atom-to-atom interactions, and a distribution of point charges is utilized to mimic the solid material's and the adsorbing molecules' polarity.

Adsorption systems have seen the application of a wide range of isotherms, including the Temkin, Langmuir, linear, Freundlich, Sips, and Brunauer, Emmett, and Teller (BET) models. According to Wang et al. (2020) [39], the linear, Freundlich, Sips, Temkin, and a few other models are empirical models that do not have strong theoretical backing. These models do not provide adsorption mechanisms. Therefore, it is important to look into the origins and physical meanings of these models. Furthermore, they claimed the isotherms have been categorized based on the quantity of model parameters or their shapes (S-, L-, H-, and C-shaped). However, there is no theoretical foundation for the classification based on the quantity of parameters. Azizian et al. (2021) [40] highlighted that the Langmuir and BET isotherms, for instance, are two-parameter models that depict chemical and physical adsorption, respectively. The quantity of model parameters is insufficient to provide the mechanism knowledge. A further drawback of the model-based classification is that most adsorption equilibrium data for liquid-solid systems have an L-shaped distribution. As a result, the isotherms ought to be categorized more sensibly in light of their physical interpretations.

2.5. Artificial Intelligence in Environmental Applications

An assessment of artificial intelligence's (AI) influence on achieving the sustainable development goals (SDGs) is necessary given its rapid expansion and wide-ranging

effects on numerous sectors. Kumari et al. (2023) [41] stated that, global economy is most affected by AI. From attaining sustainable energy and gender equality to eradicating hunger and poverty to safeguarding and preserving biodiversity, artificial intelligence (AI) is a critical component in meeting environmental sustainability goals. The environment, economy, and society make up the three categories into which the SDGs fall.

Numerous environmental fields, such as waste management, agriculture, pollution control, wildlife preservation, clean energy, and natural resource conservation, use artificial intelligence (AI). According to Konya et al. (2024) [42], AI will help energy systems that are more energy efficient and have a smaller carbon footprint—both of which are necessary to combat climate change. Effective management of the intricate ecosystem's structure and operations can be aided by AI. In addition to the aforementioned uses, it can support environmental planning, decision-making, and the identification of broad trends in desertification. The introduction of numerous new technologies has made it possible to apply AI in nations with disparate economic and cultural norms. This has made the technique more well-known worldwide.

The growing number of AI application sectors is supported by the modeling techniques' ability to handle noisy and complex data. Artificial Intelligence has been extensively employed to address issues pertaining to air pollution, modeling of water and wastewater treatment, ground water contamination, soil remediation, and SWM (Solid Waste Management) strategy planning. According to Abdallah et al. (2020) [43], pollutant and particle matter concentrations can be predicted using AI-based risk management tools including ANN (Artificial Neural Network), MLP (Multi-Layer Perception), and ANFIS (Adaptive Neuro-Fuzzy Inference System) models. Processes in water and wastewater treatment plants can be predicted and optimized with the help of ANFIS. Furthermore, they assert that ANFIS can optimize the coagulant dose for turbidity removal in a water treatment plant and precisely forecast the production of methane and effluent volatile solids from an anaerobic digester in a wastewater treatment plant.

2.5.1. Overview of ANFIS

Neural networks are used in the ANFIS (Adaptive Neuro-Fuzzy Inference System) integration system to optimize the fuzzy inference system. Lei (2017) [44] claims that to generate the specified input-output pairs, ANFIS builds a number of fuzzy if-then rules with suitable membership functions. By incorporating human understanding of the desired results into the modeling process, the initial fuzzy rules and membership functions are created. ANFIS can then modify these fuzzy if-then rules and membership functions to lower the output error measure or make the input-output relationship of the complex system more understandable. The architecture of ANFIS is described by taking into account two fuzzy if-then rules:

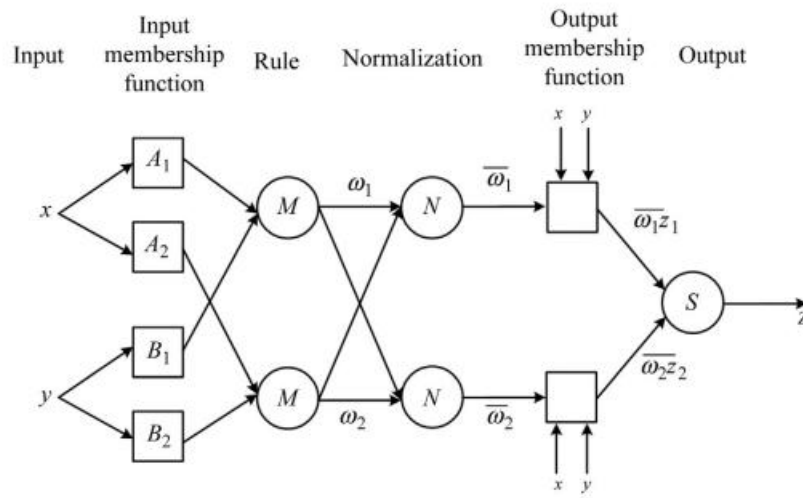


Figure 2.3:The ANFIS Architecture [44]

where the fuzzy sets are A_i and B_i , the inputs are x and y , the outputs are z_i ($i = 1, 2$) inside the fuzzy zone that the fuzzy rules have defined, and the parameters are p_i , q_i , and r_i that are established during the training phase. As seen in the above diagram, the architecture of ANFIS consists of five levels to execute these two rules. As can be observed, a circle denotes a fixed node while a square represents an adaptable node.

The ANFIS hybrid learning algorithm uses both the gradient approach and the least squares method to update the parameters. The forward pass of the learning algorithm uses the least squares estimate to determine following parameters, as noted by Çaydaş et al.

(2009) [45]. During the backward pass, the erroneous signals move backward from the output layer to the input layer. For each node output, these error signals are the derivatives of the squared error. The premise parameters are changed by the gradient descent algorithm at this backward step.



3. MATERIALS AND METHODS

3.1. Synthesis of Alginate-ZIF-8 Hydrogels

For synthesizing the alginate-ZIF-8 hydrogel, the procedure will be the following:

- First add 2%, 4% or 6% by weight of ZIF-8 and then 2.8 g of sodium alginate into 100 mL of water.
- It is mixed at 1500 RPM for one and a half hours.
- Then, this solution is added dropwise into 100 mL of pure water solution containing 1 g of calcium chloride using a pasteur pipette.
- After finishing the dropping process, the resulting mixture is left for 15 minutes, and then filtered with the help of a strainer. This is required to see the gelation of the structure.
- It is placed in the weighed petri dish and weighed again.
- Then it is left to dry in an oven at 40 degrees Celsius for 24 hours.

The quantities used for each material are as follows:

Table 3.1: The material amounts in SA – ZIF-8 Hydrogel Synthesis

Sodium Alginate (g)	ZIF-8 (g)	ZIF-8 (%)	CaCl ₂ (g)
2.8	0.056	2	1
2.8	0.112	4	1
2.8	0.168	6	1

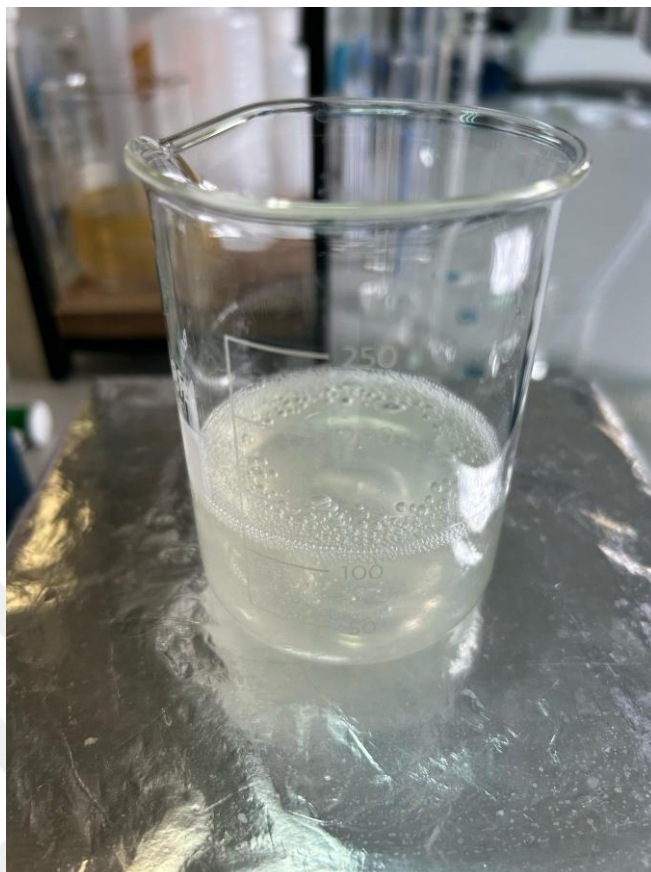


Figure 3.1:The AL@ZIF-8 Composite Solution

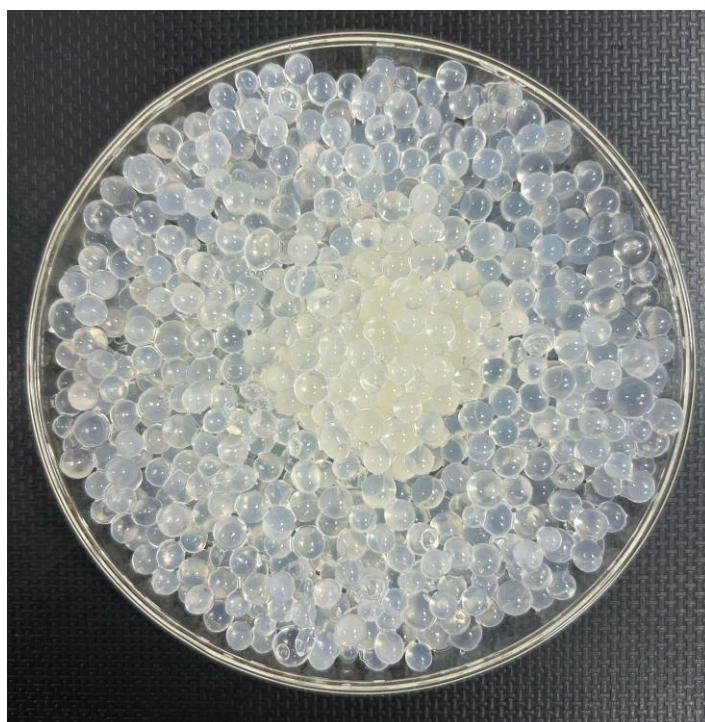


Figure 3.2:AL@ZIF-8 Composite Hydrogel

3.2. Incorporation of ZIF-8 into Alginate Hydrogels

The first step of ZIF-8 synthesis begins with the addition of 100 mL of methanol to a 600 mL beaker. In the synthesis of ZIF-8, methanol is used as an effective solvent to dissolve reagents such as zinc nitrate hexahydrate and 2-methylimidazole. This allows the formation of a homogeneous reaction mixture and increases the interactions between metal ions and organic ligands, thus enabling efficient formation of the desired MOF structure. Additionally, the low boiling point of methanol facilitates the easy evaporation of the solvent after synthesis, and the formation of the porous structure of the MOF. These properties make methanol an ideal solvent for ZIF-8 synthesis and directly increase the success of the reaction.

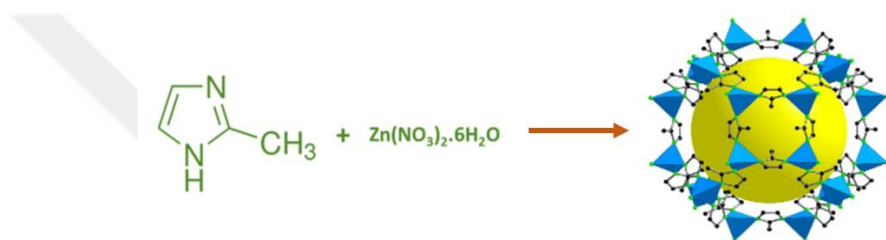


Figure 3.3: ZIF-8 Synthesis Procedure

In the second step, 0.55 g of zinc nitrate hexahydrate is measured with the help of a precision balance and added to methanol. Zinc nitrate hexahydrate provides zinc ions, the metal center of ZIF-8, and these ions form the lattice of the MOF structure. These metal centers give the structure excellent thermal and chemical stability and form ideal active sites for the selective adsorption of heavy metals such as lead from wastewater. After mixing the mixture for 5 minutes, 1.065 grams of 2-methylimidazole is measured and added to the mixture, and this organic ligand forms bonds around the zinc ions, creating a porous and stable framework structure. 2-methylimidazole controls the pore size and shape of ZIF-8, which plays a critical role in the selective adsorption of Pb(II) ions and removal of Pb(II) ions from wastewater. Adding these two components to the mixture ensures the success of ZIF-8 synthesis and provides high performance in the selection of Pb(II) ions of the material.



Figure 3.4:ZIF-8 Synthesis Processes

After the mixing process is completed, the solution is transferred to falcon tubes for the separation process of ZIF-8. The centrifugation step is performed to separate the formed ZIF-8 crystals from methanol and other substances that are insoluble in solvents such as methanol. High-speed rotation effectively separates solid and liquid phases using density differences. During this process, ZIF-8 particles are precipitated to the bottom of the tube under the influence of force in the tubes to be placed in the OMNILAB centrifuge device, which rotates at 4500 RPM for one hour. When centrifugation is complete, the supernatant clear methanol phase is carefully removed so that the ZIF-8 solid phase remains at the bottom of the tube. Methanol is added again to the solid phase and this washing process is repeated three times in total, using a centrifuge each time. Each of these steps is carried out with great care and attention

to increase the purity of ZIF-8 and hence its performance to be improved.

The final stage is the drying process of ZIF-8. After the washing process is completed, ZIF-8 removed from the falcon tubes is left to dry for 24 hours in an oven at 50 degrees Celsius. This drying process is necessary for the synthesized ZIF-8 to have the desired chemical and physical properties.



Figure 3.5:Zeolitic Imidazolate Framework-8 (ZIF-8)

ZIF-8 is formed by tetrahedral coordination of Zn(II) ions and imidazolate linkers. This coordination makes the electronic structure of Zn(II) centers suitable for interaction with Pb(II) ions. When Pb(II) ions approach the Zn(II) centers of ZIF-8, they can form coordination bonds with the metal centers of the metal-organic framework, which enables the adsorption of Pb(II) ions. Furthermore, the microporous structure of ZIF-8 allows deep penetration of Pb(II) ions at the molecular level. This diffusion process increases the interaction area on the surface and therefore increases the adsorption capacity.

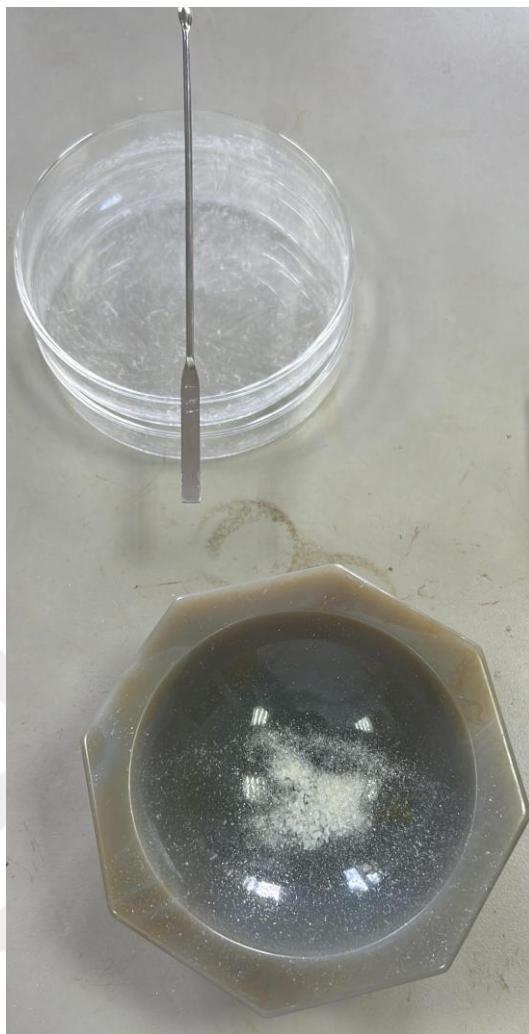


Figure 3.6: ZIF-8 after grinding in a mortar

Combining ZIF-8 with Alginate-based hydrogels further increases Pb(II) selectivity. Light metals such as sodium (Na^+) or potassium (K^+) attached to the carboxylic acid groups in alginate are replaced by Pb(II) ions. This ion exchange reaction allows Pb(II) ions to be adsorbed onto the hydrogel. Additionally, many hydroxyl and carboxyl functional groups in alginate can form complexes by forming coordination bonds with Pb(II) ions. This complex formation contributes to the binding and therefore adsorption of Pb(II) ions to the hydrogel. The addition of ZIF-8 promotes this complex formation because the microporous structure and high surface area of ZIF-8 allows more Pb(II) ions to have access to these functional groups.

3.3. Pb(II) Removal Experiments

Within the scope of this master's thesis study, more than 200 experiments were carried out for the adsorption capacity of AL@ZIF-8 against Pb(II) ions.

The experiments demonstrated the interaction of AL@ZIF-8 with lead nitrate solution at different temperatures like 23°C, 40°C, and 50°C for the removal of Pb(II) ions.

In this context, 0.1 g (depending on the amount of adsorbent) of AL@ZIF-8 is weighed and placed in eight separate 50 mL beakers. 10 mL of lead nitrate solution is added to each beaker. During the experimental process, AL@ZIF-8 was exposed to lead nitrate solution at the specified adsorbent amounts, and temperatures. Separate experiments were carried out for each adsorbent, and temperature, and this was used to understand the response of the material to temperature changes and also in thermodynamic calculations. The adsorption efficiency of the material against Pb (II) ions was evaluated in a temperature-controlled environment.

The solution was treated with EBT solution firstly, and then titration was performed with EDTA. The color change observed as a result of titration was evaluated as an indicator of the adsorption capacity of AL@ZIF-8 against Pb (II) ions.

Solutions

In this experiment, there are four different solutions that have been prepared. These are 250 mL, 0.1 M Lead (II) Nitrate ($\text{Pb}(\text{NO}_3)_2$) as a lead (heavy metal) source, 100 mL Ammonia + Ammonium Chloride solution as a buffer solution, 250 mL, 0.1 M EDTA-2NA as a titrant, and 100 mL, 0.01 M Eriochrome Black T (EBT) as indicator.

Application

At the beginning of this experiment, 0.1 g of composite hydrogel is weighed into seven 50 mL falcontubes. Then, 50 mL of lead (II) nitrate solution is added onto the composite.

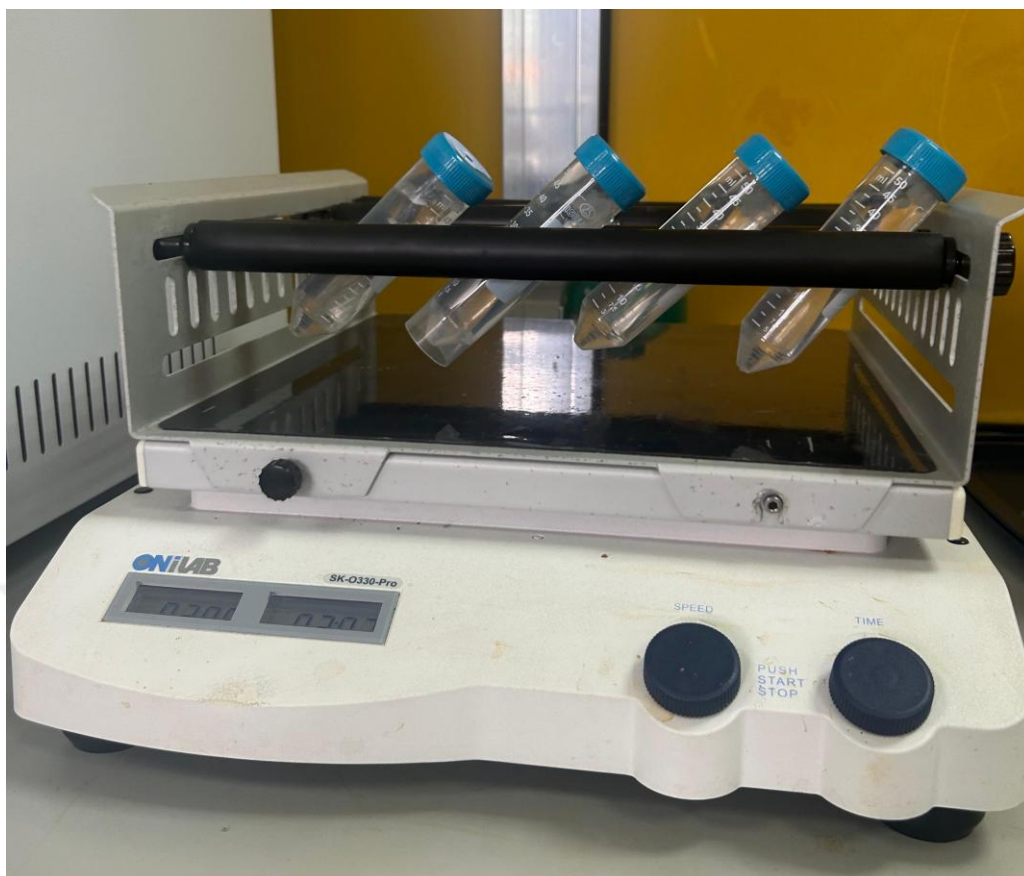
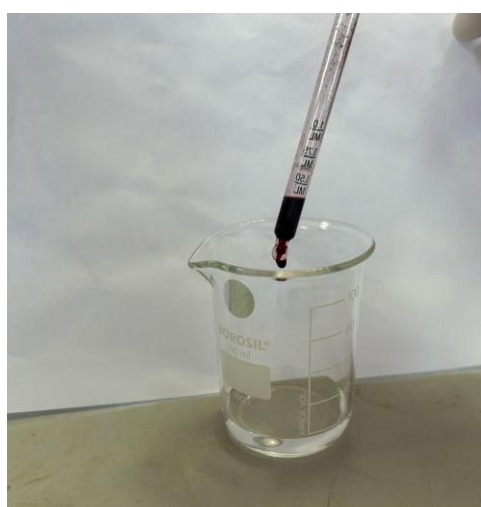


Figure 3.7:The shaking process for specified times

The composites are exposed to lead (II) nitrate solution for 10, 20, 30, 40, 50, 60, and 90 minutes. After the specified periods, 10 ml of the composite containing lead solutions are taken into 3 100 ml beakers for each falcon tube.



(a)



(b)

Figure 3.8:(a) before dropping the Indicator (EBT Solution), (b) after dropping the Indicator (EBT Solution)

Then, 5 drops of EBT solution are added to each beaker. It is made homogeneous by mixing with circular movements, as seen on Figure 3.8.

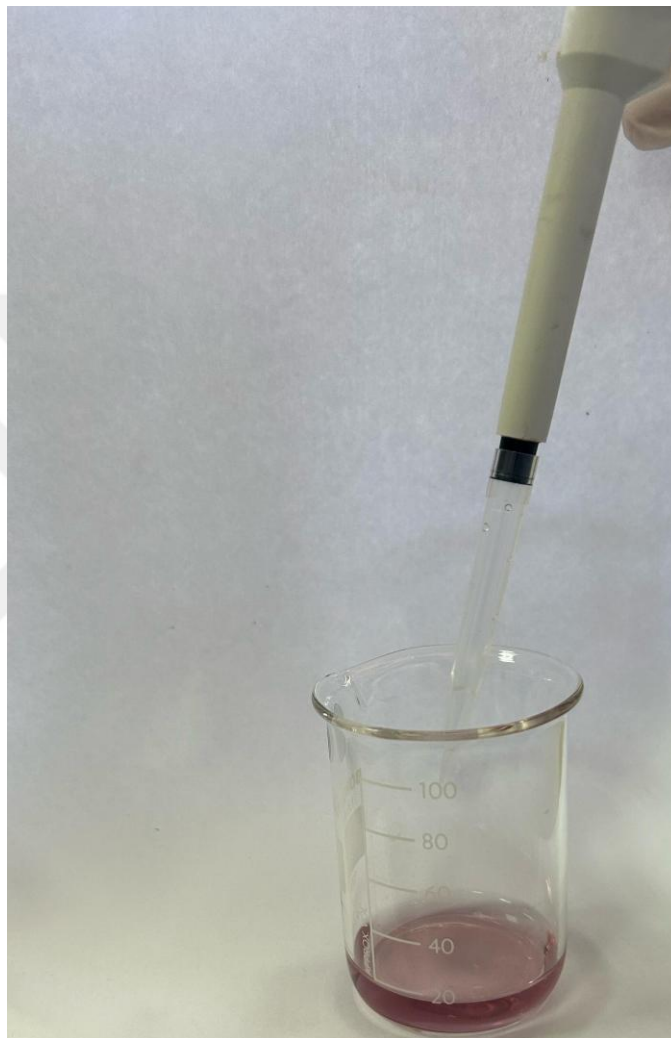


Figure 3.9:Buffer Solution Dropping to the Solution with EBT

After seeing that the indicator color is distributed homogeneously in the solution, After observing that the indicator color is homogeneously distributed in the solution, 30 μ l (i.e. 0.03 mL) of buffer solution is added to each beaker using a micropipette (as seen on Figure 3.9 above), and mixing is continued with circular movements.



Figure 3.10:The color change after the titration process

Then, the EDTA solution prepared in the beaker is transferred to a 50 ml burette and the titration process is started. The titration process is terminated when the color becomes cyan (light blue), as shown in figure 3.10 above.

3.3.1. Effect of Temperature on Pb(II) Removal

In this study, the effect of three different temperature values on lead removal was observed. Experimental sets were created at room temperature (accepted as 23°C), 40°C and 50°C, and for each of these temperatures, 0.1-gram hydrogel samples were exposed to lead solution for 10, 20, 30, 40, 50, 60 and 90 minutes. Thus, it was determined how much the composite material absorbed during these periods for each temperature.

There is a table below that provides an overview of the EDTA consumption values for each concentration at the following temperatures: 23°C, 40°C, and 50°C.

Table 3.2:EDTA Consumption values in each temperature.

Concentration (ppm)	23°C	40°C	50°C
400	1.0-1.2 mL	0.95-1.15 mL	0.8-1.0 mL
450	1.3-1.5 mL	1.05-1.2 mL	1.0-1.15 mL
500	1.35-1.5 mL	1.2-1.35 mL	1.05-1.25 mL

As the temperature rises, a notable reduction in EDTA consumption is noted. This indicates that as the temperature rises, the hydrogel's adsorption ability rises as well.

3.3.2. Impact of Contact Time on Pb(II) Removal

For this study, the impact time is arranged as 10, 20, 30, 40, 50, 60 and 90 minutes. EDTA consumption often tends to decrease as contact duration increases (between 10 and 90 minutes). This indicates that as time passes, the hydrogel adsorbs more lead ions. The same holds true for 450 parts per million. The slower rate of decline compared to 400 ppm, however, would suggest that the hydrogel is getting closer to its adsorption capacity as concentration rises.

The majority of the adsorption takes place in the first 30 to 60 minutes under all circumstances. The adsorption rate decreases and the equilibrium state is observed to be approaching after 90 minutes.

One might say that the adsorption capacity rises with increasing contact time when a fixed hydrogel amount of about 0.1 grams is employed, however saturation starts to be attained after a specific amount of time (about 60-90 minutes).

The findings suggests that, in terms of adsorption efficiency, a contact time of 60 to 90 minutes is adequate.

As a result, the contact time is an important parameter in the adsorption of lead ions with hydrogel. The first 60 minutes see the majority of the adsorption, and the system becomes

closer to equilibrium in the ninetieth minute. A contact duration of 60 to 90 minutes is advised for efficiency if process optimization is to be carried out.



4. MODELING AND OPTIMIZATION

4.1. Adsorption Kinetics

In this study, the adsorption kinetics of Pb (II) ions on AL@ZIF-8 hydrogel composites was used to investigate the time-dependent behavior of the adsorbate at different ZIF-8 loading rates (2 %, 4 % and 6 %) and different temperature settings (23 °C, 40 °C and 50 °C). This is done to determine the adsorption kinetics in different situations. Below is the mass balance equation used to determine the adsorption capacity (q_t , mg/g) based on the Pb (II) concentrations measured at specific time intervals, as described by Yu et al. (2013) [46]:

$$q_t = (C_0 - C_t) * \frac{V}{m} \quad (4.1)$$

In this equation, the initial and t-time concentrations of Pb (II) are measured in milligrams per liter (mg/L), the volume of the solution is measured in liters (L), and the quantity of adsorbent is measured in grams (g). To characterize the kinetic behavior of the adsorption system and to determine the dominant mechanisms, three different theoretical models (pseudo-first-order, pseudo-second order and Dumwald-Wagner) were applied. By integrating these models, the contributions of physical adsorption, chemical adsorption and intraparticle diffusion processes to the kinetics are systematically analyzed under specific experimental conditions. Depending on how strongly the adsorbate and substrate interact, adsorption is typically referred to as a chemisorption or physisorption process (Sims et al., 2019). Since they facilitate the bands' easy breaking, weak electrostatic interactions including London forces, dipole-dipole forces, and Van der Waals interactions encourage physisorption. Chemisorption, on the other hand, happens during the covalent bond is created by electron transferring or sharing in between the adsorbate and the substrate. Compared to physisorption, chemisorption has interactions that are two orders of magnitude greater. Adsorbate forms a monolayer on the adsorbent in chemisorption, whereas adsorbate produces a multilayer on the adsorbent in physisorption. Physisorption is reversible, has a low enthalpy, and takes place at low temperatures below the boiling point of the adsorbate. According to Singh and Kaushal (2017), chemisorption is irreversible, has a high enthalpy, and happens at all temperatures [47].

4.1.1. Pseudo-First-Order Kinetic Model

A common method for demonstrating the physico-chemical characteristics of adsorption, particularly surface adsorption at the solid-liquid interface, is the pseudo-first-order model put forth by Lagergren in 1898. The underlying assumption of this model is that the adsorption rate is precisely proportional to the difference between the capacity at a given time and the stability capacity.

According to Salvestrini (2018) [48], the differential equation of the model is

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (4.2)$$

According to Mbadcam et al. (2011) [49], the integration of this equation results in the following linearized form under the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 * t \quad (4.3)$$

The parameters of the model are determined from the slope and the intercept of the plot of $\log(q_e - q_t)$ versus t . At the molecular level, this model describes the physical adsorption processes on the adsorbent surface, as described by Simonin et al. (2016) [50]. The binding rate of adsorbate molecules to the adsorbent surface is proportional to the number of available free binding sites, and this model is valid for physical adsorption processes that require low activation energy. Pseudo-first-order kinetics characterizes physical adsorption that occurs through relatively weak interactions such as van der Waals forces, dipole-dipole interactions or hydrogen bonding.

4.1.2. Pseudo-Second-Order Kinetic Model

The kinetic pseudo-second-order model proposed by Ho and McKay (1999) [51] is used to describe chemisorption processes (chemical adsorption). According to this concept, the square of the concentration of free adsorption sites determines the adsorption rate. The differential equation is as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4.4)$$

The linearized form obtained by integration is [51]:

$$t/q_t = 1/(k_2 * q_e^2) + t/q_e \quad (4.5)$$

The parameters of this model are computed using the t/q_t versus t plot's slope and intercept. Chemisorption processes involve the formation of chemical bonds in which electrons are shared or exchanged between the adsorbate and the adsorbent. These processes usually require a high activation energy and are very sensitive to temperature.

The pseudo-second-order model describes chemical interactions at the molecular level that are defined by the exchange or transfer of electrons between the adsorbent and the adsorbate, as described by Ho and McKay (1999) [52]. The imidazolate ligands and zinc coordination centers in the ZIF-8 structure form strong chemical interactions with Pb(II) ions in AL@ZIF-8 composites. The structural properties of ZIF-8, in particular by imidazolate bridges and nitrogen-containing coordination sites. Pb(II) ions can accumulate at more active sites when the concentration of ZIF-8 increases, as there are more of these binding sites. The Zn-imidazolate bonds in ZIF-8 are susceptible to displacement processes due to the increased electropositivity of Pb(II) ions, which makes it easier for the metal ions to integrate into the structure, although the imidazolate bridges provide special binding sites with high affinity for Pb(II) ions. Above a certain concentration, however, this effect could be reversed. Excessive loading of ZIF-8 leads to agglomeration of the particles, reducing the surface area and accessibility of the binding active sites, especially in the alginate matrix.

4.1.3. Dumwald–Wagner Model

The adsorption process generally takes place in three main phases: Film diffusion (external diffusion), intraparticle diffusion and surface adsorption. The Dumwald–Wagner diffusion model analyzes whether mass transfer towards the internal structure of the adsorption particle is the rate-determining step by focusing on the intraparticle diffusion process. In the mathematical expression of this model, according to Abdul Karim et al. (2016) [53],

$$\log \left(1 - \left(\frac{q_t}{q_e} \right)^2 \right) = - \left(\frac{k}{2.303} \right) t \quad (4.6)$$

the logarithmically decreasing trend with time shows the ability of the adsorbate molecules to penetrate into the inner pores of the adsorbent. Low values for the slope (k) indicate that diffusion is slower and mass transfer is limited. Metal-organic frameworks (MOFs), such as ZIF-8, have a specific topological structure and are defined by their characteristic pore sizes. Tsai (2014) [54] claims that ZIF-8 of the SOD (sodalite) type contains pore openings with a diameter of about 3.4 Å and internal cavities with a diameter of 11.6 Å. Pb(II) ions are usually found together with the hydration sphere in aqueous solution, and the diameter of these ions is on average about 5 Å. Since this size is larger compared to the pore opening, the direct diffusion of Pb(II) ions into the pores of ZIF-8 is limited. In this case, binding to the ZIF-8 surface or to larger voids is more likely. When analyzed with the Dumwald–Wagner model, the limiting factor in this structure is the steric accessibility of the pores.

The slope values of the model decrease parallel to this difficulty of accessibility. The dispersion of ZIF-8 in a natural polymer matrix such as alginate increases the stability of the particle in aqueous systems and results in a new diffusion step being added to the system in terms of adsorption. Although the three-dimensional gel structure of alginate provides both a macroporous and ion-permeable structure, its viscosity increases at high concentrations and the movement of ions between the polymer chains can be restricted. This physical barrier creates a pre-diffusion barrier, especially for ions such as Pb(II) trying to reach the internal structures of ZIF-8. In the Dumwald–Wagner model, the low k -slope of the alginate-ZIF-8 composites suggests that such polymeric barriers limit the adsorption kinetics. This situation may be due to both the structural effects of the alginate itself and the blocking of the pores.

Adding ZIF-8 to alginate in high concentrations increases the risk of agglomeration between the particles. Agglomeration is the agglomeration of particles into large masses and the surface to volume ratio of these structures decreases. In addition, the internal pores become inaccessible because the particles stick together. These physical closures have a negative effect on both adsorption on the surface and diffusion towards the inner structure. In the Dumwald–Wagner model, this situation is described by a lower diffusion coefficient k , which indicates that the adsorption kinetics slow down significantly. The Dumwald–Wagner model not only measures the diffusion rate, but also shows which

mechanism dominates. If the value of k is high and the curve shows linearity, intraparticle diffusion processes play an important role in adsorption. Otherwise, mechanisms such as film diffusion or surface complexation may be more dominant. Coordinate binding sites on the surface of ZIF-8 can interact with Pb(II) ions. However, if these ions cannot diffuse into the inner pores, binding is limited to the surface only. In this case, the Dumwald–Wagner model allows the mechanisms to be separated by observing these constraints at the kinetic level.

4.2. Adsorption Isotherms

Isotherm models are a fundamental analytical tool to analyze the microstructural properties, the surface energy distribution, the heterogeneity of the active site and the interaction mechanisms of the adsorption system. In order to properly understand the heterogeneous nature of the adsorption process in hybrid structures such as AL@ZIF-8, different isotherm models are required. This is the only way to fully understand the mechanism.

Isotherm models provide information about the thermodynamic stability, surface morphology and molecular interaction mechanism of the system by expressing the experimental adsorption data with linear or nonlinear formulations. The isothermal parameters can be used to draw detailed conclusions about the distribution of active sites on the surface of the adsorbent, the formation of monolayers, the tendency for multilayer adsorption, the change in affinity with concentration and the limiting factors of adsorption capacity. Isothermal models are also used in the evaluation of temperature-dependent parameter changes by integrating them with thermodynamic calculations. In this way, macroscopic thermodynamic parameters such as the change in enthalpy (ΔH°), the change in entropy (ΔS°) and the change in Gibbs free energy (ΔG°) of the adsorption process can be derived from the isothermal constants, and it can be understood whether the system is under entropic or enthalpic control. In particular, the change of the isothermal constants with temperature reveals the endothermic or exothermic nature of the adsorption mechanism and provides direct information about the spontaneity of the system.

4.2.1. Langmuir Isotherm Model

The Langmuir isotherm is one of the most commonly used basic models in adsorption studies [55]. This model assumes that single-layer adsorption occurs in homogeneous active regions on the surface. The basic assumption of the model is that all adsorption regions on the adsorbent surface are energetically equal to each other and that only one adsorbent molecule can bind to each region. In addition, it is assumed that there are no horizontal (lateral) interactions between adsorbed molecules. Al-Ghouti and Da'ana (2020) [47] provided the following evidence to support this claim: Each molecule has a sorption activation energy and consistent enthalpies, indicating that adsorption is homogenous according to the Langmuir isotherm model. Adsorbate transmigration on the surface plane should be absent, and each site should have the same affinity for the adsorbate. The Langmuir hypothesis states that the intermolecular attraction forces rapidly decrease as the molecules get farther apart.

The mathematical expression for the model is:

$$q_e = q_m K_L \frac{C_e}{1 + K_L C_e} \quad (4.7)$$

Here q_e represents the amount of substance adsorbed at equilibrium; C_e represents the equilibrium concentration in the solution; q_m represents the maximum adsorption capacity and K_L represents the Langmuir constant related to the adsorption energy [56]. The conformity of Pb(II) ions to the Langmuir model in the AL@ZIF-8 hydrogel system indicates that the adsorption occurs in an energetically uniform manner at certain and specialized active centers within the ZIF-8 structure. The system's adsorption mechanism is primarily chemical (chemisorption), according to the fit to the Langmuir model, and Pb(II) ions bind exclusively to the coordination sites in the ZIF-8 structure. This binding behavior demonstrates that specific ions can interact selectively with the adsorbent's surface active spots. An indication of the binding propensity, or affinity, between the adsorbent and the adsorbate is the Langmuir constant K_L ; a high value of this constant suggests that Pb(II) ions and the AL@ZIF-8 composite have a strong interaction.

4.2.2. Freundlich Isotherm Model

The Freundlich isotherm is a widely used empirical model that was developed to explain adsorption processes that occur in particular with adsorbents with inhomogeneous surfaces [57]. This model assumes that the surface of the adsorbent consists of adsorption sites with different energy levels and that adsorption is not limited to a single layer but can also occur in a multilayer structure. The Freundlich isotherm is expressed mathematically as follows [58]:

$$q_e = K_F C_e^{1/n} \quad (4.8)$$

where;

q_e : the concentration of the adsorbate in the solid phase at equilibrium (mg/g)

K_F : Freundlich constant

$1/n$: the Freundlich exponent

The K_F constant stands for the adsorption capacity of the system, while the parameter $1/n$ is a dimensionless coefficient that reflects the heterogeneity of the surface and shows how the adsorption density changes as a function of the concentration. The agreement of Pb(II) ions in AL@ZIF-8 hydrogel composite systems with the Freundlich model shows that the active sites on the surface are not energetically equal, and the ions bind to the adsorption centers at different energy levels. This situation shows that the system has a heterogeneous adsorption character, and the adsorption mechanism is influenced by the microstructural diversity of the surface.

4.2.3. Jovanović Isotherm Model

The Jovanović isotherm was developed to explain single-layer adsorption processes and is based on some basic assumptions that differ from the Langmuir model [59]. This model assumes that the active sites are localized on the surface of the adsorbent and that there are interactions between the adsorbed species in the horizontal direction, i.e. in the lateral plane. In this respect, it offers an alternative to the assumptions of ideal homogeneity and

non-interaction of the classical Langmuir approach. The isotherm is described mathematically as follows:

$$q_e = q_m(1 - e^{(-K_J C_e)}) \quad (4.9)$$

q_m stands for the maximum adsorption capacity of the system, while the K_J constant is related to the adsorption energy and reflects the tendency of the adsorbate to bind to the surface [60]. Although the Jovanović isotherm was initially developed for gas-solid systems, it can also be successfully applied to liquid-solid phase transitions and can provide more realistic results in systems where the Langmuir model is inadequate.

The use of the Jovanović isotherm in AL@ZIF-8 composite hydrogel systems allows another aspect of the adsorption process to be understood at the molecular level. The applicability of this model draws attention to the possible lateral interactions between adsorbed Pb(II) ions and the effects of these interactions on the adsorption behavior. The magnitude of the K_J constant reveals the level of interaction energies in the system and the binding tendencies of the ions to the surface. High K_J values indicate strong adsorbent-adsorbate interactions as well as high surface affinity and energetically favorable binding conditions.

4.3. Thermodynamic Modeling

The thermodynamic investigation of adsorption processes is an important methodological tool for understanding the molecular interactions of Pb(II) ions with the surface in AL@ZIF-8 hydrogel composite systems. This study reveals not only the adsorption capacity, but also the energy transformations that occur throughout the process and the changes in disorder in the system. Thus, the extent of spontaneous adsorption, the tendency to absorb and release energy during the process and the effects of temperature changes on the adsorption mechanism can be clearly evaluated.

In this context, the applied thermodynamic modeling is performed via three basic parameters, namely the change in Gibbs free energy (ΔG°), the change in enthalpy (ΔH°) and the change in entropy (ΔS°). These parameters reflect the physico-chemical character of adsorption and play a crucial role in defining the direction, extent and nature of the interactions taking place in the system at the molecular level. In particular, the ΔG° values

indicate the spontaneity of the process; ΔH° indicates whether the process is endothermic or exothermic; ΔS° reveals the degree of disorder and the degree of molecular freedom in the system.

4.3.1. Van't Hoff Equation

One of the widely used methods for the quantitative determination of thermodynamic parameters in adsorption systems is the analytical approach based on the Van't Hoff equation. This equation defines the relationship between the thermodynamic equilibrium constant (KD) and the temperature (T) and is expressed as follows, as described by Zhukov and Karlsson (2007) [61]:

$$\ln KD = -\Delta H^\circ/RT + \Delta S^\circ/R \quad (4.10)$$

Where, the adsorption equilibrium constant (KD) is related to the standard enthalpy change (ΔH° in kJ/mol), the standard entropy change (ΔS° in J/mol K), the universal gas constant ($R = 8.314 \text{ J/mol K}$), and the absolute temperature (T in Kelvin) in a thermodynamic equation.

The KD value for the adsorption of Pb(II) ions in AL@ZIF-8 hydrogel composite systems was determined as the ratio of the adsorbed amount of Pb(II) (mg/g) to the equilibrium concentration in the solution phase (mg/L). If you use the KD values calculated at different temperatures (e.g. 296 K, 313 K and 323 K), you can obtain a linear graph by placing the $\ln KD$ values on the y-axis and the $1/T$ values on the x-axis. The slope of this diagram gives the value $-\Delta H^\circ/R$, while the y-axis intercept gives the value $\Delta S^\circ/R$. In this way, the enthalpy and entropy changes of the adsorption process can be calculated directly from the experimental data. Using the obtained ΔH° and ΔS° values, the change in Gibbs free energy (ΔG°) of the adsorption process can be calculated using the following classical thermodynamic equation, according to Linford et al. (2012) [62]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4.11)$$

Zhukov and Karlsson claim that (2007) [61] alternatively, the ΔG° value can also be determined directly from the equilibrium constant:

$$\Delta G^\circ = -RT \ln KD \quad (4.12)$$

The ΔG° values calculated at different temperatures indicate whether adsorption occurs spontaneously or not and how this spontaneous behavior changes depending on the temperature.

4.4. ANFIS Model

ANFIS will be used to model the Pb(II) interaction in wastewater of the AL@ZIF-8 hydrogel material developed within the scope of this master's thesis. Changes in Pb(II) ion removal capacities of AL@ZIF-8 composite material is depending on composite composition, composite (adsorbent) amount, temperature, and time will be examined using ANFIS. The ANFIS structure provides a structured model for managing and analyzing uncertain or imprecise data, but this model needs to be optimized for the best parameters. Therefore, within the scope of this study, the parameters of the fuzzy membership function within the FIS structure will be iteratively optimized using a genetic algorithm to increase the capacity to handle data complexities. The ANFIS architecture aims to achieve learning from input data by working simultaneously with the Artificial Neural Network (ANN) and FIS for changes in the removal of Pb(II) ions. This process creates a set of fuzzy rules based on interpreting input data and predicting changes in the resulting heavy metal removal capacity [63]. The Takagi-Sugeno inference methodology will also be integrated within the ANFIS framework. [63] This integration will facilitate the system to formulate derived fuzzy rules by mapping inputs (composite composition, composite (adsorbent) amount, temperature, and time) to outputs (heavy metal removal capacity).

ANFIS structure consists of five main layers: input layer, blurring layer, normalization layer, layer containing adaptive nodes, and output layer. These layers provide an architectural representation that describes how input data is handled and how changes in heavy metal removal capacity are predicted. [44] In the project, it is planned to use the ANFIS artificial intelligence approach optimized with a genetic algorithm, providing a way to better understand and improve the selectivity of Pb(II) ions of the AL@ZIF-8 composite.

The ANFIS structure starts with an input layer containing 'n' nodes, called Layer 0. 'n' represents the total number of inputs that can be processed by the system. The layer following the input layer is the blurring layer or called Layer 1. Each node in this layer is used to assign a membership value to a particular fuzzy variable represented by a Gaussian function. This function derives its meaning from the adjustable parameters a_i , b_i and c_i . During the learning process, these parameters are changed through a backpropagation algorithm, and as a result, the membership function value of the term of the blurring variable A_i is improved [64].

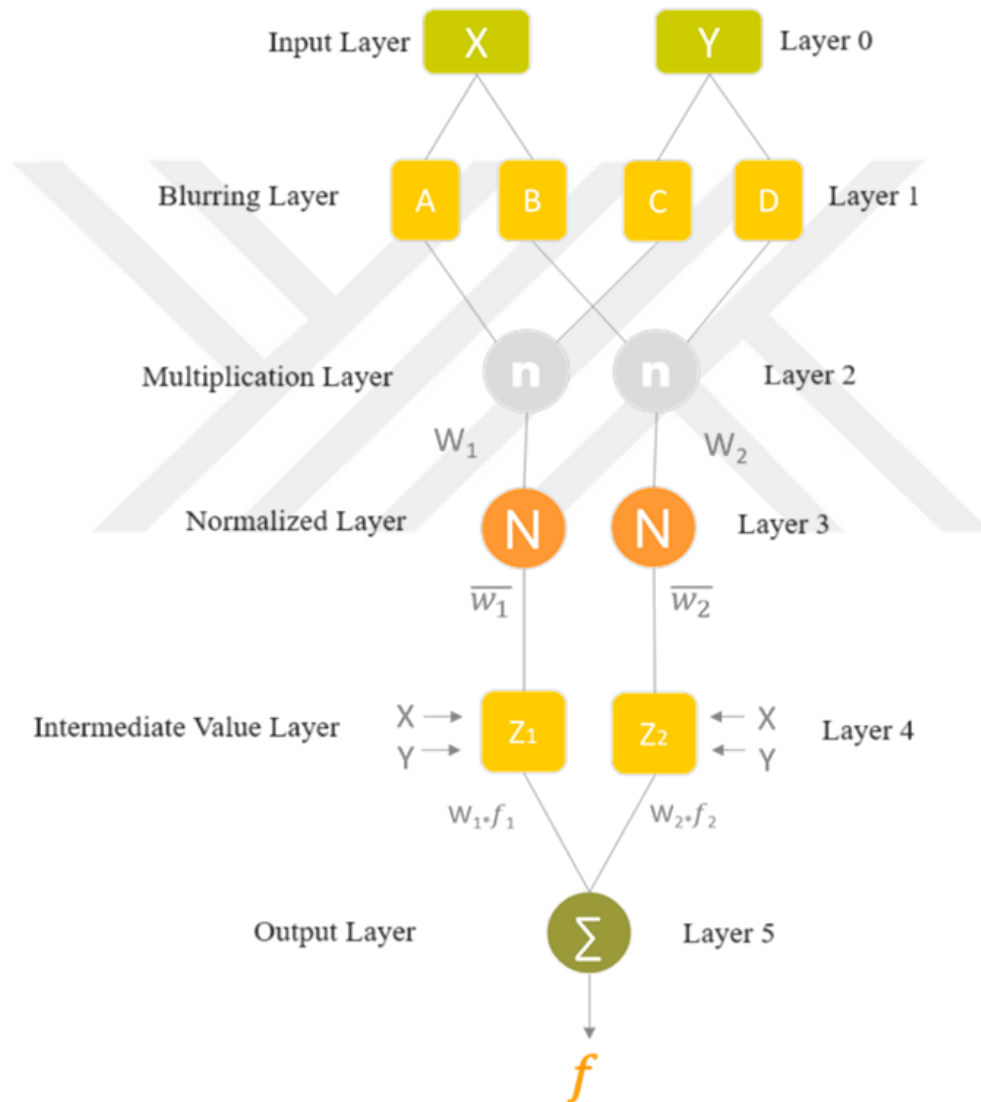


Figure 4.1:The ANFIS Model

The next layer in the network structure is layer 2. 'wi' characterizes the degree of participation of the rule specified by 'i', which is initially calculated in Layer 2. In this layer, each node calculates the ratio of the firing power of ith rule to the sum of the firing powers of all rules. The impact of each rule is calculated using a multiply or/and operation in this layer. The degree of participation of the rule is determined by multiplying the membership values represented by $\mu_{Ai}(x_0)$ and $\mu_{Bi}(x_1)$. x_0 and x_1 have the semantic values of A_i and B_i , respectively. This layer contains pn nodes, and each node symbolizes a unique rule. Here 'n' refers to the total number of input variables and 'p' refers to the total number of membership functions. The structure following this layer is layer 3 or normalization layer. Its main function is to organize the density of all rules in a mathematical formulation [64].

Layer 4 contains adaptive nodes. In this layer, a linear function is calculated at each node and the coefficients are replaced by the error function of the multilayer feedforward neural network. The π_i parameters updated during the learning phase are where i equals $n + 1$ and n refers to the total number of system inputs. The output layer is layer 5, the final component of the structure. This works by adding together the Layer 4 nodes' net outputs. The output is obtained using an equation in which the result part of Rule i is represented by the output of each node i in Layer 4. The aggregate of the outcomes of these rules yields the overall output of the neuro-fuzzy system inside the ANFIS structure.[64]

Membership functions enable the representation of inputs as fuzzy sets in the ANFIS model. The Gaussian function (gaussmf) chosen for C_0 has smooth transitions, but has only minimal effects on the model, as C_0 assumes a fixed value.

The generalized bell curve function (gbellmf) chosen for the temperature variable T ($^{\circ}\text{C}$) is particularly important as temperature often has non-linear effects on chemical and physical processes. The three-parameter structure of gbellmf (center, width and slope) is ideal for modeling the sensitivity of temperature over different ranges. The negative correlation of T with m of -0.38 shows that temperature influences mass transfer mechanisms. The reason for choosing gbellmf for the temperature variable is that the behavior of the system can differ below and above a certain threshold temperature and gbellmf can model these transitions with smooth curves. The trimf function facilitates abrupt membership transitions at designated time intervals, making it suitable for representing crucial thresholds in temporal processes. The selected trapezoidal

membership function (trapmf) for the mass variable m (g) features a flat top section that yields complete membership values within a specified range.

4.5. Modelling

In this study, Adaptive Network-Based Fuzzy Inference System (ANFIS) was used to model the multidimensional, nonlinear relationship between experimental inputs and a quantitative output variable. The modeling process was carried out with a multi-stage artificial intelligence computing architecture extending from data preparation, statistical feature extraction, variable importance analysis, data normalization, hyperparameter optimization, training of both inferential and grid-based FIS structures, ensemble modeling and structure analysis of the best model. Data normalization was performed with a robust statistics-based approach instead of traditional min-max or z-score standardization methods. A scaling independent of weak distribution assumptions was performed using median and interquartile range (IQR) for each feature. This process was preferred in order to minimize the damage of extreme values to the learning process in model training. After normalization, the scale unity of the inputs was ensured, and membership function parameterization and trainability of the model were optimized.

Correlation-based analysis was applied in feature selection, and the Pearson correlation coefficient between each independent variable and the target variable was calculated. The obtained correlation values were both visually presented with a bar chart and used as a reference in deriving variable importance weights. With the variance-based analysis, the information contribution rates of the variables were determined, and instead of eliminating low-variance features, they were balanced with the number of membership functions. The modeling process was based on two-stage FIS creation approaches: (1) Subtractive Clustering and (2) Grid Partitioning. Subtractive clustering transformed the feature vectors into cluster centers depending on the density distribution on the data space, and transformed these centers into Gaussian-like membership functions. The kernel influence radius (`ClusterInfluenceRange``) variability was selected between 0.3 and 0.5, and a model was derived for each radius value. The outputs of these models; training and test root mean square error (RMSE) and coefficients of determination (R^2) were evaluated.

In grid-based approaches, the model was structured with predefined membership function (MF) types (gaussmf, gbellmf, trapmf, trimf) and MF number combinations. MF numbers were determined dynamically according to variable importance levels; for example, by defining more MFs for a variable with high correlation, the input space was segmented with higher resolution. This approach increases the discrimination power of the model in the feature space and allows it to make more precise inferences. The model hyperparameters, namely training epoch number, learning rate (`StepSize`), learning rate reduction factor (`StepSizeDecreaseFactor`), were tested with different combinations. The combinations were cross-matched with each MF type and number combination, the ANFIS model was trained for each configuration, and the resulting accuracy and error metrics were recorded. During training, an early stopping mechanism was also integrated using the validation set.

In the ensemble modeling process, models that exceed a certain success threshold in the test set were selected and the outputs of these models were combined with weights inversely proportional to RMSE. This approach aimed to produce a prediction output with lower variance by reducing the random components in the errors of individual models. The final model decision was made according to the general success criteria by comparing the test success of each individual model with the success of the ensemble model. The membership function structure (type, parameters), inference rules (rule base), surface responses and sensitivity analyses of the best performing model were visualized in detail. As a result of these analyses, the response of the model in the feature space, optimum decision regions and stability ranges of the system were determined.

5. RESULTS AND DISCUSSION

In this section, the performance of AL@ZIF-8 composite hydrogel in the removal of Pb(II) was discussed in detail in light of the experimental data and the modeling results supported by artificial intelligence. The effects of different ZIF-8 loading rates, temperature conditions and initial Pb(II) concentrations on the adsorption kinetics and thermodynamic parameters were investigated, revealing that the adsorption mechanism is characterized by both surface chemical reactions and diffusion processes based on mass transfer. The ANFIS model was used as an approach for artificial intelligence. In order to train the AI model, experimental data from the adsorption process of Pb(II) ions using the AL@ZIF-8 composite was carefully selected. Comprehensive kinetic and thermodynamic evaluations led the selection process to improve the model's prediction capabilities and dependability while also accurately representing the adsorption properties.

5.1. Correlation Model for Pb(II) Removal by AL@ZIF-8

To accurately measure the Pb (II) removal performance of AL@ZIF-8 hydrogel composites, a reliable correlation equation was developed based on the complexometric titration of the amount of Pb (II) in pure water. The complexometric titration was carefully designed to ensure high accuracy and reproducibility. A key aspect of this experimental procedure was the precise preparation of the reagent solutions, including the indicator solution, the buffer solution and the titration solution.

To establish the correlation model, Pb (II) nitrate solutions were systematically prepared at concentrations of 1000 ppm, 800 ppm, 600 ppm, 400 ppm and 200 ppm. Each solution was prepared by dissolving certain amounts of lead (II) nitrate calculated according to its molar mass (331.2 g/mol) and the corresponding lead ion content (207.21 g/mol). As indicated in Table 5.1, for example, exactly 0.1656 g of lead (II) nitrate was dissolved in 100 ml of pure water to obtain a 1000 ppm lead ion solution. This precision ensured an accurate representation of the theoretical Pb (II) content, which is crucial for reliable correlation data.

Table 5.1: Pb (II) Concentrations and Corresponding EDTA Consumption

Lead (II) Nitrate Amount Exp.(g)	Pb(II) Concentration (ppm)	Trial No.	EDTA (mL)
0,1662	996.426	1	2,5
		2	2,6
		3	2,6
		4	2,75
		5	2,65
		6	2,7
		7	2,7
		8	2,6
		9	2,65
		10	2,65
0,1333	795.108	1	2,35
		2	2,25
		3	2,25
		4	2,25
		5	2,2
		6	2,2
		7	2,2
		8	2,25
		9	2,25
		10	2,25
0,0997	597.976	1	1,6
		2	1,75
		3	1,75
		4	1,65
		5	1,8
		6	1,6
		7	1,7
		8	1,7
		9	1,75
		10	1,75
0,0662	400.256	1	1,25
		2	1,25
		3	1,2
		4	1,25
		5	1,25
		6	1,25
		7	1,2
		8	1,25
		9	1,3
		10	1,25
0,0332	199.525	1	0,5
		2	0,5
		3	0,5
		4	0,5
		5	0,5
		6	0,5
		7	0,5
		8	0,55
		9	0,6
		10	0,55

The table above shows the titration experiment data for lead removal experiments. Indicator, buffer solution and EDTA solution were used in titration experiments. EBT (Eriochrome Black T) was prepared as indicator, Ammonium Chloride and Ammonia solution in pure water was prepared as buffer solution, and EDTA (Ethylene Diamine Tetraacetic Acid) solution was prepared for use in the titration process. The buffer solution was formed by adding 3.4 grams of ammonium chloride and 28.5 ml of ammonia to 100 ml of pure water. EDTA solution was formed by adding 1.86 grams of EDTA to 250 ml of pure water. EBT was used as 5 drops for each experiment. EBT solution was obtained by mixing 0.1 gram of EBT with 1 ml of ethanol in 100 ml of pure water.

Each experiment set in this table consists of 10 pieces and lead (II) nitrate was used in each experiment. First, lead (II) nitrate aqueous solutions are prepared. For lead (II) nitrate aqueous solutions, lead (II) nitrate is weighed as 1000ppm, 800ppm, 600ppm, 400ppm and 200ppm, respectively, and the solution is prepared with 100 mL of pure water. The relevant amounts are selected according to the amount of lead in this solution. The ionization equation of the lead (II) nitrate solution is as follows [65]:



According to this equation, 1 mole of lead ion is obtained from 1 mole of lead nitrate solution. Since the molecular weight of lead (II) nitrate is 331.2 g/mol and the molecular weight of lead is 207.21 g/mol, 0.1656 g of lead (II) nitrate will contain 0.1036 g of lead, when 0.1656 g of lead (II) nitrate is added to 100 ml of water, a 1000 ppm lead solution is obtained.

Experiments are also conducted for 800, 600, 400, and 200 ppm, respectively, and the amount of EDTA consumed is determined as a result of titration. The average of the consumption values obtained for these five different ppm values is found. The graph showing the lead consumption correlation curve is as follows:

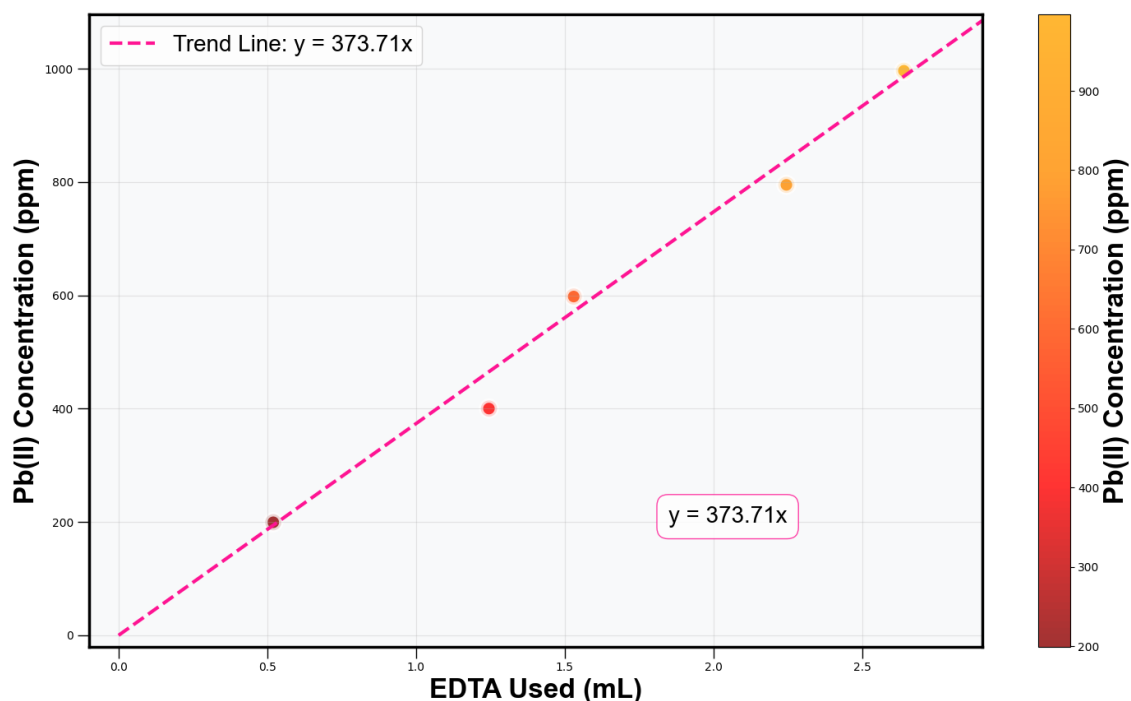


Figure 5.1:The Lead Consumption Correlation Curve

The average consumption value calculated for each experiment in these 5 different experimental sets is shown on the x-axis in the graph. The averages of the amounts used for each experiment are; 2.64, 2.245, 1.705, 1.245, and 0.52 mL, respectively. Since it is not easy to calculate the theoretical and experimental weights one-to-one, the calculated experimental data were multiplied by 1000, 800, 600, 400, and 200 ppm, respectively, after being proportioned to the theoretical data, the experimental ppm values were calculated, which is also the verification of these experiments, and these values are shown on the y-axis. These values were calculated as 996.4, 795.1, 597.97, 400.26, and 199.52 ppm as a result of the operations $1000 \times (0.1656/0.1662)$, $800 \times (0.1324848/0.1333)$, $600 \times (0.0994/0.0997)$, $400 \times (0.06624/0.0662)$ and $200 \times (0.03312/0.0332)$, respectively. This graph shows how consistent and with little error the correlation curve of the consumption in the study and the amount of lead used in the experiment was obtained.

5.2. Baseline Experiments

Metal-organic framework (MOF) structured composite hydrogels cause consumption in EDTA titration even when interacting with pure water containing no Pb(II). This situation is due to the dynamic physicochemical interactions exhibited by AL@ZIF-8 in aqueous

medium. The zinc ions (Zn^{2+}) in the ZIF-8 structure are separated from the framework structure under certain conditions in aqueous medium and pass into the solution. This metal ion release varies depending on factors such as the pH value of the water, the ionic strength and the interaction time. Zn^{2+} ions that pass into solution, like Pb(II) ions, form stable complexes with EDTA in the presence of EBT indicator and cause a color change during titration. The structural stability of ZIF-8 is an important, critical parameter in aqueous media. The coordination bonds between organic linkers, which consist of imidazole rings and zinc metal centers, are particularly sensitive to pH changes. As a result of hydrolysis reactions, partial degradation of the framework structure can occur and both zinc ions and organic ligands are released into the solution. Even when immobilized in polymer matrices such as alginate, the high surface/volume ratio of the nanoscale ZIF-8 particles accelerates these hydrolysis reactions. As the amount of composite material increases, the concentration of these chemical species released into the solution also increases, resulting in increased EDTA consumption.

The polymeric components in the hydrogel composite structure itself also have the ability to complex metal ions. Alginate is a polysaccharide that contains carboxyl groups, and these groups interact with divalent metal ions. The cross-linking metal ions (usually Ca^{2+}) used in the formation of the hydrogel network can be partially released into the aqueous environment and are released into the environment through the ion exchange mechanism. In addition, the carboxyl groups in the alginate chains change the pH of the medium due to protonation/deprotonation equilibria, which affects the stability of ZIF-8 and the kinetics of metal ion release.

Ion exchange mechanisms also play an important role in this phenomenon. During the synthesis and storage of the composite material, various metal ions or other cationic species in its structure pass into solution according to the principles of ion exchange when they come into contact with pure water. In particular, the fact that the reagents used in the synthesis of the ZIF-8 structure were not completely removed or the presence of metal ions used to crosslink the alginate gel prepares the ground for such ion exchange reactions. In addition, various ions trapped in the micro/nanopores of the composite structure enter the solution by diffusion over time and cause consumption during EDTA titration. Therefore, even if Pb(II) is not added from the beginning, it causes an unexpected

consumption in the EDTA titration. For a correct calculation of the adsorption capacity, it is therefore mandatory to obtain initial values prepared with different amounts of composite material in order to obtain scientifically accurate results. This approach makes it possible to distinguish the EDTA consumption resulting from the composite material from the consumption resulting from the actual Pb(II) adsorption. When evaluating the influence of the AL@ZIF-8 composite on Pb(II) adsorption, it is crucial to refer to the basic diagram shown in Figure 5.2. The presence of the composite material as an adsorbent interferes with the EDTA titration as quantitatively shown in this diagram. The baseline study confirms the existence of components that pass from the composite material into the solution and interact with EDTA in the complexometric titration, and characterizes the change in these effects over time.

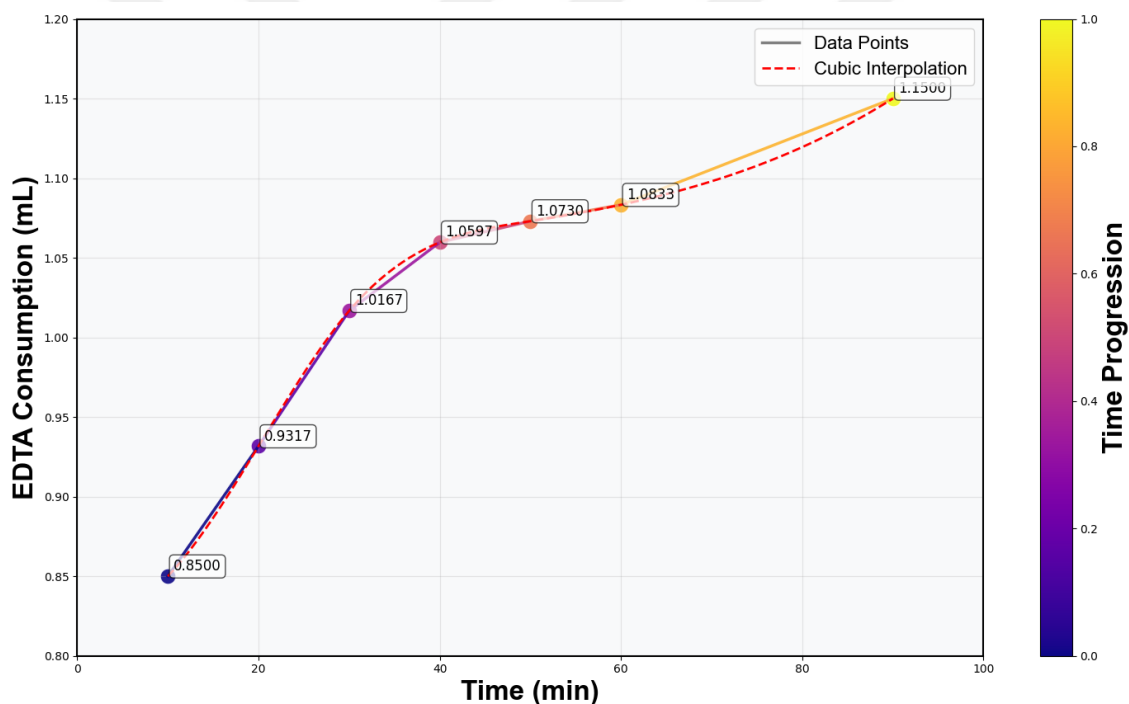


Figure 5.2: Baseline Values of EDTA consumption of AL@ZIF-8 composite before Pb(II) adsorption

In the experimental studies conducted to determine the baseline, 0.1 grams of AL@ZIF-8 composite material was suspended in 50 ml of deionized water and complexometric titrations were performed at different contact times (10, 20, 30, 40, 50, 60 and 90 minutes). At each time point, titration was performed with a standardized EDTA solution

and the indicator EBT (Eriochrome Black T). The variation of the obtained titration consumption with time reflects the kinetic profile of the ions released from the composite material to the medium. The accuracy of the experimental data and the interpolation of the titration curve were achieved using the cubic interpolation method. With this mathematical approach, the EDTA consumption at intermediate time points could be estimated with high accuracy.

5.3. Adsorption Efficiency of Lead Ions on AL@ZIF-8

The effectiveness of the AL@ZIF-8 composite in eliminating Pb(II) ions from aqueous solutions was methodically investigated under various experimental conditions. Table 5.2 shows remarkable differences in the removal of lead ions as a function of ZIF-8 concentration (2%, 4% and 6%), temperature (23°C, 40°C and 50°C) and contact time (10-90 minutes).

Table 5.2: Pb(II) ion adsorption performance of AL@ZIF-8 composite material at different ZIF-8 ratios, temperature and contact time conditions

Lead Amount (PPM)	ZIF-8 Amount (%)	T (°C)	Composite Amount (g)	t(min)	Lead Amount (mg/L)
400	2	23	0,1003	10	244,58
400	2	23	0,1004	20	171,8173277
400	2	23	0,1007	30	67,25937771
400	2	23	0,1003	40	241,0273269
400	2	23	0,1004	50	83,27649728
400	2	23	0,1001	60	0
400	2	23	0,1005	90	0

Table 5.2 continued

400	4	23	0,1004	10	79,4885
400	4	23	0,1002	20	129,0158277
400	4	23	0,1006	30	67,25937771
400	4	23	0,1003	40	45,36332688
400	4	23	0,0999	50	34,36049728
400	4	23	0,0997	60	61,14512229
400	4	23	0,1008	90	0
400	6	23	0,1	10	79,4885
400	6	23	0,1001	20	25,06932771
400	6	23	0,1007	30	0
400	6	23	0,1007	40	0
400	6	23	0,1002	50	0
400	6	23	0,1006	60	30,57262229
400	6	23	0,0998	90	0
400	2	40	0,1003	10	128,4045
400	2	40	0,0996	20	73,98532771
400	2	40	0,101	30	33,01817771
400	2	40	0,0995	40	14,79082688

Table 5.2 continued

400	2	40	0,0997	50	22,13149728
400	2	40	0,099	60	0
400	2	40	0,0998	90	0
400	4	40	0,1005	10	85,603
400	4	40	0,0999	20	18,95482771
400	4	40	0,0998	30	0
400	4	40	0,0994	40	0
400	4	40	0,0993	50	0
400	4	40	0,101	60	0
400	4	40	0,1008	90	12,229
400	6	40	0,0995	10	152,8625
400	6	40	0,1003	20	6,72582771
400	6	40	0,1002	30	30,57237771
400	6	40	0,1004	40	0
400	6	40	0,1004	50	52,70399728
400	6	40	0,1002	60	0
400	6	40	0,0999	90	0
400	2	50	0,1003	10	122,29

Table 5.2 continued

400	2	50	0,1	20	73,98532771
400	2	50	0,1	30	0
400	2	50	0,1003	40	0
400	2	50	0,1001	50	0
400	2	50	0,0997	60	0
400	2	50	0,0999	90	0
400	4	50	0,1002	10	0
400	4	50	0,0995	20	98,44332771
400	4	50	0,1004	30	48,91587771
400	4	50	0,1	40	0
400	4	50	0,1004	50	22,13149728
400	4	50	0,0997	60	12,22912229
400	4	50	0,1007	90	0
400	6	50	0,1003	10	140,6335
400	6	50	0,0998	20	104,5578277
400	6	50	0,0995	30	0
400	6	50	0,0995	40	0
400	6	50	0,1	50	0

Table 5.2 continued

400	6	50	0,1001	60	0
400	6	50	0,1003	90	0
450	2	23	0,1001	10	214,0075
450	2	23	0,1004	20	184,0463277
450	2	23	0,1006	30	158,9768777
450	2	23	0,1005	40	161,5388269
450	2	23	0,1001	50	40,47499728
450	2	23	0,1	60	122,2901223
450	2	23	0,0995	90	24,458
450	2	23	0,1004	120	42,80137771
450	2	23	0,1005	140	0
450	2	23	0,1005	180	0
450	2	23	0,1009	220	0
450	2	23	0,0998	240	0
450	4	23	0,1002	10	122,29
450	4	23	0,0998	20	55,64182771
450	4	23	0,0995	30	24,45787771
450	4	23	0,1004	40	20,90532688

Table 5.2 continued

450	4	23	0,1004	50	132,1924973
450	4	23	0,1004	60	158,9771223
450	4	23	0,1005	90	48,916
450	4	23	0,0996	120	24,45787771
450	4	23	0,101	140	0
450	4	23	0,0997	180	0
450	4	23	0,1008	220	0
450	4	23	0,0995	240	0
450	6	23	0,0998	10	220,122
450	6	23	0,1002	20	226,8478277
450	6	23	0,1008	30	214,0073777
450	6	23	0,101	40	88,16482688
450	6	23	0,1006	50	144,4214973
450	6	23	0,1009	60	146,7481223
450	6	23	0,0993	90	0
450	6	23	0,1003	120	42,80137771
450	6	23	0,101	140	0
450	6	23	0,1009	180	0

Table 5.2 continued

450	6	23	0,1	220	0
450	6	23	0,0997	240	18,34362229
450	2	40	0,0995	10	214,0075
450	2	40	0,1006	20	57,67999438
450	2	40	0,1002	30	14,26704438
450	2	40	0,1001	40	0
450	2	40	0,1001	50	0
450	2	40	0,1001	60	0
450	2	40	0,0999	90	0
450	4	40	0,1005	10	122,29
450	4	40	0,1006	20	92,32882771
450	4	40	0,0999	30	158,9768777
450	4	40	0,0999	40	75,93582688
450	4	40	0,1005	50	28,24599728
450	4	40	0,1007	60	36,68712229
450	4	40	0,1004	90	0
450	6	40	0,0996	10	103,9465
450	6	40	0,0999	20	67,87082771

Table 5.2 continued

450	6	40	0,1002	30	36,68687771
450	6	40	0,1003	40	0
450	6	40	0,0999	50	0
450	6	40	0,1005	60	30,57262229
450	6	40	0,1	90	18,3435
450	2	50	0,1001	10	110,061
450	2	50	0,0995	20	104,5578277
450	2	50	0,1002	30	61,14487771
450	2	50	0,0995	40	14,79082688
450	2	50	0,0996	50	0
450	2	50	0,1002	60	0
450	2	50	0,1005	90	0
450	4	50	0,1001	10	116,1755
450	4	50	0,0997	20	92,32882771
450	4	50	0,1004	30	103,9463777
450	4	50	0,0999	40	45,36332688
450	4	50	0,1002	50	0
450	4	50	0,1	60	0

Table 5.2 continued

450	4	50	0,1001	90	0
450	6	50	0,1	10	85,603
450	6	50	0,1003	20	147,3593277
450	6	50	0,1005	30	116,1753777
450	6	50	0,0996	40	39,24882688
450	6	50	0,1	50	40,47499728
450	6	50	0,0998	60	0,00012229
450	6	50	0,1	90	0
500	2	23	0,0999	10	201,7785
500	2	23	0,1001	20	171,8173277
500	2	23	0,1005	30	128,4043777
500	2	23	0,1003	40	118,7373269
500	2	23	0,1	50	138,3069973
500	2	23	0,1001	60	91,71762229
500	2	23	0,1006	90	30,5725
500	4	23	0,1001	10	177,3205
500	4	23	0,1004	20	159,5883277
500	4	23	0,1003	30	165,0913777

Table 5.2 continued

500	4	23	0,1	40	118,7373269
500	4	23	0,1004	50	73,08566395
500	4	23	0,1007	60	59,10695562
500	4	23	0,1009	90	36,687
500	6	23	0,0998	10	220,122
500	6	23	0,1004	20	196,2753277
500	6	23	0,1005	30	158,9768777
500	6	23	0,1008	40	106,5083269
500	6	23	0,1009	50	71,04749728
500	6	23	0,0998	60	36,68712229
500	6	23	0,0999	90	30,5725
500	2	40	0,1004	10	152,8625
500	2	40	0,1	20	116,7868277
500	2	40	0,1003	30	73,37387771
500	2	40	0,1005	40	45,36332688
500	2	40	0,1003	50	64,93299728
500	2	40	0,1004	60	61,14512229
500	2	40	0,1002	90	30,5725

Table 5.2 continued

500	4	40	0,0998	10	134,519
500	4	40	0,1006	20	110,6723277
500	4	40	0,1009	30	85,60287771
500	4	40	0,1001	40	63,70682688
500	4	40	0,0998	50	52,70399728
500	4	40	0,1002	60	48,91612229
500	4	40	0,1007	90	42,8015
500	6	40	0,1009	10	146,748
500	6	40	0,1005	20	116,7868277
500	6	40	0,0995	30	85,60287771
500	6	40	0,1	40	39,24882688
500	6	40	0,1007	50	22,13149728
500	6	40	0,1003	60	0
500	6	40	0,1004	90	36,687
500	2	50	0,0995	10	134,519
500	2	50	0,1	20	129,0158277
500	2	50	0,1003	30	134,5188777
500	2	50	0,0997	40	8,676326876

Table 5.2 continued

500	2	50	0,0995	50	46,58949728
500	2	50	0,1005	60	18,34362229
500	2	50	0,1004	90	18,3435
500	4	50	0,0995	10	146,748
500	4	50	0,1004	20	122,9013277
500	4	50	0,0995	30	48,91587771
500	4	50	0,0999	40	20,90532688
500	4	50	0,0996	50	22,13149728
500	4	50	0,0998	60	36,68712229
500	4	50	0,0996	90	36,687
500	6	50	0,1004	10	158,977
500	6	50	0,1001	20	190,1608277
500	6	50	0,1	30	152,8623777
500	6	50	0,0995	40	94,27932688
500	6	50	0,1003	50	83,27649728
500	6	50	0,0995	60	42,80162229
500	6	50	0,0998	90	55,0305

At an initial lead concentration of 400 mg/L, the composite containing 2% ZIF-8 provided complete removal in 60 minutes, while the composite containing 6% ZIF-8 showed the same effect in only 30 minutes. This shows that the composite containing 6% ZIF-8 has an average increase in adsorption capacity of 100. This significant improvement in adsorption efficiency can be explained by the fact that the higher ZIF-8 content in the composite matrix provides more active centers and pore spaces to which lead ions can bind. When investigating the effect of temperature on adsorption kinetics, it was found that the removal time decreased from 60 minutes to 40 minutes, especially for composites containing 2% ZIF-8, when the temperature was increased from 23°C to 40°C. This corresponds to an increase in adsorption efficiency. This corresponds to an increase in the adsorption rate of about 33. The increase in the kinetic energy of the ions with the increase in temperature increases the diffusion rate into the pores of the composite and facilitates the access of the lead ions to the active sites. At 50°C, the time of complete removal decreased to 30 minutes for the composite with 2% ZIF-8. From a thermodynamic perspective, this result demonstrates that adsorption becomes more advantageous at higher temperatures and validates the endothermic nature of the adsorption process.

When the lead concentration was increased to 450 mg/L, significant changes in the adsorption dynamics were observed. Composites containing 2% ZIF-8 provided complete removal in 140 minutes at 23°C, while this period was set at 140 minutes for composites containing 4% ZIF-8 and 90 minutes at the same temperature for composites containing 6% ZIF-8. This 12.5% increase in the concentration at the beginning increased the adsorption time by 2.33 times. This situation can be explained by the faster saturation of the active sites and the increase in diffusion barriers at high concentrations. At 40°C and 50°C, the composites generally showed faster adsorption, especially the composites containing 6% ZIF-8 reduced the lead concentration to 18.3435 mg/L in 90 minutes at 40°C (approximately 96% removal efficiency).

At the highest test concentration of 500 mg/L, no composite material could be completely removed within the test period. The lowest residual lead concentrations were measured at 18.3435 mg/L (after 90 minutes) for the composite with 2% ZIF-8 at 50°C and 30.5725 mg/L (after 90 minutes) for the composite with 6% ZIF-8 at 23°C. These results correspond to removal efficiencies of 96.3% and 93.9% respectively.

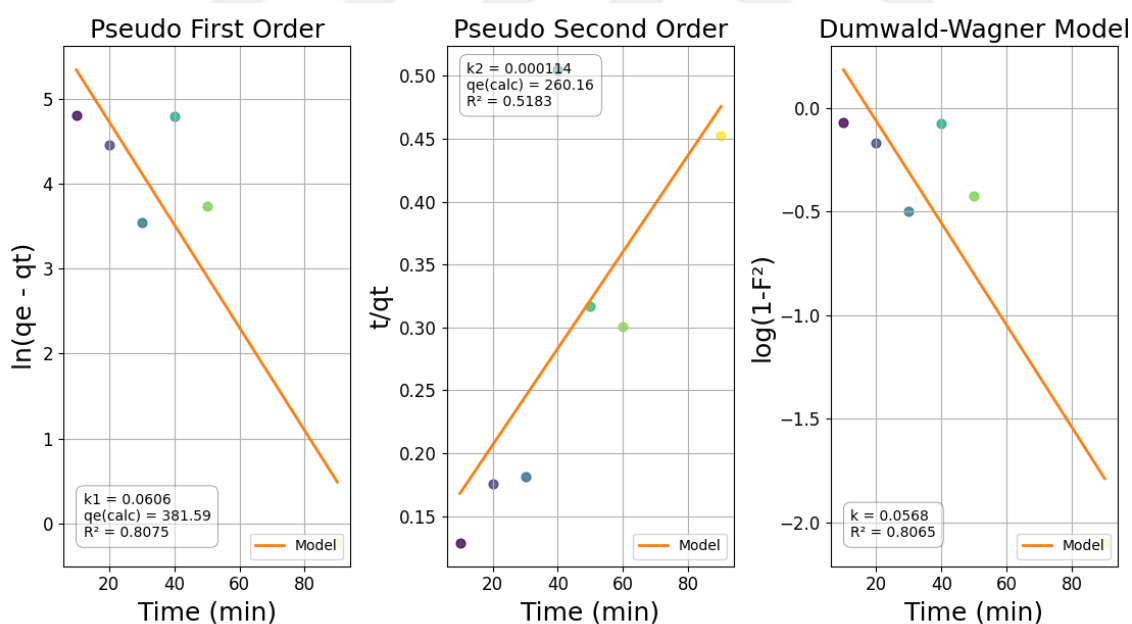
The adsorption effect of the AL@ZIF-8 composite can be explained by many physicochemical processes. The imidazolate ligands and the zinc(II) centers in the ZIF-8 structure tend to establish robust coordination interactions with lead ions. The carboxyl groups in the alginate matrix can form chelates with lead ions. With increasing temperature, both the swelling of the composite matrix and the diffusion coefficient of the lead ions increase. As the ZIF-8 concentration increases, the porosity and the specific surface area in the composite structure also increase, making more active adsorption centers available. As the adsorption time increases, the lead ions diffuse into deeper pores, maximizing the adsorption capacity. From the interaction of all these factors, it can be concluded that the AL@ZIF-8 composite material exhibits optimal adsorption performance, especially with a 6% ZIF-8 loading at 40°C and 60 minutes or longer contact times.

5.4. Kinetic Studies

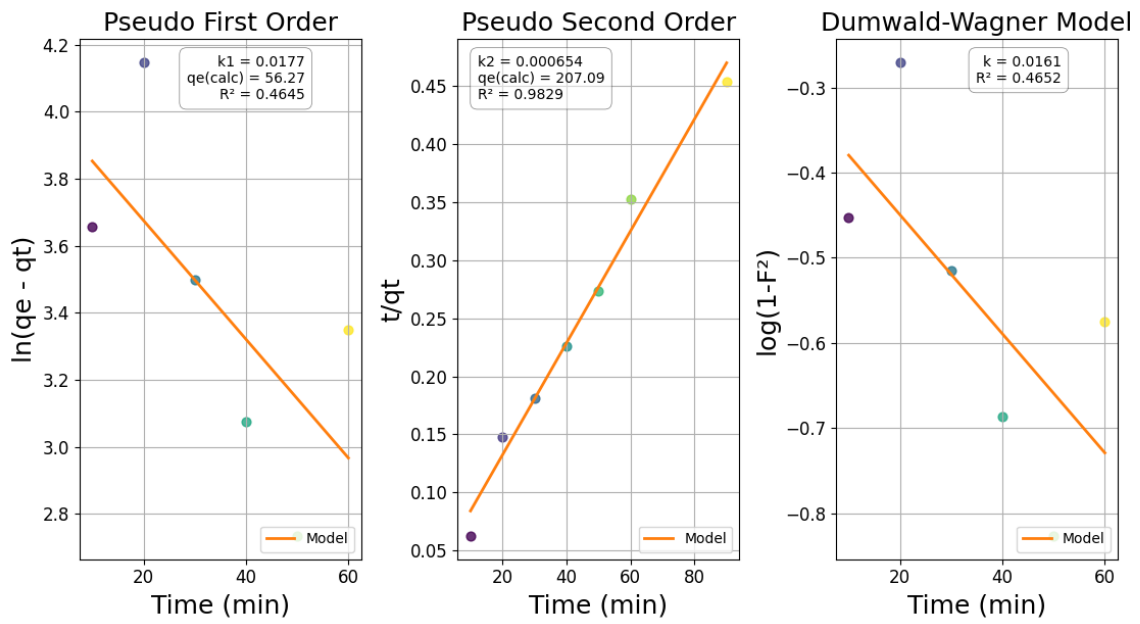
5.4.1. Kinetic Analysis of Pb(II) Adsorption on AL@ZIF-8 at 400 mg/L: Effects of Temperature and ZIF-8 Loading Ratio

The kinetic analyses performed to determine the adsorption mechanism of Pb(II) ions on AL@ZIF-8 hydrogel composites clearly show the effects of different ZIF-8 loading rates (a) 2%, (b) 4% and (c) 6%) on the adsorption behaviour. As can be seen in **Figure 5.3.**, it was observed that the adsorption process at a low ZIF-8 loading rate (2%) agrees better with the pseudo-first order kinetic model ($R^2 = 0.8075$) and the Dumwald-Wagner diffusion model ($R^2 = 0.8065$). This indicates that adsorption at low ZIF-8 concentration is controlled by both chemical reactions and intraparticle diffusion. The higher calculated k_1 value (0.0606 min^{-1}) compared to other loading rates proves that the adsorption reactions at the surface are faster at low ZIF-8 rates. However, the equilibrium adsorption capacity calculated using the pseudo-second order model ($q_e = 260.16 \text{ mg/g}$) showed a lower correlation coefficient ($R^2 = 0.5183$) than other models. Upon increasing the ZIF-8 rate to 4%, it was detected that the adsorption process was mainly consistent with the pseudo-second-order kinetic model ($R^2 = 0.9829$). This finding indicates that the adsorption mechanism was determined by chemisorption with increasing ZIF-8 rate and the interactions between Pb(II) ions and the adsorbent surface became dominant by valence forces, electron exchange or exchange. The calculated k_2 value (0.000654 g/mg-

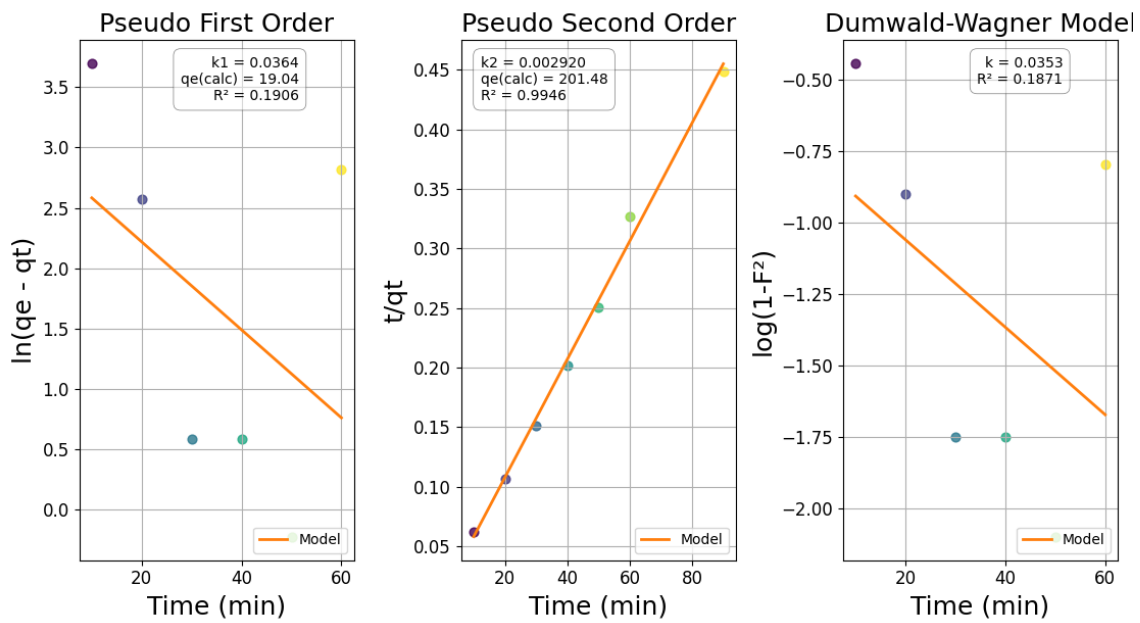
min) increased 5.7-fold compared to the 2% ZIF-8 rate. The significant decrease in the correlation coefficient ($R^2 = 0.4652$) of the Dumwald-Wagner model, which represents the diffusion-driven mechanisms, confirms that intraparticle diffusion is less effective in the adsorption process. The theoretical equilibrium adsorption capacity calculated under these conditions was determined to be 207.09 mg/g. Upon raising the ZIF-8 loading rate to 6%, the pseudo-second-order kinetic model showed excellent correlation ($R^2 = 0.9946$), proving that the adsorption process was almost completely carried out by the chemisorption mechanism. The k_2 value, which was calculated as 0.00292 g/mg-min, increased by a factor of 4.5 compared to the 4% loading rate. This observation indicates that the chemisorption rate increased dramatically when the ZIF-8 rate was increased. The equilibrium adsorption capacity, which was predicted to be 201.48 mg/g, had a value relatively close to the 4% loading rate. The fact that the correlation coefficients of the Dumwald-Wagner model and the pseudo-first order model decreased to values of 0.1871 and 0.1906, respectively, is evidence that the contribution of diffusion processes and physical adsorption to the adsorption mechanism has decreased significantly.



(a)



(b)

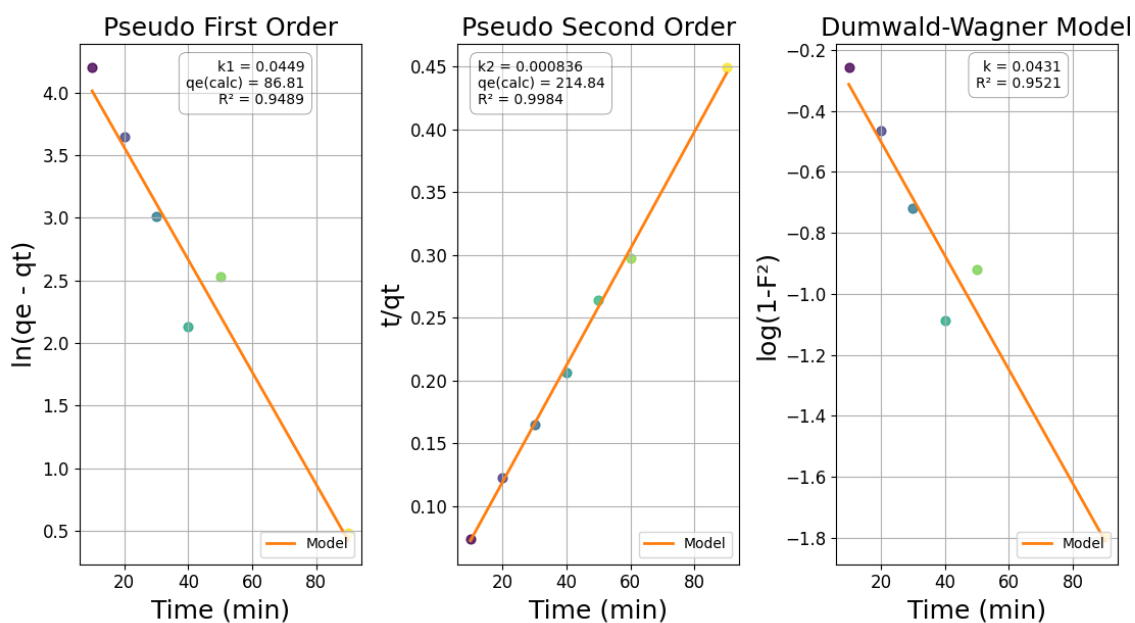


(c)

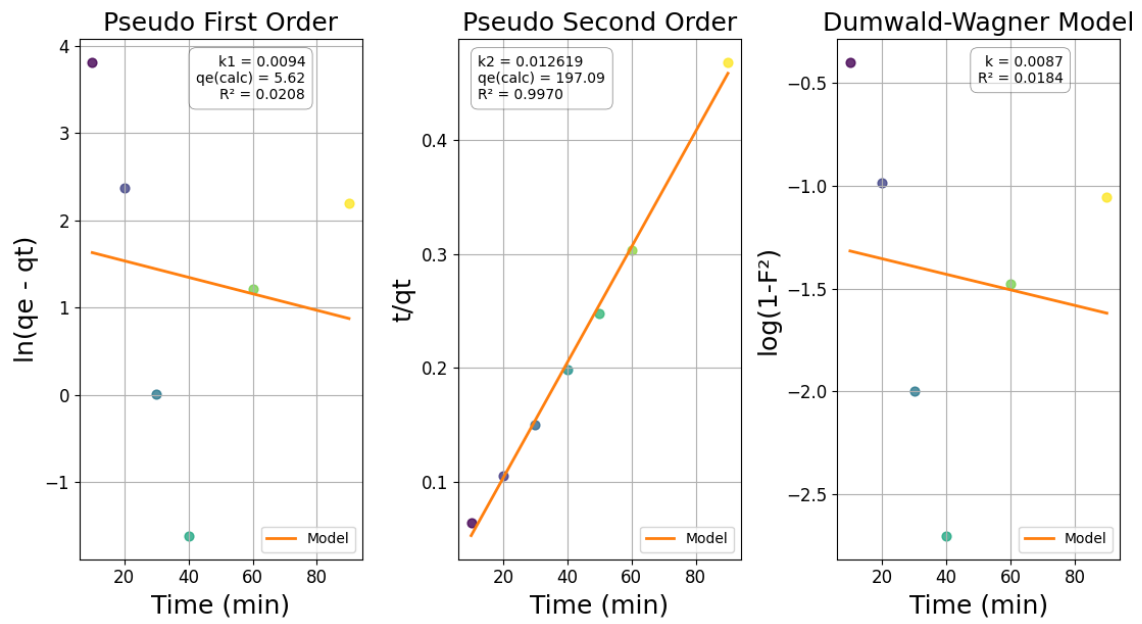
Figure 5.3: Adsorption kinetic analysis for determining predominant adsorption mechanism of Pb(II) ions onto AL@ZIF-8 using chemical reaction and intraparticle diffusion models: Effect of ZIF-8 loading ratios (a) 2%, (b) 4%, and (c) 6% at initial Pb(II) concentration of 400 mg/L and Temperature of 23°C.

The kinetic analysis to study the adsorption mechanism of Pb(II) ions on AL@ZIF-8 hydrogel shows that an increase in temperature (from 23°C to 40°C) leads to significant changes in the adsorption mechanism. For the experiments performed at 40°C, the pseudo-second order kinetic model was found to be the best fit ($R^2 = 0.9984$, 0.9970 and 0.9863, respectively) at all ZIF-8 loading rates (2%, 4% and 6%). This clearly shows that the adsorption process shifts towards a predominantly chemical adsorption mechanism with increasing temperature. In particular, at a ZIF-8 loading of 2, the adsorption process, which corresponds to the pseudo-first order model at 23°C ($R^2 = 0.8075$), fits perfectly to the pseudo-second order model at 40°C ($R^2 = 0.9984$), which proves that the adsorption mechanism clearly changes from physical adsorption to chemical adsorption with increasing temperature. When investigating the kinetic parameters, significant changes in the pseudo second-order rate constants (k_2) are observed with increasing temperature. While the k_2 value at 23°C was 0.000114 g/mg-min, it reached 0.000836 g/mg-min at 40°C, which is about 7.33 times at 2% ZIF-8. Similarly, at 4% ZIF-8 loading, the k_2 value increased from 0.000654 g/mg-min to 0.012619 g/mg-min, which is a remarkable increase (19.30-fold). These results show that increasing the temperature significantly accelerates the adsorption kinetics and changes the reaction mechanism. However, at 6% ZIF-8 loading, the k_2 value decreased from 0.00292 g/mg-min to 0.001062 g/mg-min (approximately 64% decrease), showing an unexpected trend. This suggests that an increase in temperature at high ZIF-8 concentrations may have a different mechanism of action on adsorption kinetics. When examining the correlation coefficients of the Dumwald-Wagner model, which represents the effect of diffusion mechanisms, the effect of increasing temperature on diffusion processes differed depending on the ZIF-8 loading rate. At 2% ZIF-8 loading, the R^2 value of the Dumwald-Wagner model increased from 0.8065 to 0.9521, while it decreased from 0.4652 to 0.0184 at 4% loading. At 6 loading, it increased from 0.1871 to 0.3499. As for the equilibrium adsorption capacities (q_e), at low ZIF-8 loadings (2 and 4), reduction in the ability for adsorption was observed with the rising temperature (from 260.16 mg/g to 214.84 mg/g and from 207.09 mg/g to 197.09 mg/g), while a slight increase (from 201.48 mg/g to 209.12 mg/g) was observed at high ZIF-8 loadings (6%). It is hypothesized that this situation is due to the activation of new adsorption sites at high ZIF-8 concentrations with the increase in temperature. When comparing the adsorption behavior at 23°C and 40°C, it was found that the most

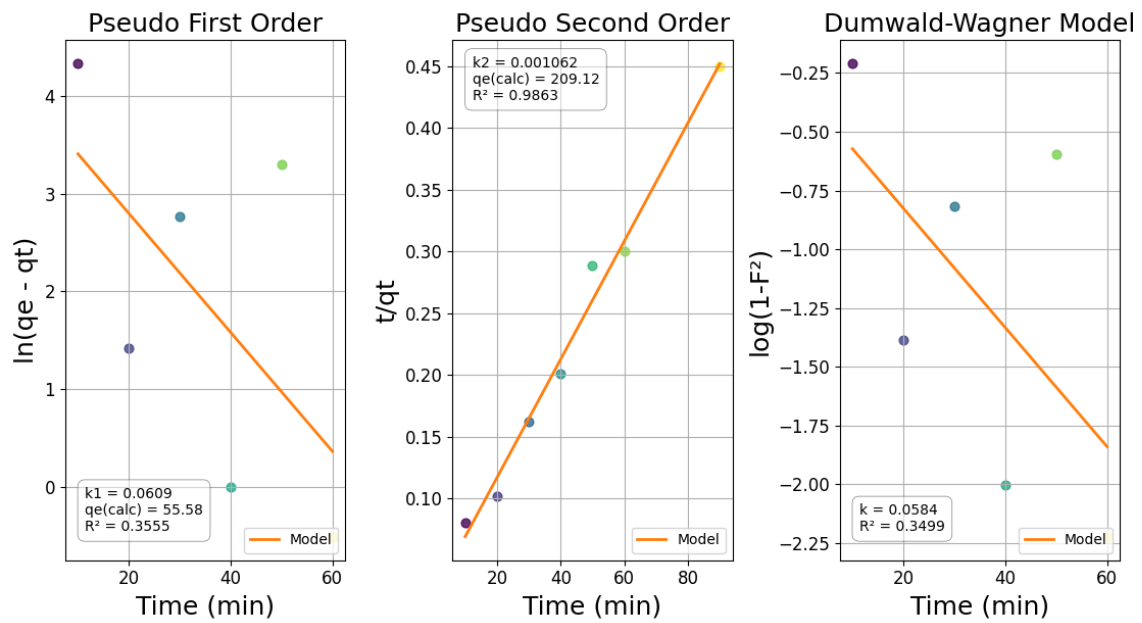
significant effect of temperature increase was observed at a ZIF-8 loading of 2. While both physical adsorption and intraparticle diffusion were effective at this concentration at low temperature (23°C), the adsorption mechanism clearly shifted to chemical adsorption with the increase in temperature (40°C). The coefficient of correlation of the pseudo-second order model increased from 0.5183 to 0.9984, clearly indicating this change in the reaction mechanism. These results scientifically confirm that the adsorption of Pb(II) on the AL@ZIF-8 composite is an endothermic process and that increasing the temperature significantly affects the adsorption efficiency and mechanism, especially at low ZIF-8 concentrations.



(a)



(b)



(c)

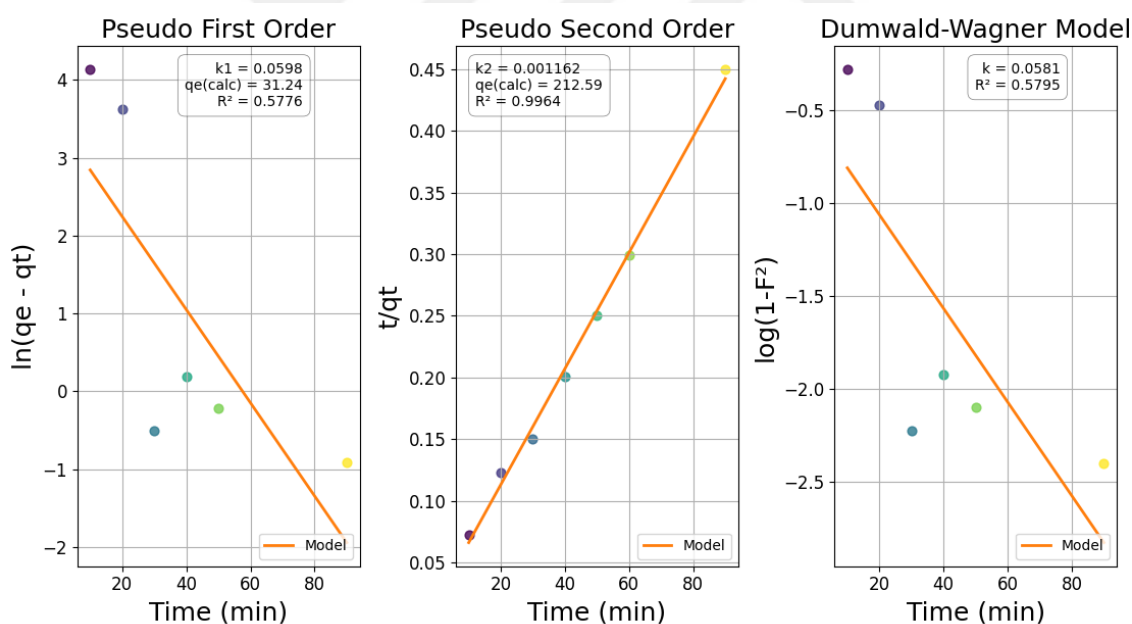
Figure 5.4: Adsorption kinetic analysis for determining predominant adsorption mechanism of Pb(II) ions onto AL@ZIF-8 using chemical reaction and intraparticle diffusion models: Effect of ZIF-8 loading ratios (a) 2%, (b) 4%, and (c) 6% at initial Pb(II) concentration of 400 mg/L and Temperature of 40°C.

The adsorption mechanism of Pb(II) ions at an initial concentration of 400 mg/L on AL@ZIF-8 composite hydrogel showed a significant temperature dependence as a result of kinetic analyses performed at different temperatures (23°C, 40°C and 50°C). Under these fixed initial concentration conditions, the pseudo-second order kinetic model was found to have near perfect correlation coefficients ($R^2 = 0.9964, 0.9923$ and 0.9912 , respectively) at all ZIF-8 loading rates (2%, 4% and 6%) in the experiments performed at 50°C. These results indicate a significant shift from the diffusion-driven adsorption mechanism at low temperatures (23 degrees Celsius) to the chemical adsorption mechanism at high temperatures (40 degrees Celsius and 50 degrees Celsius with temperature difference). In particular, the small fit of the pseudo second-order model at 23 degrees Celsius ($R^2 = 0.5183$) increased to 0.9984 and 0.9964 at 40 degrees Celsius and 50 degrees Celsius, respectively, when the ZIF-8 concentration was 2%. This shows how high temperatures change adsorption.

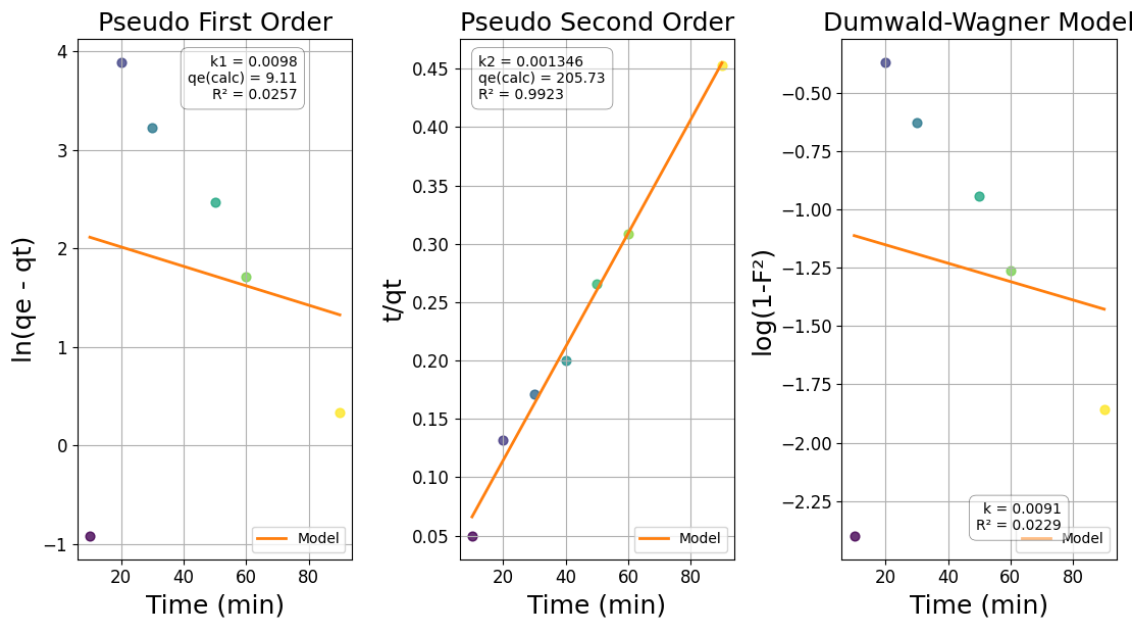
A consistent increase in the pseudo second-order rate constant (k_2) was observed at 2% ZIF-8 loading with increasing temperature: The k_2 value increased from 0.000114 g/mg-min at 23°C to 0.000836 at 40°C (7.33-fold) and 0.001162 at 50°C (10.19-fold). This situation shows that the adsorption kinetics are clearly endothermic at a low ZIF-8 ratio. At 4% ZIF-8 loading, a dramatic increase in k_2 value (19.30-fold) was observed from 23°C to 40°C, but an unexpected decrease was observed at 50°C. Similarly, at 6% ZIF-8 loading, a continuous downward trend in k_2 values was observed with the increase in temperature (0.00292 at 23°C, 0.001062 at 40°C, and 0.00086 g/mg-min at 50°C). This situation indicates that the adsorption mechanism is more effective at high ZIF-8 ratios at low temperatures and that increasing the temperature may have a negative effect on the reaction kinetics. When the equilibrium adsorption capacities (q_e) were evaluated at three different temperatures, a continuous downward trend was observed for 2 ZIF-8 with the increase of temperature (260.16 mg/g at 23°C, 214.84 mg/g at 40°C and 212.59 mg/g at 50°C). In contrast, when 6 ZIF-8 was loaded, the opposite trend was observed and the capacity of adsorption rose continuously with rising in temperature (201.48 mg/g at 23°C, 209.12 mg/g at 40°C and 216.12 mg/g at 50°C). For 4% ZIF-8, a decrease in capacity was observed at 40°C, but a renewed increase at 50°C. These different behaviours indicate that the adsorption mechanism has a complex interaction with temperature

depending on the ZIF-8 loading rate.

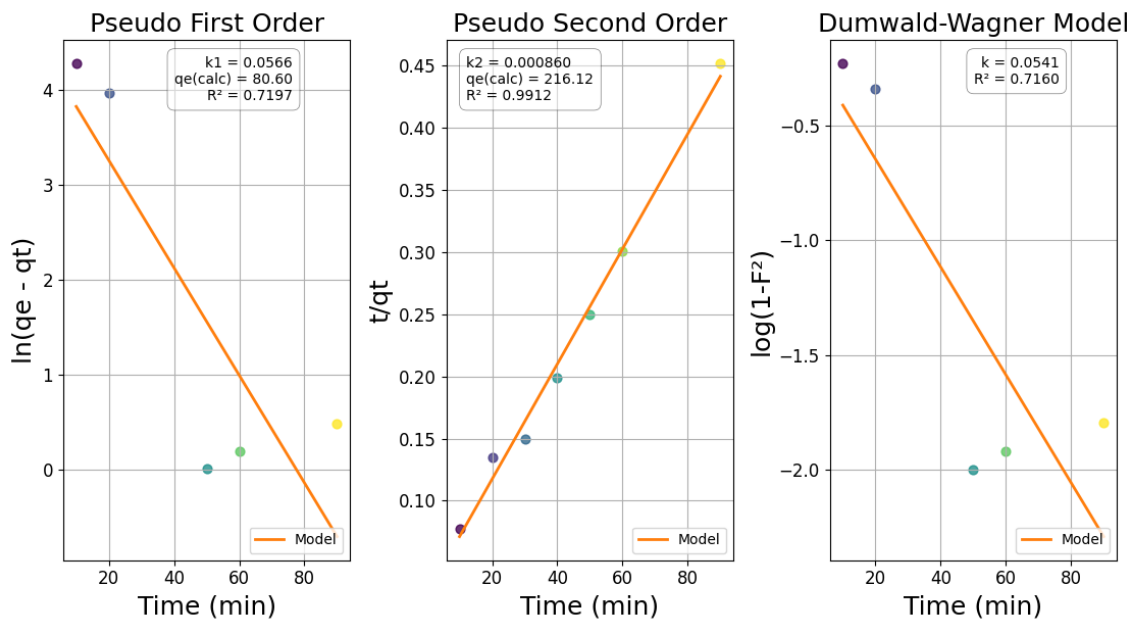
The competition between diffusion and chemical reaction mechanisms showed significant changes with increasing temperature. When this competition was evaluated by the ratio between the R^2 value of the pseudo second-order model and the R^2 value of the Dumwald-Wagner model, this ratio increased from 0.64 at 23°C to 1.05 at 40°C and 1.72 at 50°C for a ZIF-8 content of 2, proving that chemical adsorption becomes increasingly dominant with increasing temperature. In contrast, at a ZIF-8 content of 4, this ratio showed values of 2.11 at 23°C, 54.18 at 40°C and 43.33 at 50°C with a dramatic increase. Similarly, at 6% ZIF-8, the chemical adsorption to diffusion ratio was 5.32 at 23°C, while at higher temperatures it decreased to 2.82 at 40°C and 1.38 at 50°C. These results show that at low ZIF-8 loading, chemical adsorption becomes more dominant with increasing temperature, while at high ZIF-8 loading, the relative importance of diffusion mechanisms increases with increasing temperature.



(a)



(b)



(c)

Figure 5.5: Adsorption kinetic analysis for determining predominant adsorption mechanism of Pb(II) ions onto AL@ZIF-8 using chemical reaction and intraparticle diffusion models: Effect of ZIF-8 loading ratios (a) 2%, (b) 4%, and (c) 6% at initial Pb(II) concentration of 400 mg/L and Temperature of 50°C.

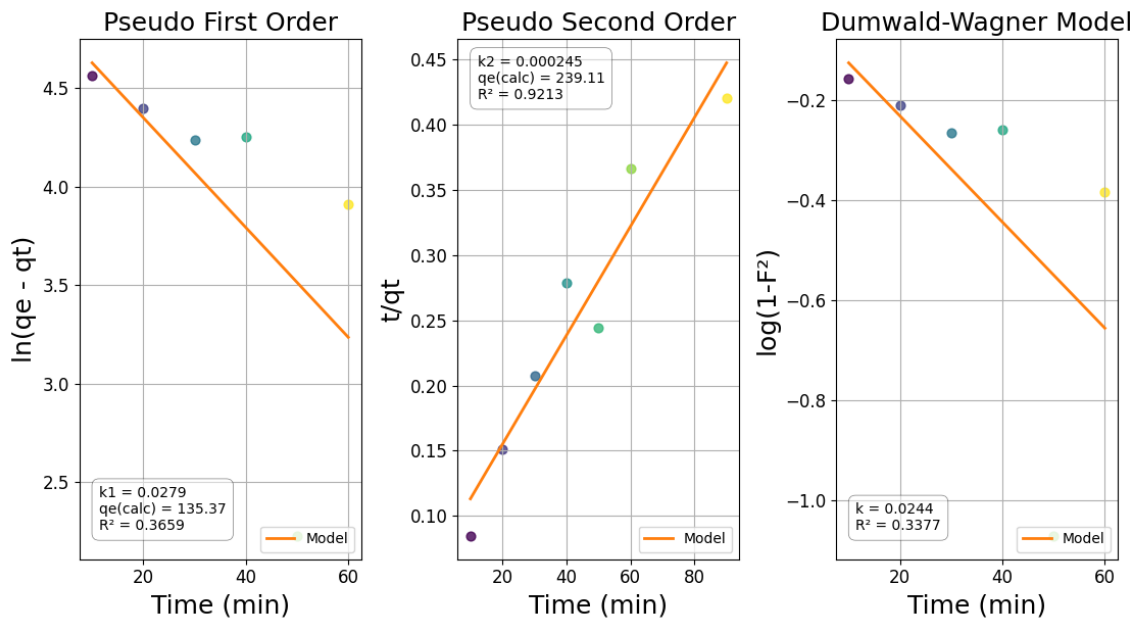
5.4.2. Kinetic Analysis of Pb(II) Adsorption on AL@ZIF-8 at 450 mg/L: Effects of Temperature and ZIF-8 Loading Ratio

The adsorption mechanism of Pb(II) ions on AL@ZIF-8 composite hydrogel at an initial concentration of 450 mg/L was investigated by kinetic analysis performed at different ZIF-8 loading rates (2%, 4% and 6%) at 23°C. Compared to the previously studied initial concentration of 400 mg/L at the same temperature (23°C), it was found that increasing the initial concentration resulted in significant changes in the adsorption mechanism. At 450 mg/L, it was found that the pseudo-second order kinetic model showed the best fit at all ZIF-8 loading rates ($R^2 = 0.9213$, 0.9142 and 0.8302 , respectively). This differs from the result where the pseudo-first order model showed a better fit ($R^2 = 0.8075$) at 400 mg/L with 2% ZIF-8. This result shows that the adsorption mechanism shifts from physical adsorption to chemical adsorption with increasing initial concentration.

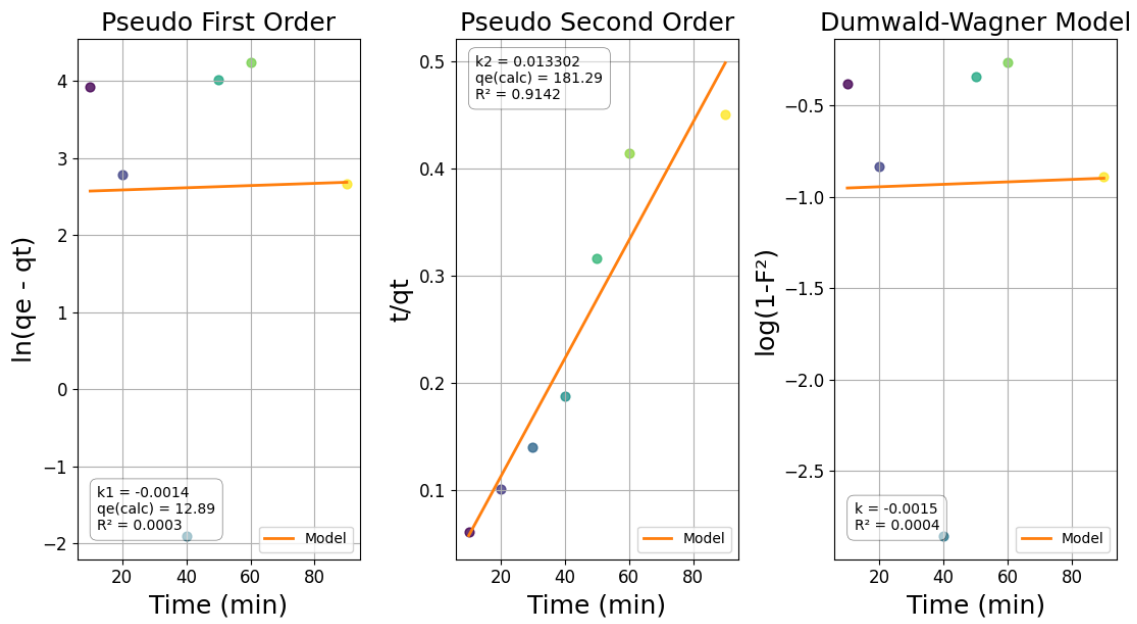
When the pseudo-second order rate constants (k_2) were examined, significant increases in adsorption rates were observed at 2% and 4% ZIF-8 loadings when the initial concentration increased from 400 mg/L to 450 mg/L. While the k_2 value at 2% ZIF-8 increased from 0.000114 g/mg-min to 0.000245 g/mg-min, a 2.15-fold increase, this increase was much more dramatic at 4% ZIF-8, where the k_2 value increased from 0.000654 g/mg-min to 0.013302 g/mg-min, a 20.34-fold increase. However, at 6% ZIF-8 loading, an opposite trend was observed, where the k_2 value decreased from 0.00292 g/mg-min to 0.000155 g/mg-min, a decrease of approximately 95%. According to these findings, at low ZIF-8 loadings, the adsorption kinetics speeds up with the starting concentration, whereas at high ZIF-8 loadings, it decreases. When evaluated by equilibrium adsorption capacities (q_e), a decrease in adsorption capacities was observed at 2% and 4% ZIF-8 with the increase in initial concentration (from 260.16 mg/g to 239.11 mg/g and from 207.09 mg/g to 181.29 mg/g, respectively), and a significant increase was observed at 6% ZIF-8 (from 201.48 mg/g to 255.02 mg/g). This shows that the adsorbent is able to bind more Pb(II) ions, even with increasing initial concentration at high ZIF-8 content. This increase observed at high ZIF-8 loadings could be due to the activation of previously inaccessible adsorption sites at high concentrations. Examining the changes in the goodness of fit of the different kinetic models, it can be seen that the fit of the pseudo-second order model increases significantly ($R^2 = 0.5183$ to 0.9213) with the increase of

the initial concentration at a ZIF-8 ratio of 2 , while it decreases slightly at the ratios of 4 % and 6 %. These findings demonstrate how the ZIF-8 loading rate affects how the initial concentration affects the adsorption mechanism.

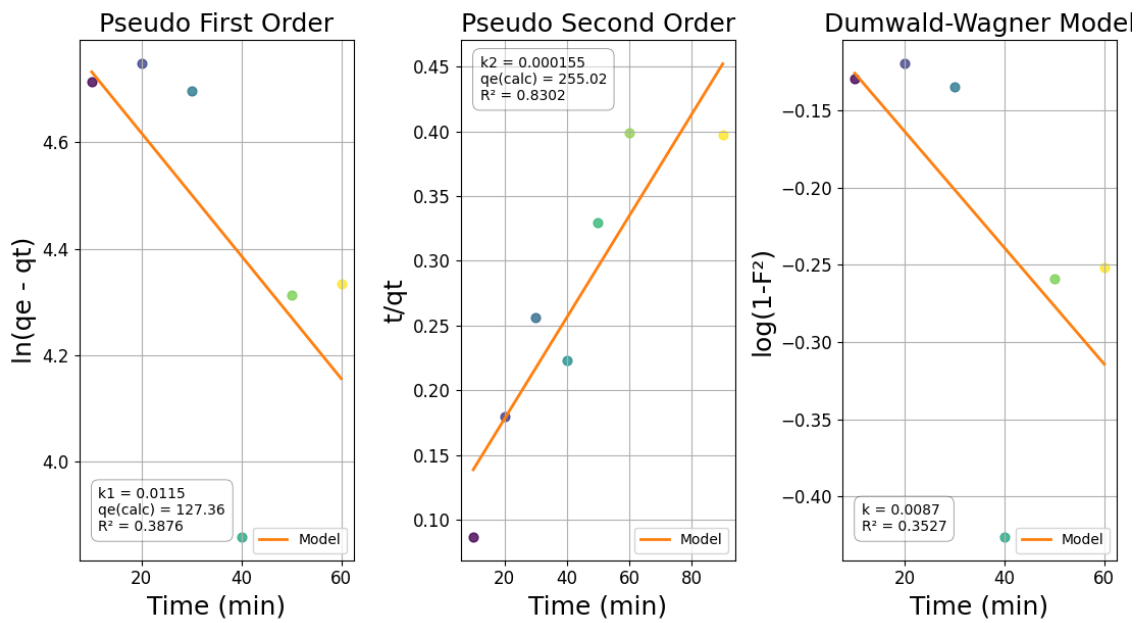
Examining the competition between diffusion and chemical reaction mechanisms, it is found that chemical adsorption clearly dominates with increasing initial concentration, especially at ZIF-8 ratios of 2% and 4%. At a ZIF-8 ratio of 2, the ratio of the pseudo-second order model to the Dunwald-Wagner model increased from 0.64 to 2.73 and at 4% from 2.11 to a much higher value of 2285.50. Comparing the experiments performed at 23°C with the results at 40°C and 50°C, it is found that increasing the initial concentration changes the adsorption mechanism in favor of chemisorption, especially at low temperatures and low ZIF-8 loadings. This shows that the chemisorption mechanism, which is already predominant at 40°C and 50°C, also comes to the fore at 23°C with increasing initial concentration. As a result, both the temperature and the initial concentration together with the ZIF-8 loading ratio should be considered when determining the optimum conditions for Pb(II) adsorption on AL@ZIF-8 composites. It is clear that at high initial concentrations such as 450 mg/L, a 6% ZIF-8 loading provides the highest adsorption capacity but has the slowest kinetics; low ZIF-8 loadings provide faster adsorption kinetics but have lower adsorption capacities.



(a)



(b)

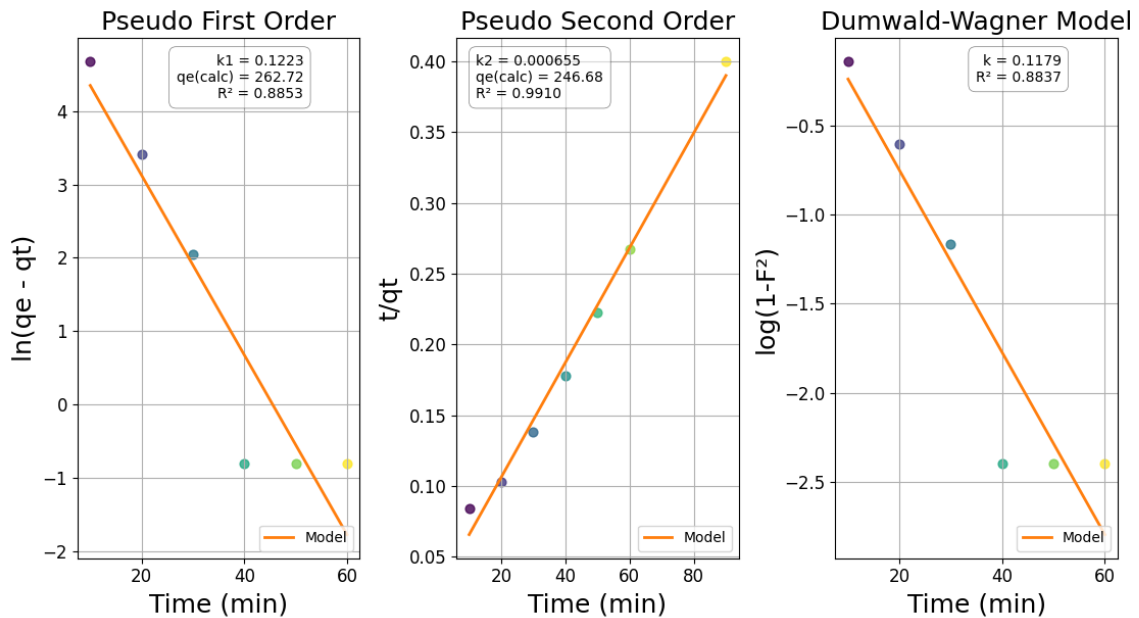


(c)

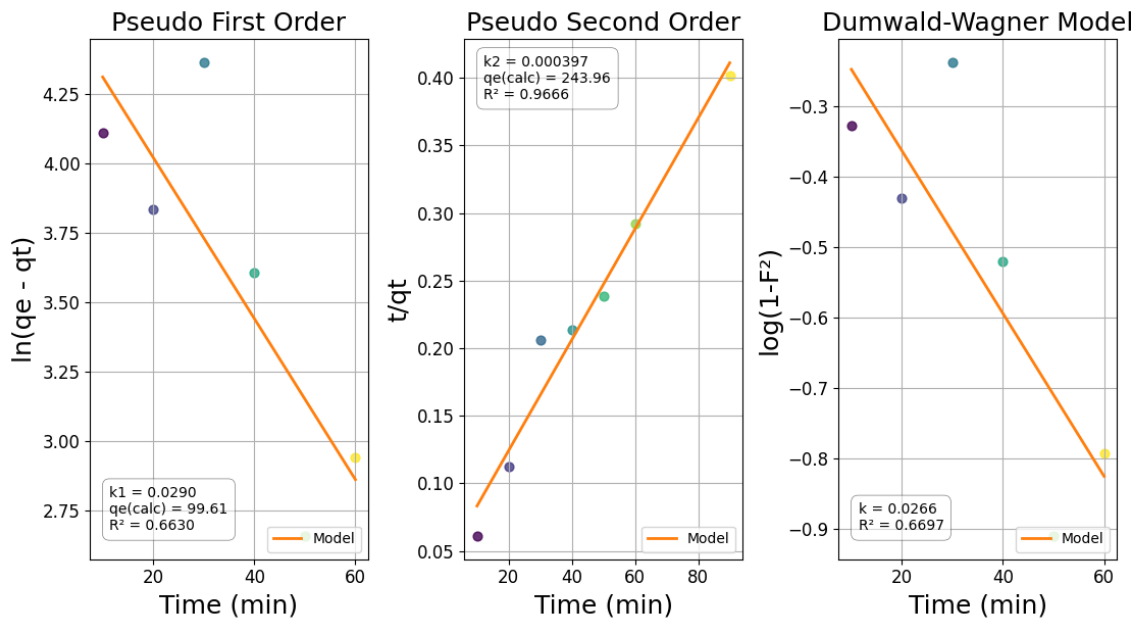
Figure 5.6: Adsorption kinetic analysis for determining predominant adsorption mechanism of Pb(II) ions onto AL@ZIF-8 using chemical reaction and intraparticle diffusion models: Effect of ZIF-8 loading ratios (a) 2%, (b) 4%, and (c) 6% at initial Pb(II) concentration of 450 mg/L and Temperature of 23°C.

When the adsorption behavior of Pb(II) ions on AL@ZIF-8 composite hydrogel was investigated at an initial concentration of 450 mg/L and a temperature of 40°C, it was found that the pseudo-second-order kinetic model showed the best fit at all ZIF-8 loading rates ($R^2 = 0.9910, 0.9666$ and 0.9956 , respectively). These results indicate that the adsorption mechanism at an initial concentration of 450 mg/L and a temperature of 40°C was significantly controlled by chemical adsorption. Comparison of the experiments performed at the same initial concentration (450 mg/L) but different temperatures (23°C and 40°C) showed that increasing the temperature had significant effects on the adsorption kinetics. At 2% ZIF-8 loading, the pseudo-second order rate constant (k_2) increased 2.67-fold from 0.000245 g/mg-min to 0.000655 g/mg-min with increasing temperature. At 6% ZIF-8 loading, this increase was much more dramatic: the k_2 value increased 14.12-fold from 0.000155 g/mg-min to 0.002189 g/mg-min. In contrast, the k_2 value surprisingly dropped from 0.013302 g/mg-min to 0.000397 g/mg-min when the ZIF-8 loading was 4%. This corresponds to a decrease of 97%. These results show that the effect of temperature increase on adsorption kinetics varies depending on the ZIF-8 loading rate when the initial concentration is high (450 mg/L). When equilibrium adsorption capacities (q_e) were examined, a rising in adsorption capacities was observed with the rising in temperature at 2 % and 4 % ZIF-8 loadings (from 239.11 mg/g to 246.68 mg/g and from 181.29 mg/g to 243.96 mg/g, respectively), while a decrease was observed at 6 % ZIF-8 loading (from 255.02 mg/g to 222.57 mg/g). In particular, the increase of 62.67 mg/g at 4% ZIF-8 loading shows that temperature has a significant positive effect on adsorption capacity at this loading rate. In addition, an improvement in the correlation coefficients (R^2) of the pseudo-second order model was observed at all ZIF-8 loading rates with the increase in temperature, and this improvement was more pronounced at 6% loading with an increase from 0.8302 to 0.9956. Comparisons carried out at the same temperature (40°C) but different initial concentrations (400 mg/L and 450 mg/L) clearly show the effects of increasing concentration on the adsorption parameters. An increase in equilibrium adsorption capacities was observed at all ZIF-8 loading rates with the increase in initial concentration: from 214.84 mg/g to 246.68 mg/g (31.84 mg/g increase) at 2% loading, from 197.09 mg/g to 243.96 mg/g (46.87 mg/g increase) at 4% loading, and from 209.12 mg/g to 222.57 mg/g (13.45 mg/g increase) at 6% loading. These results show that increasing the initial concentration at 40°C significantly increases the

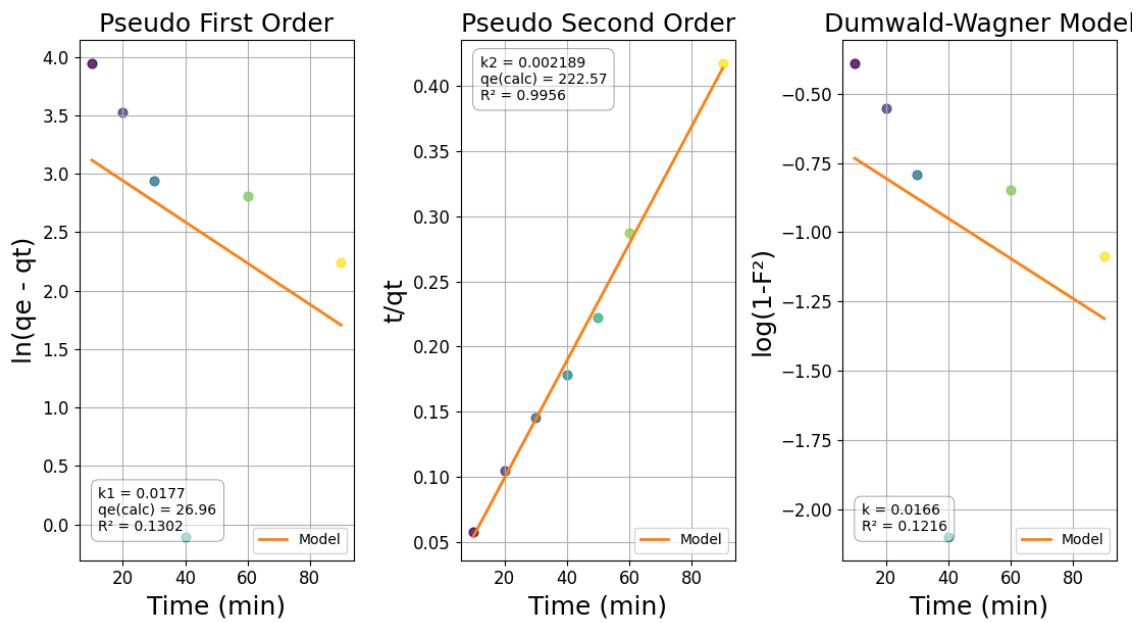
adsorption capacity, but this increase varies depending on the ZIF-8 loading rate. When the effect of initial concentration was examined in relation to the adsorption rate constants, a decrease in k_2 values was observed at 2% and 4% ZIF-8 loadings (22% and 97%, respectively), while an increase was observed at 6% loading (106%). This shows that a 6% ZIF-8 loading has more favorable adsorption kinetics at high concentrations. When comparing the correlation coefficients (R^2), a slight decrease was observed at 2% and 4% loading and a slight increase at 6% loading. These results show that increasing the initial concentration did not significantly change the fit of the model, but led to a slight improvement at 6% ZIF-8 loading. When the competition of diffusion and chemical reaction mechanisms is analyzed together with temperature and concentration changes, interesting results are obtained. When the initial concentration was risen from 400 mg/L to 450 mg/L at 23°C, the ratio of chemical adsorption to diffusion increased dramatically from 2.11 to 2285.50 at 4 ZIF-8 loading. At 40°C, this ratio decreased from 54.18 to 1.44 at 4% ZIF-8 loading and increased from 2.82 to 8.19 at 6% loading. These results show that the adsorption mechanism is affected differently depending on ZIF-8 loading at high temperatures and high concentrations.



(a)



(b)

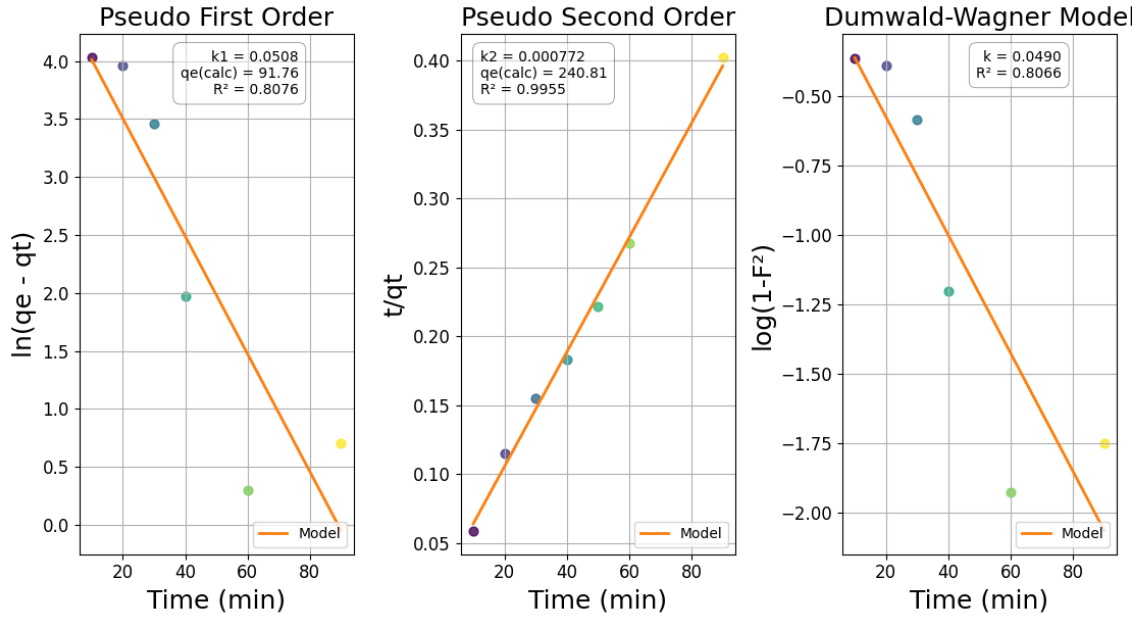


(c)

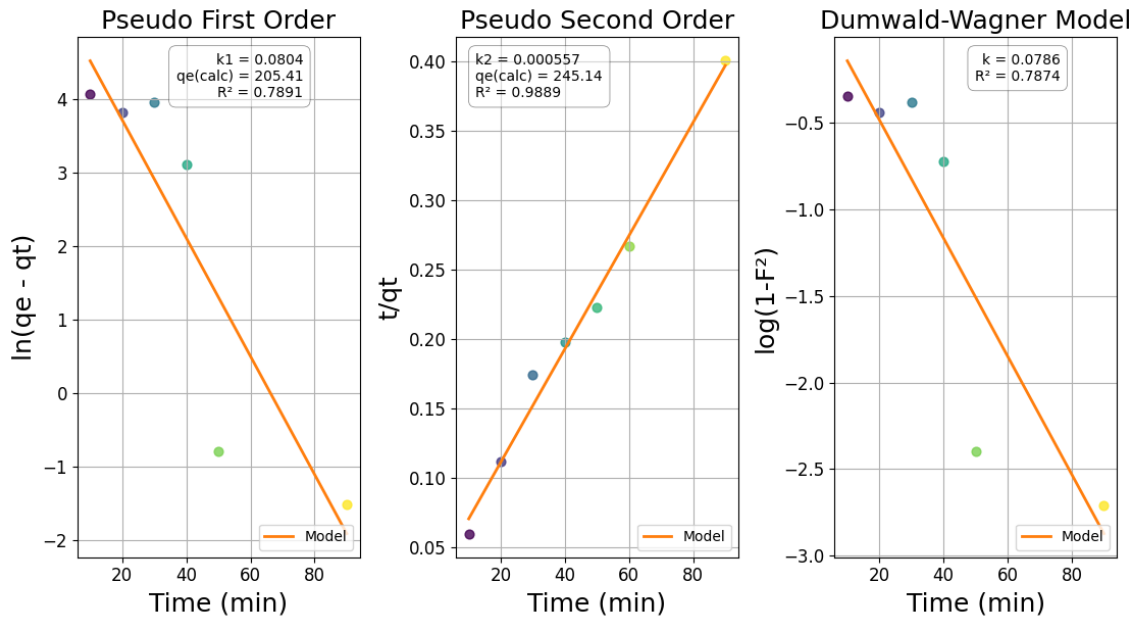
Figure 5.7: Adsorption kinetic analysis for determining predominant adsorption mechanism of Pb(II) ions onto AL@ZIF-8 using chemical reaction and intraparticle diffusion models: Effect of ZIF-8 loading ratios (a) 2%, (b) 4%, and (c) 6% at initial Pb(II) concentration of 450 mg/L and Temperature of 40°C.

When the experimental results at 50°C are compared with the adsorption data at similar concentration (450 mg/L) at lower temperatures (23°C and 40°C), the obvious effects of temperature on the adsorption kinetics and mechanism can be observed. At 2% ZIF-8 loading, the pseudo-second-order rate constant (k_2) showed a continuous increase with increasing temperature: the k_2 value, which was 0.000245 g/mg-min at 23°C, increased to 0.000655 g/mg-min (2.67-fold increase) at 40°C and to 0.000772 g/mg-min (3.15-fold increase) at 50°C. This result shows that the adsorption kinetics at low ZIF-8 content was clearly endothermic. A complex kinetic behavior as a function of temperature was observed at 4% ZIF-8 loading. The k_2 value decreased from 0.013302 g/mg-min to 0.000397 g/mg-min (97% decrease) from 23°C to 40°C, while it increased from 40°C to 50°C to 0.000557 g/mg-min (40% increase). Similarly, at 6% ZIF-8 loading from 40°C to 50°C, the k_2 value decreased from 0.002189 g/mg-min to 0.000424 g/mg-min (81% decrease). These results show that the adsorption kinetics at high ZIF-8 loadings do not respond monotonically to the temperature increase. The adsorption capabilities were investigated and it was found that the adsorption capacity increased significantly with increasing temperature at 4% ZIF-8 loading. The q_e value, which was 181.29 mg/g at 23°C, increased to 243.96 mg/g at 40°C and to 245.14 mg/g at 50°C. This result shows that the adsorption capacity at this loading rate improved with increasing temperature. At 6% ZIF-8 loading, the adsorption capacity was 255.02 mg/g at 23°C, decreased to 222.57 mg/g at 40°C, but increased again to 248.82 mg/g at 50°C, showing a U-shaped trend. This shows that the adsorption capacity tends to increase again with high ZIF-8 loading at high temperatures (50°C). A striking observation at 50°C is that the correlation coefficients and kinetic parameters of the pseudo-first order and Dumwald-Wagner models are quite close to each other. For all ZIF-8 loading rates, the ratio of the k_1 values in the pseudo-first order model to the k values in the Dumwald-Wagner model varies between about 1.02-1.04. The difference between the R^2 values is also quite small (0.0010-0.0024). This indicates that both intraparticle diffusion and surface reactions during the adsorption process occur at similar rates at high temperatures (50°C) and jointly contribute to the adsorption mechanism. To investigate the relative contributions of the diffusion and chemical reaction processes, the R^2 ratios of the pseudo second-order model and the Dumwald-Wagner model are compared. It is found that these ratios typically decrease as the temperature increases from 23°C to 50°C. For a 4% ZIF-8

loading, the ratio was 2285.50 at 23°C, decreasing to 1.44 at 40°C and further decreasing to 1.26 at 50°C. Similarly, with a 6% ZIF-8 loading, the ratio was 8.19 at 40°C and decreased to 1.12 at 50°C. These results show that at high temperatures (50°C), chemisorption is still the predominant mechanism, but the contribution of diffusion increases relatively.



(a)



(b)

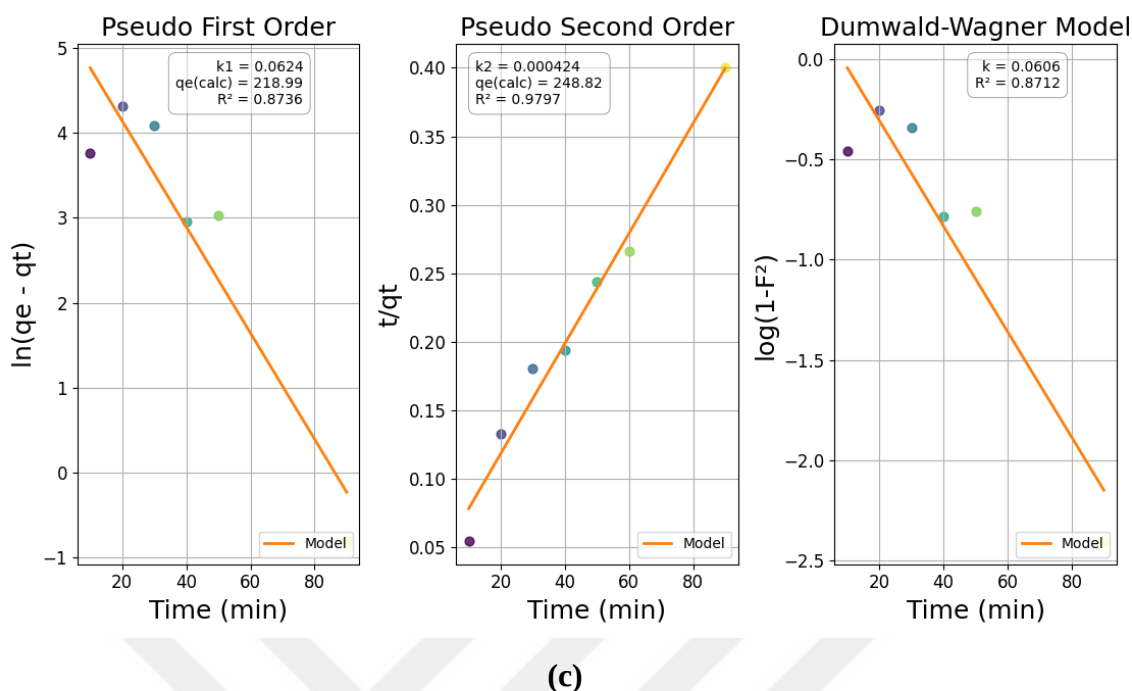


Figure 5.8: Adsorption kinetic analysis for determining predominant adsorption mechanism of Pb(II) ions onto AL@ZIF-8 using chemical reaction and intraparticle diffusion models: Effect of ZIF-8 loading ratios (a) 2%, (b) 4%, and (c) 6% at initial Pb(II) concentration of 450 mg/L and Temperature of 50°C.

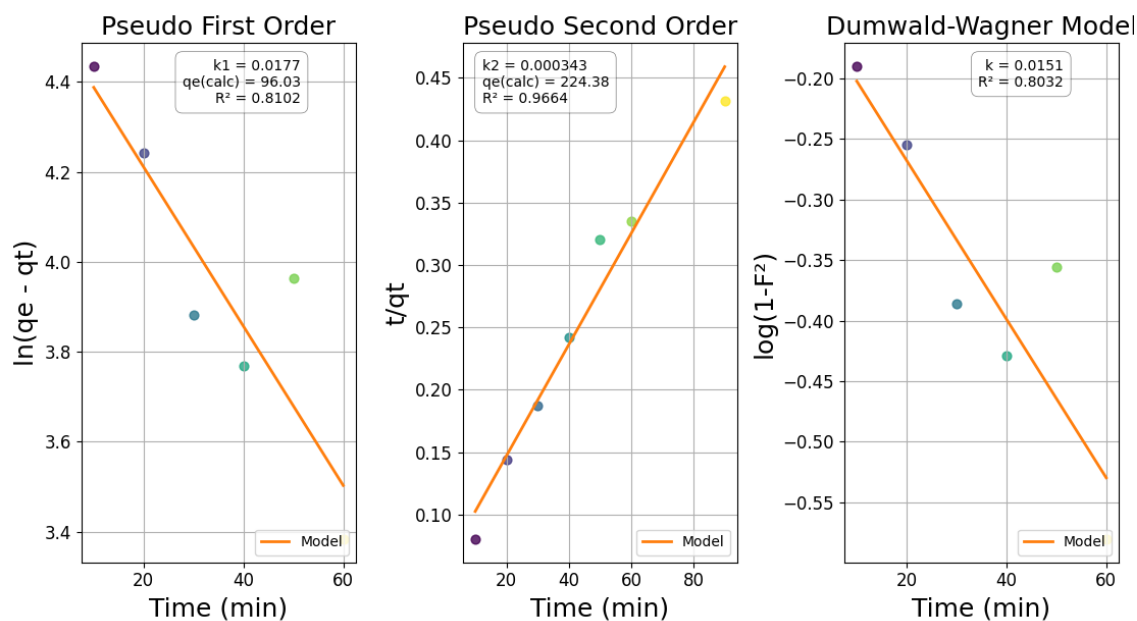
5.4.3. Kinetic Analysis of Pb(II) Adsorption on AL@ZIF-8 at 500 mg/L: Effects of Temperature and ZIF-8 Loading Ratio

The investigation of Pb(II) ion adsorption on AL@ZIF-8 hydrogel at an initial concentration of 500 mg/L and a temperature of 23°C revealed that the pseudo-second-order kinetic model provided the optimal fit across all ZIF-8 loading rates ($R^2 = 0.9664$, 0.9812, and 0.9814, respectively). Compared to the lower initial concentrations (400 mg/L and 450 mg/L), an improvement in the accuracy of the pseudo-second order model was observed at 500 mg/L, especially at 2% ZIF-8 loading. This improvement was particularly evident at the higher dose. It was observed that the R^2 value of the pseudo-second order model increased from 0.5183 at 400 mg/L to 0.9213 at 450 mg/L and then to 0.9664 at 500 mg/L when the loading rate was increased to this level. This situation shows that the adsorption mechanism at low ZIF-8 ratio clearly shifts from physical

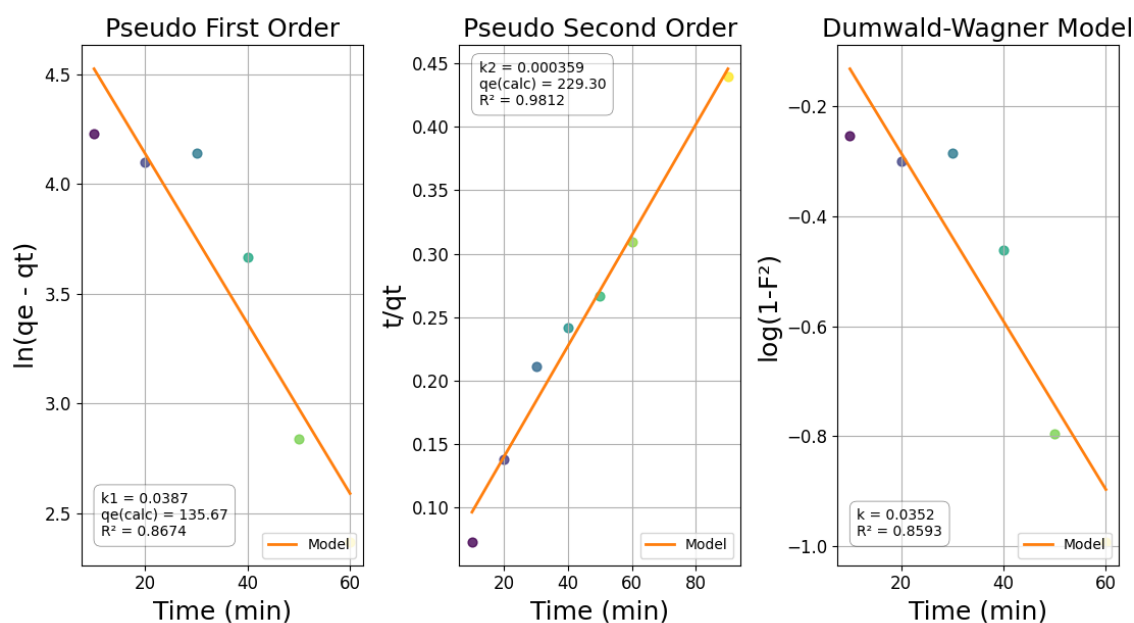
adsorption to chemical adsorption with increasing initial concentration. When the adsorption rate constants (k_2) were examined, a continuous increase was observed with the increase of the initial concentration at a 2% ZIF-8 loading: The k_2 value, which was 0.000114 g/mg-min at 400 mg/L, increased to 0.000245 g/mg-min at 450 mg/L (2.15-fold increase) and to 0.000343 g/mg-min at 500 mg/L (3.01-fold increase). This result shows that increasing the initial concentration at low ZIF-8 loading accelerates the adsorption kinetics. On the other hand, a fluctuating change in k_2 values was observed with increasing concentration at 4% and 6% ZIF-8 loading. At 4% ZIF-8 loading, the k_2 value increased 20.34-fold from 400 mg/L to 450 mg/L and decreased again at 500 mg/L. Similarly, at 6% loading, a general downward trend was observed with increasing concentration. This complex behavior indicates that the adsorption kinetics at high ZIF-8 loadings respond nonlinearly to the initial concentration. When evaluated using the equilibrium adsorption capacities (q_e), a continuous downward trend in adsorption capacity was observed with increasing initial concentration at 2% ZIF-8 loading: The q_e value, which was 260.16 mg/g at 400 mg/L, decreased to 239.11 mg/g at 450 mg/L and to 224.38 mg/g at 500 mg/L. This could be due to the saturation of the adsorption sites when the concentration increases at a low ZIF-8 ratio. The adsorption capacity increased from 181.29 mg/g to 229.30 mg/g when the initial concentration was increased from 450 mg/L to 500 mg/L at a 4% ZIF-8 loading.

The capacity was 201.48 mg/g at 400 mg/L, increased to 255.02 mg/g at 450 mg/L and decreased slightly to 251.39 mg/g at 500 mg/L after a 6% ZIF-8 loading. These results show that the adsorption capacity is better maintained at high concentrations and high ZIF-8 loadings. When the competition between diffusion and chemical reaction mechanisms was investigated, a significant decrease in the R^2 ratios of the pseudo-second-order and Dumwald-Wagner models was observed at all ZIF-8 loading rates with the increase in initial concentration from 450 mg/L to 500 mg/L. For example, at 4% ZIF-8 loading, this ratio was 2285.50 at 450 mg/L, while it decreased to 1.14 at 500 mg/L. Similarly, the ratio, which was 2.35 at 450 mg/L for a 6 ZIF-8 loading, decreased to 1.27 at 500 mg/L. This shows that the percentage contribution of the diffusion mechanism to the adsorption process increases at high initial concentrations such as 500 mg/L. Such concentrations are considered too high. Another noteworthy point is that the rate constants and correlation coefficients of the pseudo-first-order model and the Dumwald-Wagner

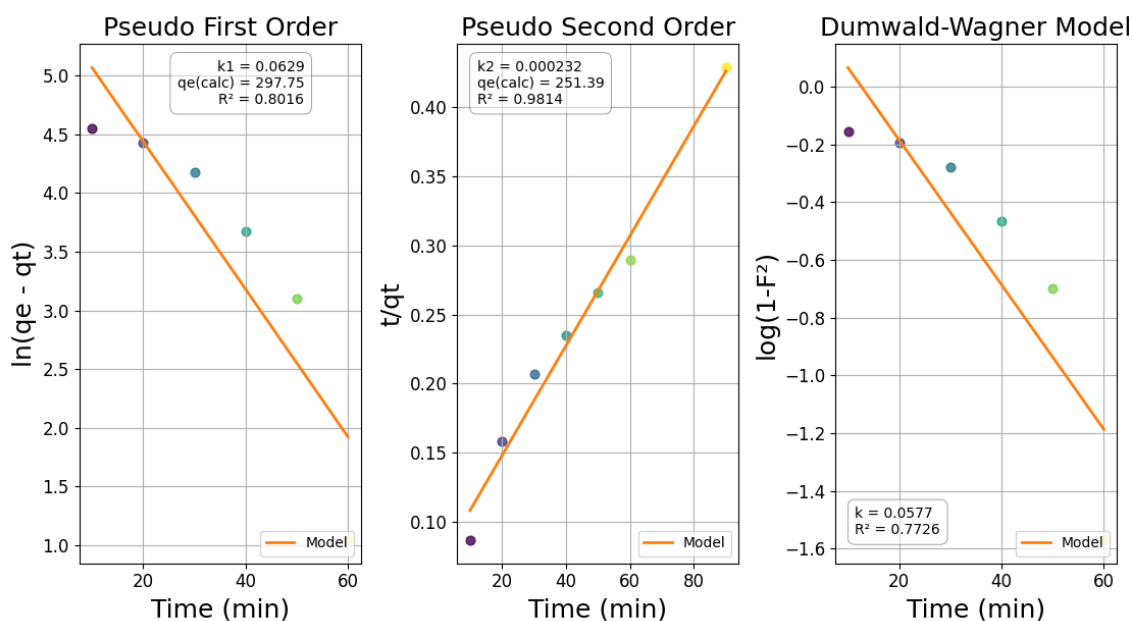
model are remarkably similar at the initial concentration of 500 mg/L. For all ZIF-8 loading rates, the ratio of the k_1 values in the pseudo-first order model to the k values in the Dumwald-Wagner model varies between about 1.09 and 1.17. The difference between the R^2 values is also very small (0.0070-0.0290). These findings suggest that both intraparticle and film diffusion are significant factors in the adsorption process at the high starting concentration of 500 mg/L.



(a)



(b)



(c)

Figure 5.9: Adsorption kinetic analysis for determining predominant adsorption mechanism of Pb(II) ions onto AL@ZIF-8 using chemical reaction and intraparticle diffusion models: Effect of ZIF-8 loading ratios (a) 2%, (b) 4%, and (c) 6% at initial Pb(II) concentration of 500 mg/L and Temperature of 23°C.

Comparison of experiments performed at the same concentration (500 mg/L) but different temperatures (23°C and 40°C) shows significant effects of temperature increase on adsorption kinetics. For all ZIF-8 loading rates, a significant increase in the pseudo second-order rate constant (k_2) was observed with increasing temperature: 2.44-fold increase at 2% loading, 3.03-fold increase at 4% loading and 3.84-fold increase at 6% loading. This result shows that at a high initial concentration (500 mg/L), temperature increase in temperature significantly accelerates the adsorption kinetics and that this acceleration becomes more pronounced as the ZIF-8 loading rate increases. Furthermore, as the temperature increased, the correlation coefficients (R^2) also improved, suggesting that a high temperature improves the adsorption process's chemisorption feature.

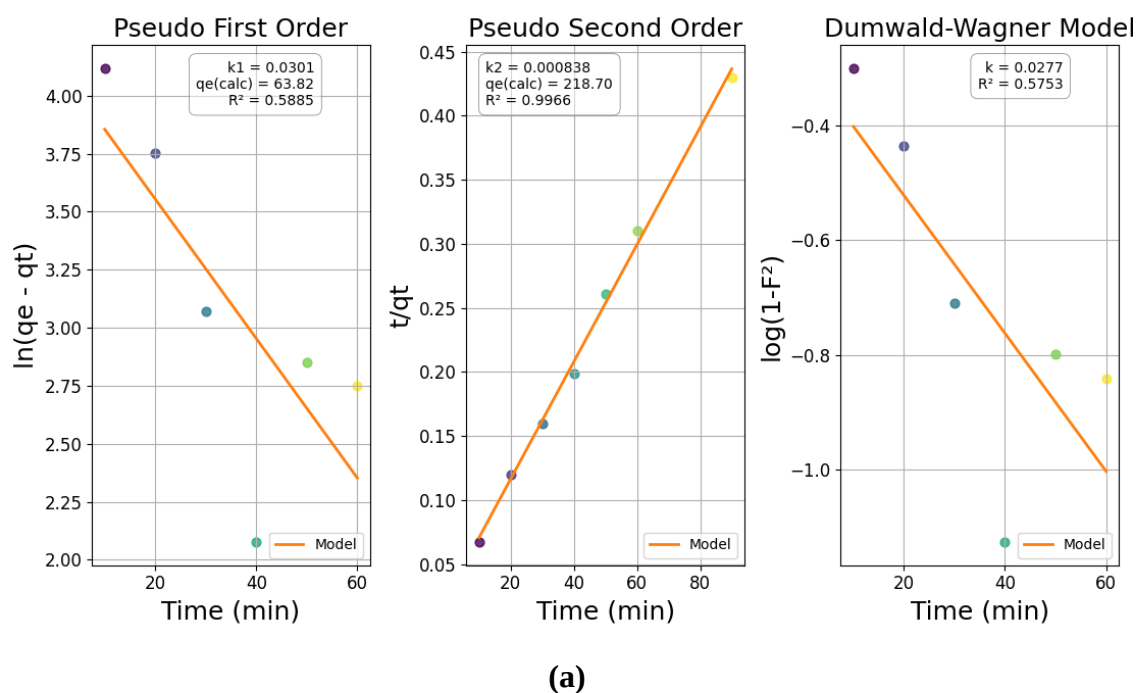
When evaluating the equilibrium adsorption capacities (q_e), a decrease in adsorption capacities with increasing temperature was observed for all ZIF-8 loading rates: 5.68

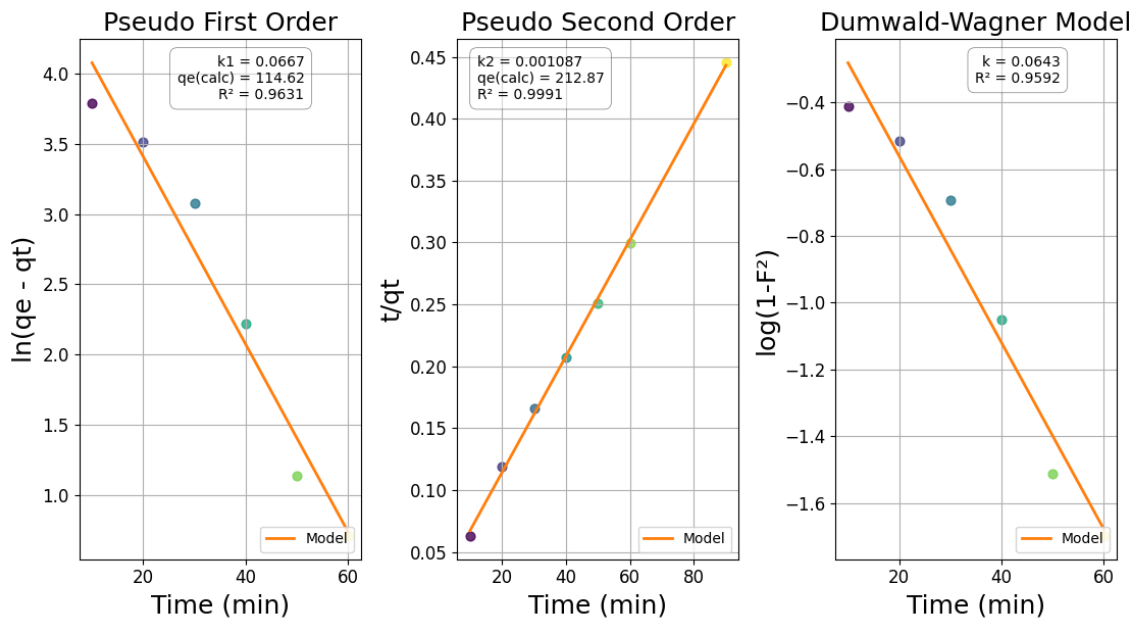
mg/g at 2% loading, 16.43 mg/g at 4% loading and 26.05 mg/g at 6% loading. This decrease shows that adsorption at a high initial concentration (500 mg/L) has an exothermic character and that an increase in temperature negatively affects the adsorption capacity. The fact that the decrease becomes more pronounced with increasing ZIF-8 loading indicates the existence of an adsorption mechanism that is more sensitive to thermal effects at high ZIF-8 content.

Comparisons carried out at the same temperature (40°C) but different initial concentrations (450 mg/L and 500 mg/L) clearly show the effects of increasing concentration on the adsorption parameters. At 2% and 4% ZIF-8 loadings, an increase in the adsorption rate constant (k_2) values was observed with the increase in initial concentration (1.28 and 2.74 times, respectively), while a decrease (59%) was observed at 6% loading. This shows that different ZIF-8 ratios lead to different kinetic responses to the increase in concentration. In addition, the equilibrium adsorption capacities decreased with the increase in concentration at 2 % and 4 % loadings (27.98 mg/g and 31.09 mg/g decrease, respectively), while a slight increase (2.77 mg/g) was observed at 6 % loading. These results show that the higher ZIF-8 ratio better maintains the adsorption capacity at high concentrations. When examining the competition between diffusion and chemical reaction mechanisms, an increase in the R^2 ratios of the pseudo second-order models and the Dumwald-Wagner models was observed with the increase in temperature at 2% and 6% ZIF-8 loadings (from 1.20 to 1.73 and from 1.27 to 1.80, respectively), while a slight decrease was observed at 4% loading (from 1.14 to 1.04). Similarly, this ratio increased with a load of 2 % and 6 %, while it decreased with a load of 4 %. From these results it can be deduced that the adsorption process reacts differently to temperature and concentration fluctuations and that this reaction depends on the ZIF-8 loading ratio.

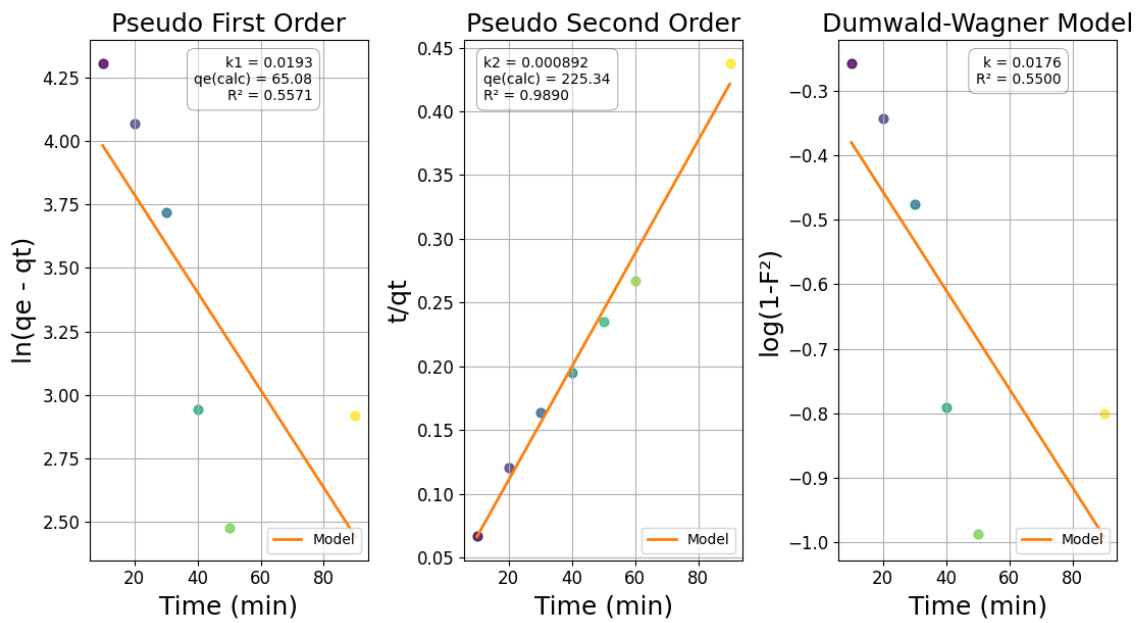
At 500 mg/L and 40°C, large similarities are observed between the rate constants (k_1 and k) and the correlation coefficients of the pseudo-first order and Dumwald-Wagner models. The ratios of the rate constants (k_1/k) were between 1.04-1.10 for all loading rates, while the differences between the R^2 values were quite small (0.0039-0.0132). These findings suggest that under high concentration and temperature circumstances, both intraparticle and film diffusion are significant factors in the adsorption process. In a general evaluation, it can be said that the optimum ZIF-8 loading rate for Pb(II) adsorption

of AL@ZIF-8 composites is 4 at an initial concentration of 500 mg/L and a temperature of 40°C. This loading rate provides the highest correlation coefficient ($R^2 = 0.9991$) and 3.03-fold accelerated kinetics, while the decrease in adsorption capacity remains at a reasonable level. Moreover, under these conditions, there is a nearly balanced relationship ($R^2(\text{PSO})/R^2(\text{DW}) = 1.04$) between chemical adsorption and diffusion mechanisms, indicating that the adsorption process is controlled by both surface chemistry and mass transfer.





(b)



(c)

Figure 5.10: Adsorption kinetic analysis for determining predominant adsorption mechanism of Pb(II) ions onto AL@ZIF-8 using chemical reaction and intraparticle diffusion models: Effect of ZIF-8 loading ratios (a) 2%, (b) 4%, and (c) 6% at initial Pb(II) concentration of 500 mg/L and Temperature of 40°C.

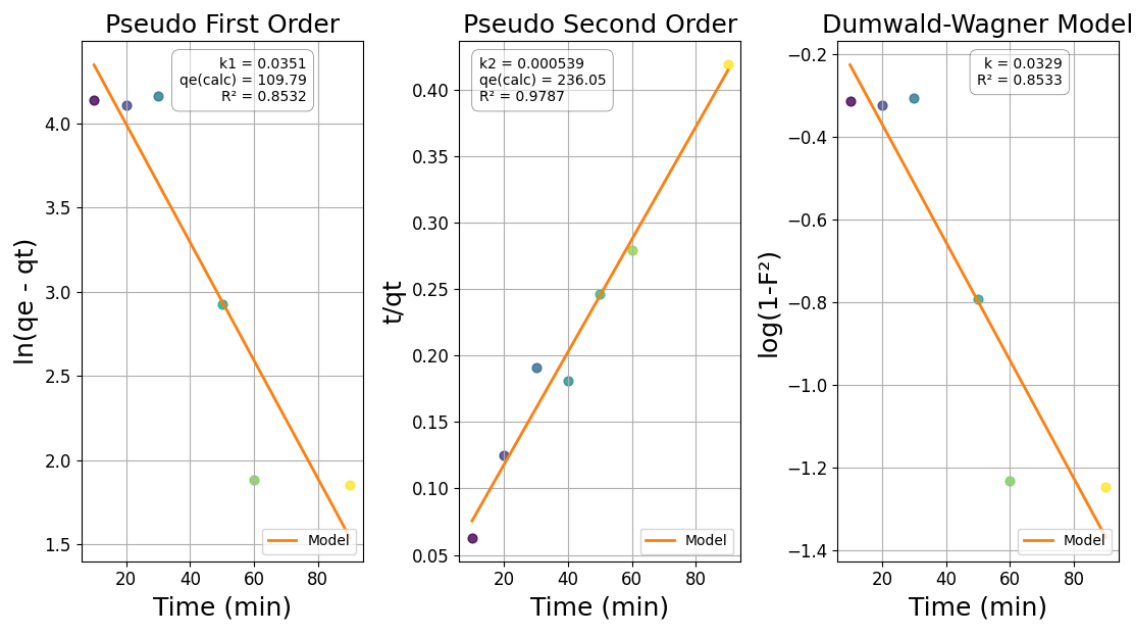
The adsorption mechanism of Pb(II) ions on AL@ZIF-8 composite hydrogel at an initial concentration of 500 mg/L and a temperature of 50°C was investigated in detail at different ZIF-8 loading rates (2%, 4% and 6%). According to the kinetic analysis results, at all ZIF-8 loading rates, the pseudo-second order kinetic model exhibited the highest correlation coefficients ($R^2 = 0.9787, 0.9933, \text{ and } 0.9798$, respectively). These results confirm that the adsorption process is mainly controlled by the chemical adsorption mechanism under high temperature and concentration conditions.

An increase in the pseudo second-order rate constant (k_2) was observed with the increase in temperature from 23°C to 50°C for all ZIF-8 loading rates. This increase was 1.57-fold at 2% loading, 3.31-fold at 4% loading and 1.82-fold at 6% loading. This was found when investigating the effect of temperature on adsorption kinetics. However, a small increase of nine percent was observed at 4% loading, although the k_2 values decreased by 36 percent and 53 percent at 2% and 6% ZIF-8 loading at temperatures between 40 and 50 degrees Celsius, respectively. From these results, it can be deduced that the adsorption kinetics in the range of 40°C to 50°C exhibit different behaviors depending on the ZIF-8 loading rate considered. One of the most favorable rates in terms of kinetics under these conditions is a 4% ZIF-8 loading, which has the largest rate constant (0.001187 g/mg-min) at 50°C. This rate also happens to be the most favorable rate.

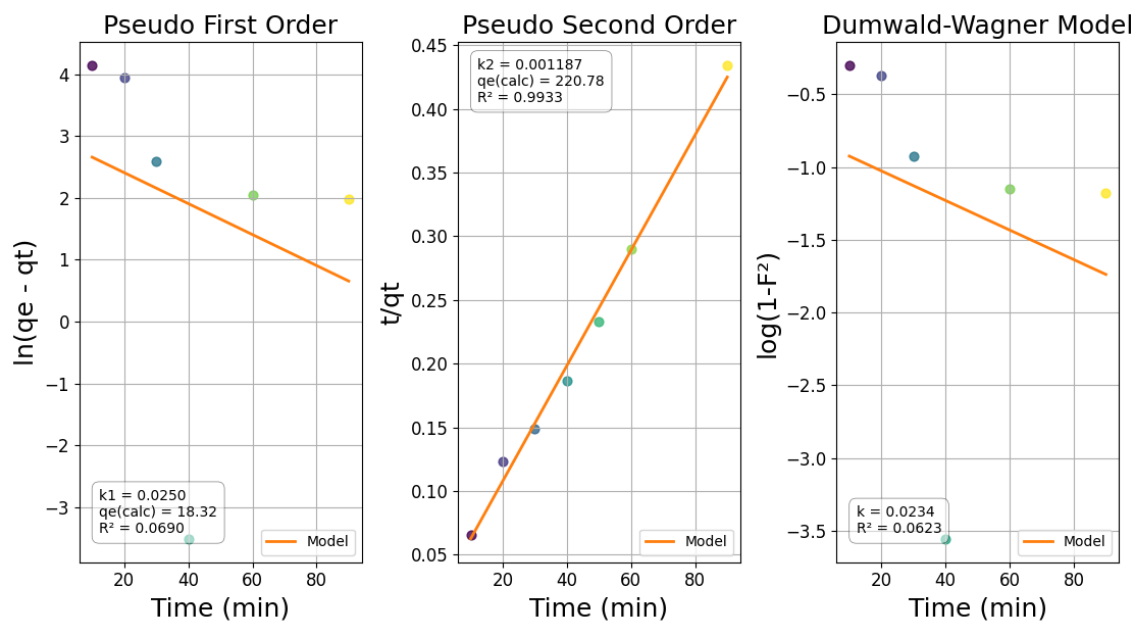
The investigation of the equilibrium adsorption capacities (q_e) showed that the temperature increase has different effects depending on the ZIF-8 loading rate. When the temperature was increased from 23 degrees Celsius to 50 degrees Celsius, the adsorption capacity increased by 5.2%, from 224.38 mg/g to 236.05 mg/g. This occurred when the ZIF-8 loading was 2%. In contrast, when the temperature was raised to a higher level, there was a decrease in capacity observed at both 4 and 6 times loading. The loss amounted to 3.7% and 10.9% respectively. When the temperature was increased from 40 degrees Celsius to 50 degrees Celsius, it was observed that the adsorption capacity increased to 17.35 mg/g and 7.91 mg/g at 2 and 4 ZIF-8 loading, respectively. According to these findings, the rate of 2% ZIF-8 loading is the most appropriate in terms of adsorption capacity when the temperature is at a high level (50 degrees Celsius). When the correlation coefficients were examined, minimal changes in the R^2 values of the pseudo-second order model were observed with the increase in temperature from 23°C to

50°C. Slight decreases were recorded at all loading rates from 40°C to 50°C. This shows that the adsorption mechanism at high temperatures such as 50°C is still mainly controlled by chemical adsorption, but the contribution of other mechanisms also increases. When the competition between diffusion and chemical reaction mechanisms was studied, different behaviors were observed depending on the ZIF-8 loading. At 2% ZIF-8 loading, the ratio $R^2(\text{PSO})/R^2(\text{DW})$ was 1.20 at 23°C, increased to 1.73 at 40°C and decreased to 1.15 at 50°C, indicating that chemical adsorption is more dominant at intermediate temperatures (40°C), while the contribution of diffusion relatively increases at high temperatures (50°C). For a 4% ZIF-8 loading, this ratio was 1.14 at 23°C and 1.04 at 40°C, while it increased to 15.94 at 50°C. This dramatic increase shows that the adsorption process at this loading ratio is almost completely controlled by chemical reactions at high temperatures. At 6% loading, this ratio was 1.80 at 40°C and decreased to 1.04 at 50°C, indicating that the contribution of diffusion mechanisms increases at high temperatures. When the rate constants and correlation coefficients of the pseudo-first order and Dumwald-Wagner models are examined at 50°C, it is found that these two models have very similar values at all ZIF-8 loading rates. While the ratios of the rate constants (k_1/k_2) vary between 1.07-1.08, the differences between the R^2 values are very small (between -0.0059 and 0.0067). The nearly similar R^2 values of these two models (the difference is only -0.0001), particularly at a loading of 2%, demonstrate that both surface reactions and intraparticle diffusion are equally significant in high-temperature adsorption.

The essential importance of optimizing the ZIF-8 loading rate becomes clear when the adsorption capacity and rate at an initial concentration of 500 mg/L and a high temperature setting of 50°C are examined together. This concentration and temperature combination is used for the evaluation. While a ZIF-8 loading of 2% results in the maximum adsorption capacity (236.05 mg/g), a ZIF-8 loading of 4% leads to the highest adsorption rate ($k_2 = 0.001187$ g/mg-min). At a loading of 6%, the performance decreases, both in terms of capacity and rate of the system.



(a)



(b)

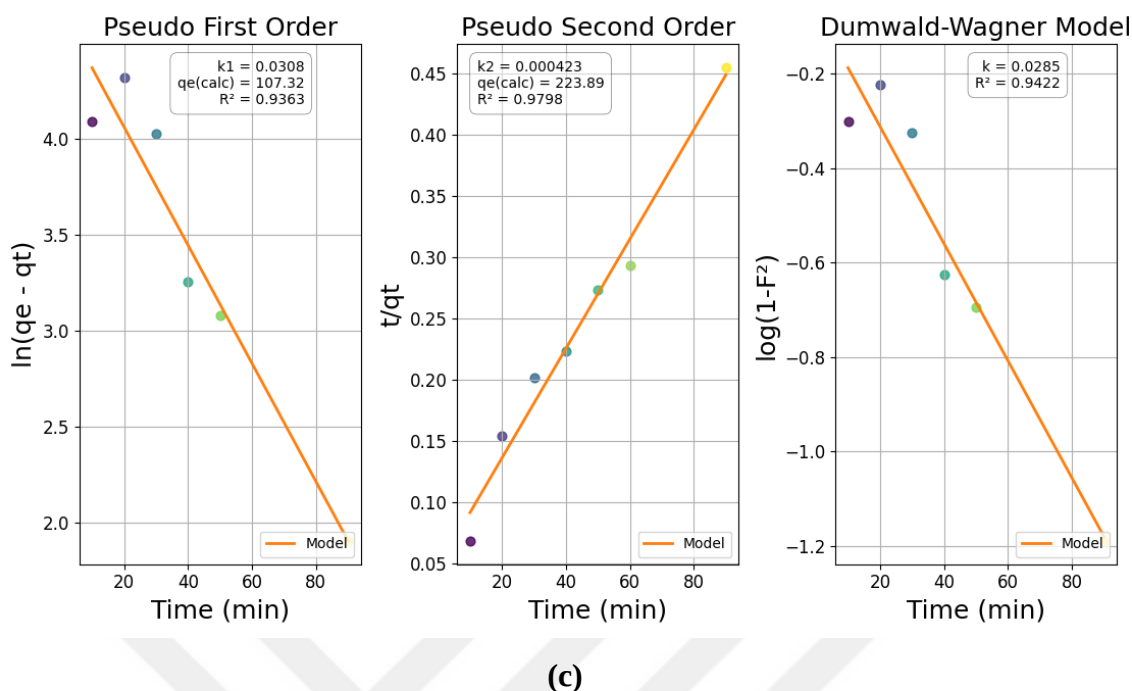


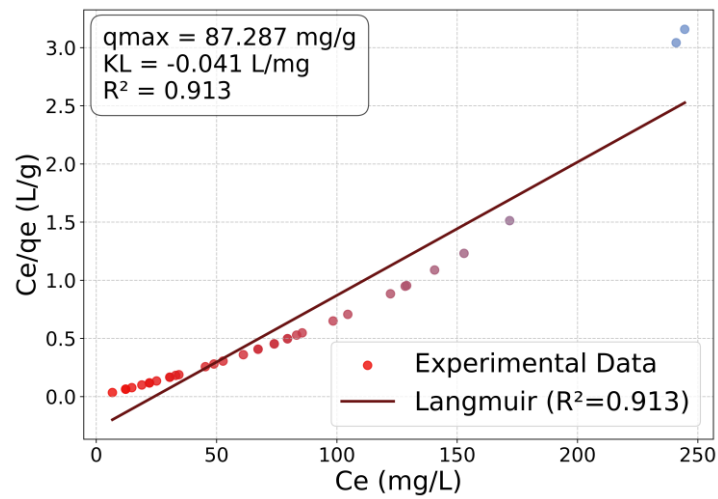
Figure 5.11: Adsorption kinetic analysis for determining predominant adsorption mechanism of Pb(II) ions onto AL@ZIF-8 using chemical reaction and intraparticle diffusion models: Effect of ZIF-8 loading ratios (a) 2%, (b) 4%, and (c) 6% at initial Pb(II) concentration of 500 mg/L and Temperature of 50°C.

5.5. Thermodynamic Analysis

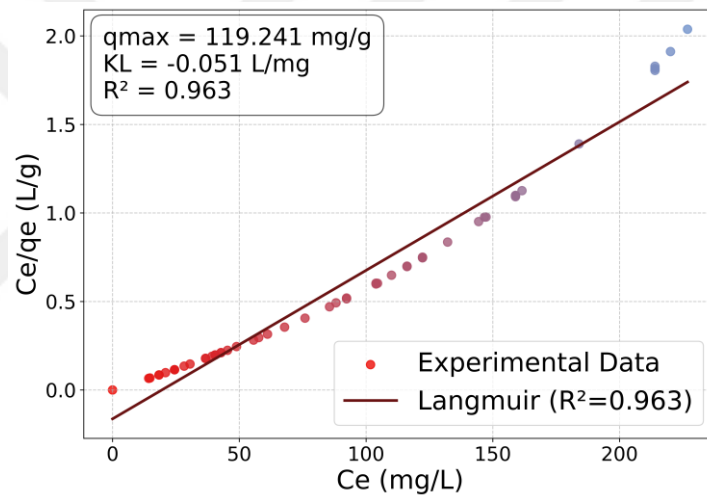
5.5.1. Adsorption Isotherms

5.5.1.1. Langmuir Adsorption Isotherm Curves

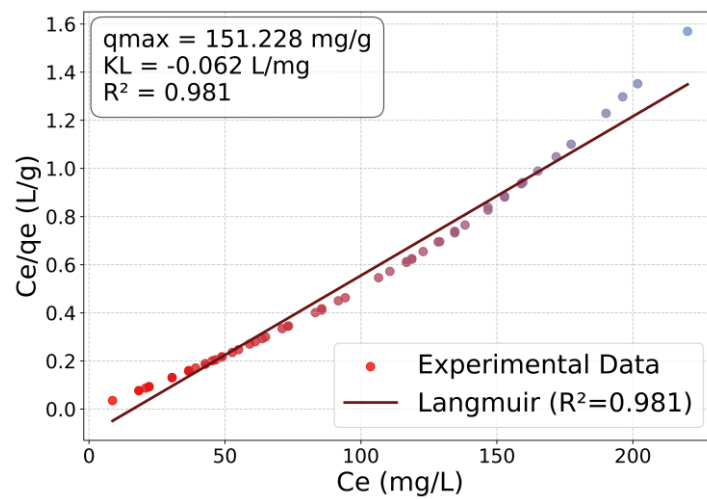
The Langmuir isotherms determined for the removal of Pb(II) using AL@ZIF-8 composite material provide important information about both the maximum adsorption capacity of the material and the adsorption mechanism.



(a)



(b)



(c)

Figure 5.12: Langmuir Isotherm Curves: (a) 400 mg/L, (b) 450 mg/L, (c) 500 mg/L

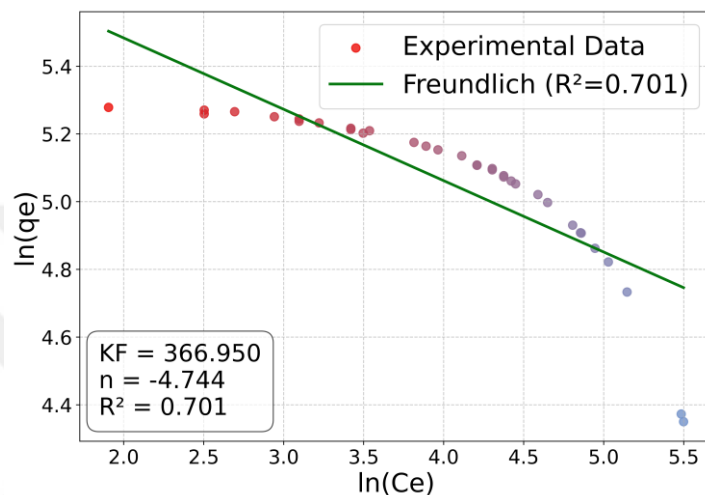
Examining the graph (or experimental conditions) in **Figure 5.12**, it is clear that the $q_{\max}$, K_L and R^2 values for three different initial Pb(II) concentrations (400 mg/L, 450 mg/L and 500 mg/L) change as a function of the initial concentration. For a Pb(II) concentration of 400 mg/L, $q_{\max}$ was determined as 87.287 mg/g, K_L as -0.041 L/mg and R^2 as 0.913 according to the Langmuir isotherm. At 450 mg/L Pb(II) concentration, these values were determined as $q_{\max} = 119.241$ mg/g, $K_L = -0.051$ L/mg and $R^2 = 0.963$. At 500 mg/L Pb(II) concentration, $q_{\max}$ was 151.228 mg/g, K_L -0.062 L/mg and R^2 0.981. The $q_{\max}$ value represents the monolayer capacity, which is described as the maximum capacity of the AL@ZIF-8 composite to remove Pb(II). On the other hand, the K_L value determines the adsorption affinity or strength of the AL@ZIF-8 composite. It can be seen that the AL@ZIF-8 composite exhibits an increasing affinity for Pb(II) ions and gradually conforms to the Langmuir model. The increase in the $q_{\max}$ value from 87.287 mg/g to 151.228 mg/g with the increase in the initial Pb(II) concentration indicates that the maximum adsorption capacity of the composite continues to increase; the increase in the absolute values of the K_L values (albeit with a negative sign) indicates that the interaction between the adsorbent and Pb(II) is enhanced. The increase in the R^2 value from 0.913 to 0.981 is also important to show that the fit of the experimental data to the Langmuir model is gradually improving.

Alginate is a natural polysaccharide that exhibits high interactions with heavy metal ions due to the many carboxyl groups in its structure. Positively charged Pb(II) ions may engage with the carboxylate groups of alginate via coordinative bonding and electrostatic attraction. ZIF-8 is a highly porous metal-organic framework (MOF) composed of coordinated Zn(II) ions and imidazolate ligands. The large internal surface area of ZIF-8 facilitates the transport and retention of heavy metal ions to the surface. While the polyanionic structure of alginate attracts heavy metal ions to the surface, the porous internal structure and nitrogen-containing ligands of ZIF-8 increase the adsorption capacity by creating additional binding sites. As a result, the high $q_{\max}$ values and the increased R^2 ratios indicate that AL@ZIF-8 is a very effective and efficient material for the adsorption of heavy metals. Therefore, the AL@ZIF-8 composite can be evaluated as

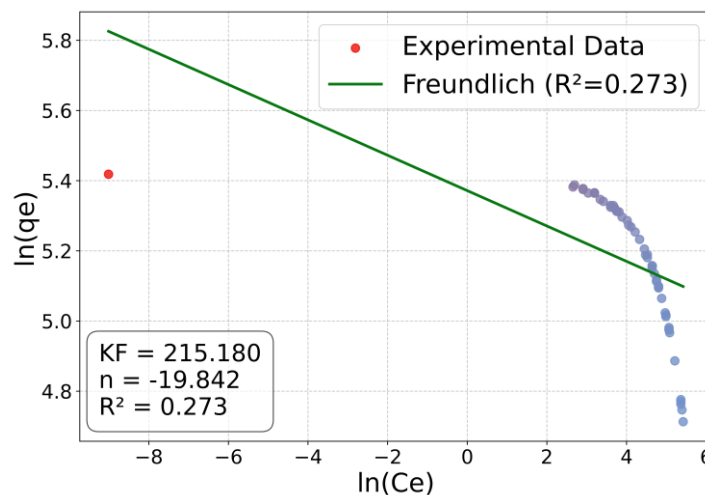
a strong adsorbent for various applications in water treatment, especially for the removal of Pb(II).

5.5.1.2. Freundlich Adsorption Isotherm Curves

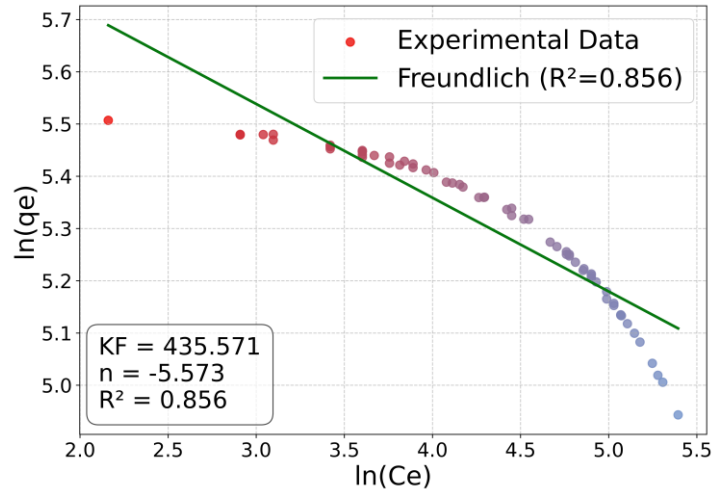
The adsorption behavior of AL@ZIF-8 composite material at different initial Pb(II) concentrations (400, 450 and 500 mg/L) was evaluated using the Freundlich isotherm.



(a)



(b)



(c)

Figure 5.13: Freundlich Isotherm Curves: (a) 400 mg/L, (b) 450 mg/L, (c) 500 mg/L

The KF value for a concentration of 400 mg/L Pb(II) was calculated as 366.950 (mg/g)(L/mg)^(1/n). This high KF value shows that the AL@ZIF-8 composite has a high adsorption capacity at this concentration. However, the negative value of n (-19.842) indicates a significant deviation from the classical Freundlich assumptions. Contrary to expectations, this negative value shows a decreasing tendency of the adsorption capacity with increasing Pb(II) concentration and is the result of lateral interactions between the ions and the saturation of the high-energy regions. The R² value determined at this concentration (0.701) shows moderate agreement with the Freundlich model.

At a concentration of 450 mg/L, the KF value decreased significantly to 215.180 (mg/g)(L/mg)^(1/n). The more pronounced negative n value shows that the adsorption mechanism is in a transitional state at this concentration and the energetic heterogeneity of the adsorption areas increases. The R² value of 0.748 shows that the adsorption behavior at this concentration can be explained to a limited extent by the Freundlich model. At 500 mg/L, the KF value increased to 435.571 (mg/g)(L/mg)^(1/n), and the n value reached -5.573. This increase in the KF value indicates that the adsorption capacity increased again. At this point, effective filling may have occurred in the adsorption regions of the AL@ZIF-8 composite (especially in the ZIF-8 pores). In addition, the increase in the R² value to 0.972 indicates that the adsorption behavior became more

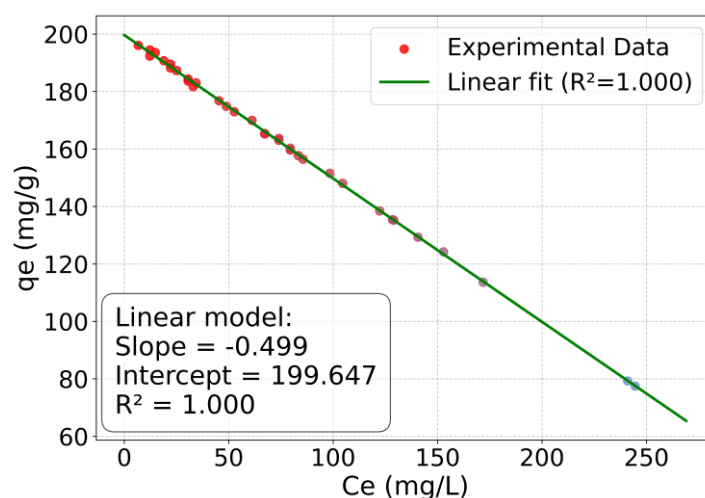
homogeneous again at this concentration and the agreement with the Freundlich model increased.

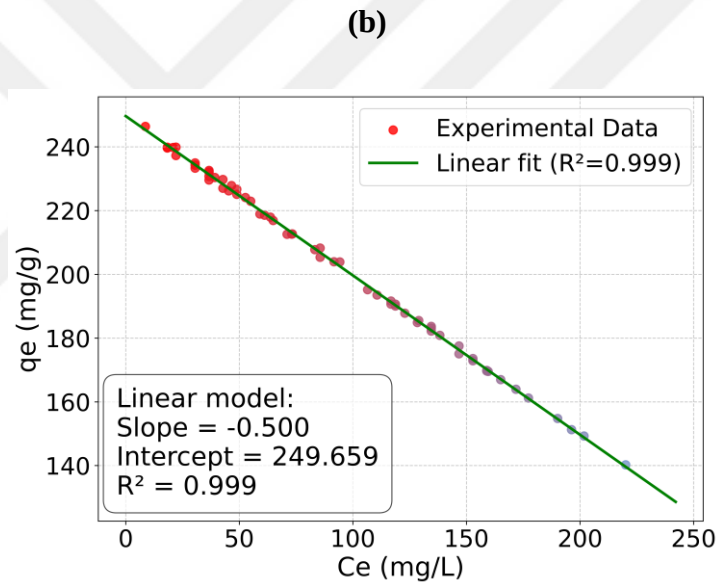
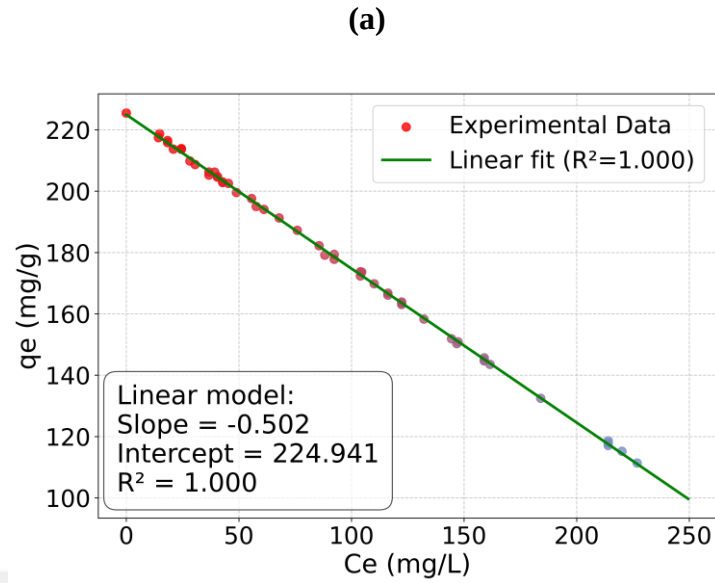
The observed change in R^2 values as a function of concentration (400 mg/L: 0.701, 450 mg/L: 0.273, 500 mg/L: 0.856) technically shows the heterogeneous structure and the transitional stages of the adsorption mechanism. The low R^2 value observed at a concentration of 450 mg/L indicates the critical region where surface heterogeneity is greatest and adsorption exhibits complex transition mechanisms. When examined at the molecular level, at low concentrations the Pb(II) ions adsorb mainly on the carboxylate groups of the high-affinity G-blocks in the alginate structure, while at medium and high concentrations diffusion occurs towards the pores of ZIF-8. At high concentrations, the adsorption mechanism is more in the form of physical adsorption and surface precipitation. This situation provides a technical evaluation that explains the multi-layered and heterogeneous adsorption capacity of the AL@ZIF-8 composite in different concentration ranges.

5.5.1.3. Jovanović Adsorption Isotherm Curves

Examining the graphs in Figures 1-3, it is clear that the $q_{\max}$, slope, and R^2 values for three different initial Pb(II) concentrations (400 mg/L, 450 mg/L, and 500 mg/L) change systematically as a function of the initial concentration. Pb(II) concentration of 450 mg/L (Figure 2), these values were determined as $q_{\max} = 224.941$ mg/g, slope = -0.502 and $R^2 = 1.000$. At a Pb(II) concentration of 500 mg/L (Figure 3), $q_{\max}$ increased to 249.659 mg/g with a slope of -0.500 and $R^2 = 0.999$. The Jovanović model, expressed mathematically as $q_e = q_{\max}(1 - e^{(-KJCe)})$, assumes monolayer adsorption with possible mechanical contacts between the adsorbate molecules. The linearized form $\ln(q_e) = \ln(q_{\max}) - KJCe$ gives the values for slope (-KJ) and intercept ($\ln(q_{\max})$) observed in the figures. The consistent slopes of about -0.500 L/mg at all concentrations indicate that the Pb(II) ions interact with the AL@ZIF-8 composite material via a uniform binding energy distribution and suggest homogeneous adsorption sites despite the heterogeneous structure of the composite material. The adsorption process may be described at the molecular level by the coordination chemistry that exists between the functional groups and the lead ions that are present in the AL@ZIF-8 composite. In the structure of alginate, the G-blocks are composed of α -L-gluronate residues that are bonded to axial-axial (a,a)

glycosidic linkages. These G-blocks also create cavities that are shaped like egg cartons and have certain geometric patterns. The formation of these cavities occurs when divalent cations, such as lead ions, coordinate with surrounding G-blocks. Typically, each lead ion coordinates with four carboxylate oxygen atoms and two hydroxyl groups, resulting in the formation of a deformed octahedral coordination sphere. The sodalite structure (SOD) of ZIF-8, which is defined by the tetrahedral coordination of Zn^{2+} ions with four 2-methylimidazolate ligands, offers extra adsorption sites. This is the case simultaneously. It is possible for the lone pairs that are present in the nitrogen atoms of the imidazolate rings to establish coordination bonds with the ions of Pb^{2+} . The size of the pore opening (3.4 Å) and the larger inner cavity (11.6 Å) of ZIF-8 enable size-selective adsorption, while the hydrophobic nature of the inner cavity creates a favorable environment for the sequestration of metal ions after passing through the pore openings. The increase in q_{max} values with increasing initial Pb^{2+} concentration (from 199.647 to 249.659 mg/g) can be attributed to the improved mass transfer kinetics. Higher concentration gradients allow higher diffusion rates of Pb^{2+} ions out of the boundary layer surrounding the AL@ZIF-8 particles and into the inner porous network. This phenomenon follows Fick's law of diffusion, where the flux is proportional to the concentration gradient. From a thermodynamic point of view, the adsorption process is exothermic, as evidenced by the negative gradients. The adsorption energy ($\Delta G^{\circ}_{\text{ads}}$) can be related to the Jovanovic constant (KJ) via the relationship $\Delta G^{\circ}_{\text{ads}} = -RT \ln(\text{KJ})$. The consistent KJ values at different concentrations indicate that adsorption is determined by similar energetic parameters regardless of the initial concentration.





(c)

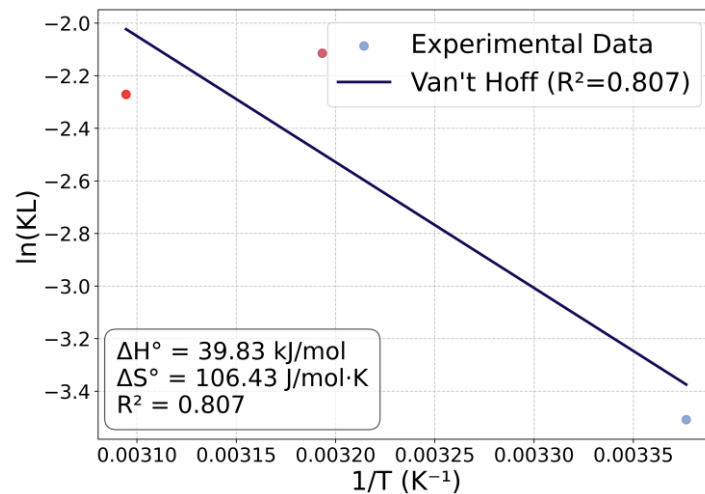
Figure 5.14:Jovanović Isotherm Curves: (a) 400 mg/L, (b) 450 mg/L, (c) 500 mg/L

The excellent fit to the Jovanović model indicates that the adsorption process involves significant surface interactions where the distribution of binding energies plays an important role. The polyanionic structure of alginate attracts Pb(II) ions to the surface, while ZIF-8's porous framework and nitrogen-containing ligands create additional binding sites that become increasingly utilized at higher initial Pb(II) concentrations.

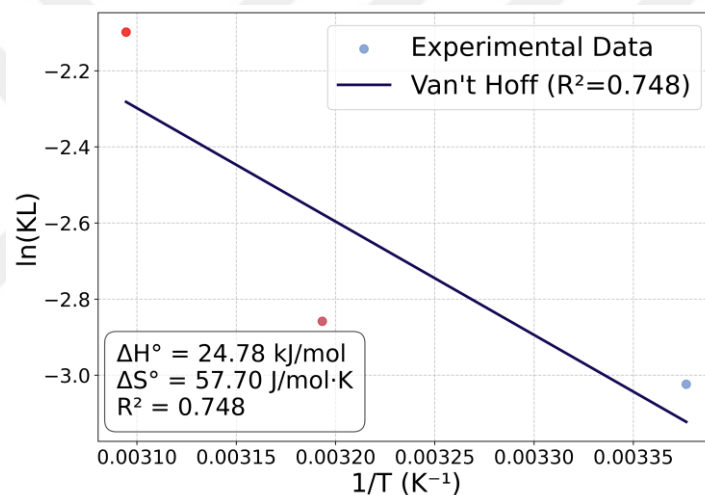
5.5.2. Thermodynamic Analysis

The adsorption mechanism of AL@ZIF-8 composite towards Pb(II) ions was thermodynamically investigated at different initial concentrations (400, 450 and 500 mg/L). It was observed that the enthalpy (ΔH°) and entropy (ΔS°) values, calculated using the Van't Hoff equation, changed systematically with increasing concentration.

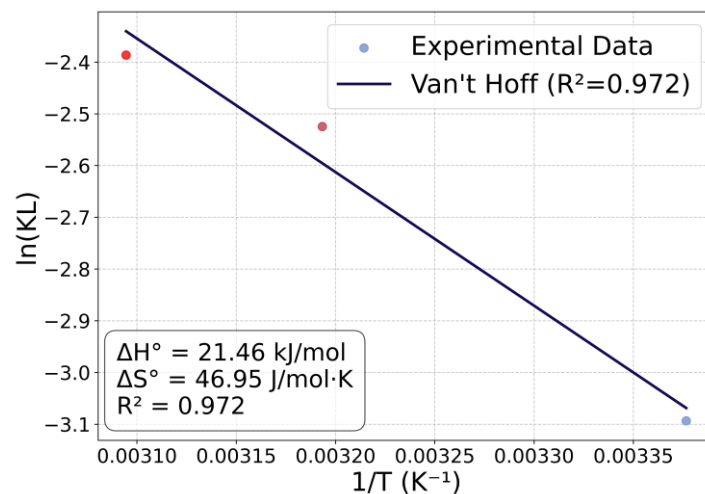
The ΔH° value determined at a Pb(II) concentration of 400 mg/L was 39.83 kJ/mol, indicating that the adsorption was clearly endothermic. At this stage, the Pb(II) ions bind to high-energy regions by forming strong electrostatic interactions and coordination bonds with the carboxylate groups (-COO-) of the alginate. During this binding, the hydration shells of the Pb(II) ions are removed, which requires a lot of energy. At a concentration of 450 mg/L Pb(II), the ΔH° value decreases to 24.78 kJ/mol, indicating that the adsorption mechanism has changed. As the high-energy regions fill up, the Pb(II) ions move towards the porous structure of ZIF-8 and the lower affinity regions. Both the strength and the energy level of the coordination contacts made with the imidazolate nitrogen atoms in ZIF-8 are lower. When the concentration of ΔH° drops to 500 mg/L, the value of ΔH° drops even further to 21.46 kJ/mol. At this concentration, the Pb(II) ions can penetrate into the micropores and the inner parts of ZIF-8. Physical adsorption, van der Waals interactions and weak coordination interactions are in the foreground in these areas. In addition, lateral interactions between Pb(II) ions and surface precipitation mechanisms come into play. The entropy changes (ΔS°) decrease with increasing concentration (106.43 J/mol K at 400 mg/L, 57.70 J/mol K at 450 mg/L, 46.95 J/mol K at 500 mg/L). The high entropy increase at a concentration of 400 mg/L is due to the release of a large number of water molecules by the removal of the hydration shells of the Pb(II) ions. As the concentration increases, the surface areas are filled up and the freedom of movement of the ions decreases, which limits the entropy increase.



(a)



(b)



(c)

Figure 5.15: Van't Hoff Thermodynamic Calculations: (a) 400 mg/L, (b) 450 mg/L, (c) 500 mg/L

The mechanism at the molecular level can be explained as follows: At low concentrations, the Pb(II) ions bind to the "egg-box" structures in the high-affinity G-blocks of the alginate, while at high concentrations they bind to the M-blocks and monodentate carboxylate groups. While the pore openings of ZIF-8 initially show only limited interaction, the diffusion of Pb(II) ions into the inner pores increases at high concentrations. The adsorption rate also increases with increasing concentration. While a diffusion-limited process prevails at low concentrations, mass transport accelerates at high concentrations. In addition, the possible decrease in the pH value of the solution at high Pb(II) concentrations can change the adsorption mechanism from electrostatic interactions to coordination bonds. With increasing concentration, the R^2 values first decreased and then increased (400 mg/L: 0.807, 450 mg/L: 0.748, 500 mg/L: 0.972). The low value at 450 mg/L indicates that the adsorption is in the transition phase, while the high value at 500 mg/L indicates that the adsorption mechanism is becoming more stable.

5.6. Artificial Intelligence

The interpretation of the data obtained from experimental studies and the determination of the optimum adsorption conditions are of crucial importance for increasing the efficiency of the process. Especially in adsorption processes, where complex and non-linear relationships exist, it can be difficult to make predictions with the desired accuracy using classical statistical methods. At this point, advanced approaches such as ANFIS (Adaptive Network Based Fuzzy Inference System), a combination of techniques such as artificial intelligence-based methods, in particular fuzzy logic and artificial neural networks, come to the fore.

In this thesis, an ANFIS-based model was developed to more accurately and reliably analyse and predict the effectiveness of AL@ZIF-8 composite hydrogels in the removal of Pb(II) ions. In the modelling phase, the experimental data were first divided into training and test data sets, and then the internal consistency and representativeness of

these data sets were evaluated with statistical analyses. Correlation matrix analyses and joint plot analyses were used to demonstrate the quality and suitability of the data selected for the ANFIS model. In this way, a solid data infrastructure was created to accurately and consistently represent the dynamics of the adsorption process and the interactions between the parameters. In the final phase, the ANFIS model was trained, the predictive success of the model was evaluated and its ability to predict the optimal conditions for Pb(II) adsorption performance was demonstrated.

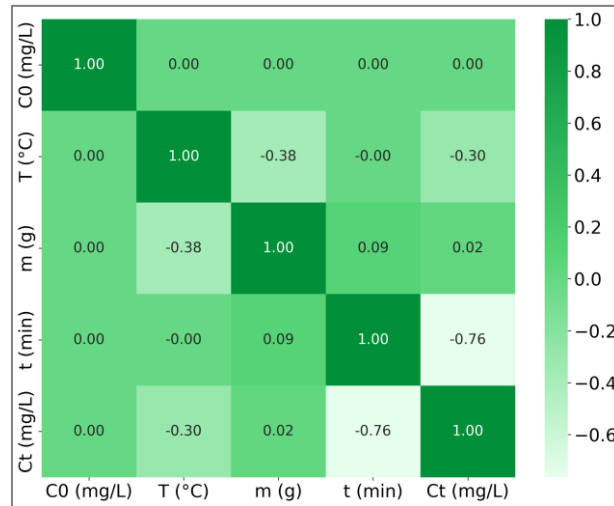
5.6.1. Data Analysis for ANFIS

As a result of the kinetic and thermodynamic analyses, it was observed that the best adsorption results for the initial concentration (C_0) were obtained at 500 mg/L, which provided the best result in terms of performance, was preferred to be used in the prediction studies as an artificial intelligence approach to be carried out with the ANFIS model. Thus, it was aimed to increase the accuracy and prediction ability of the model. In this context, training ($n=53$) and test ($n=10$) datasets, which are randomly separated from the experimental dataset for 500 mg /L in MATLAB, are used to verify the effectiveness and generalizability of the ANFIS model. This separation allows the model to be trained with training data and the performance of the trained model to be evaluated on an independent dataset with test data. On the other hand, it is crucial to do a statistical analysis on the experimental data set, as well as the training and test data sets that were randomly divided in the MATLAB environment, before building the ANFIS model. At this stage, correlation matrix analysis (heat maps) and joint plot analysis are used to evaluate the internal consistency and representativeness of the data sets. Correlation matrix analysis enables the determination of the critical parameters affecting Pb (II) adsorption performance by quantifying the strength and direction of the relationship between the parameters. Joint plot analysis, on the other hand, visually shows the relationships between two parameters and the marginal distributions of these parameters and allows the quality of the split of the data sets and the statistical compatibility of different data sets to be assessed. In this context, the relationships between operating parameters such as contact time, temperature and adsorbent mass and the final Pb (II) concentration are expressed numerically, and the robustness and suitability of the data sets for ANFIS modeling is checked.

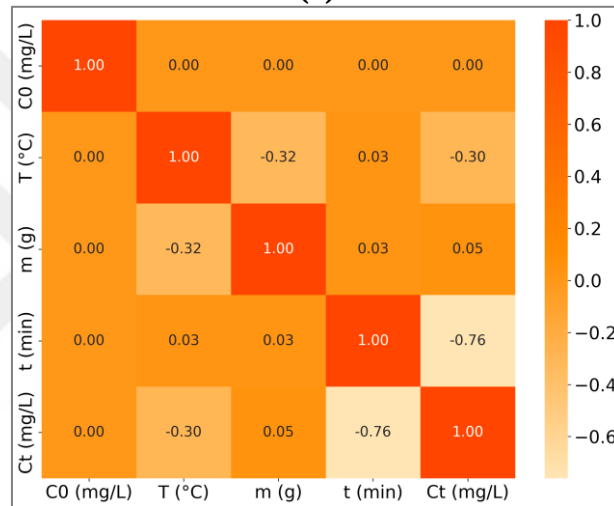
5.6.1.1. Correlation Matrice Analysis

Correlation matrices or heatmaps show visually and quantitatively the relationships between the parameters that influence the adsorption performance of AL@ZIF-8 composite material in the removal of Pb (II). The training (n=53) and test (n=10) datasets obtained from the experimental dataset and randomly separated in the MATLAB environment for the development of the ANFIS model clearly show the consistency of the correlations between the parameters. According to the matrices values in the experimental dataset (green), test (blue) and training (orange) datasets, the strongest relationship is the negative correlation between contact time (t) and adsorption concentration (Ct).

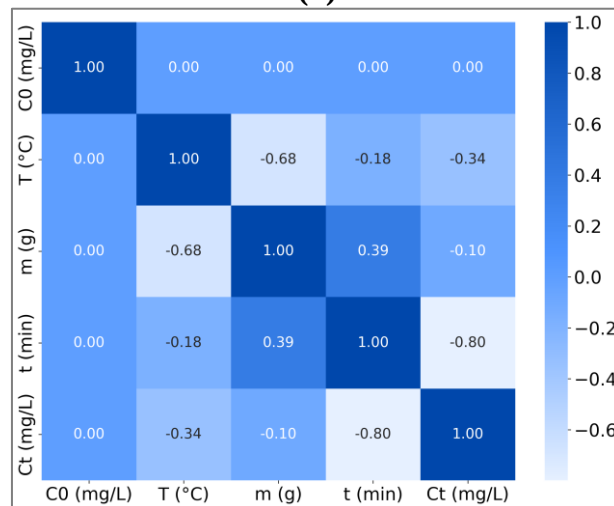
Figure 5.16. Correlation matrices (heat maps) for Pb (II) removal using AL@ZIF-8 composite material: (a) experimental dataset (green), (b) training dataset (orange) and (c) test dataset (blue). Temperature (T) shows a slightly negative relationship with Ct, with correlation coefficients of -0.30 in the combined dataset, -0.34 in the test dataset and -0.30 in the training dataset. This means that increasing the temperature increases the adsorption efficiency but does not have as strong an effect as the contact time. The mass of adsorbent (m) shows a very low and inconsistent correlation with Ct in the combined (0.02), test (-0.10) and training (0.05) data sets. The relationship between temperature and adsorbent mass is shown with strongly negative (-0.68) correlation values in the test data set, moderately negative (-0.38) in the combined data set and moderately negative (-0.32) in the training data set. This illustrates the temperature-mass relationship, which should be considered when planning the experiment.



(a)



(b)



(c)

Figure 5.16: Prediction Density Counter: (a) All Dataset, (b) Training Data, (c) Test Data

The similarity of the correlation coefficients in the training and test data sets (e.g. -0.76 in training and -0.80 in test for t-Ct; -0.30 in training and -0.34 in test for T-Ct) confirms the reliability of the data partitioning. This consistency indicates that the data sets are randomly and correctly partitioned to represent the dynamics of the AL@ZIF-8 adsorption process and that the model is capable of providing reliable results in practical applications. In summary, these correlation analyses quantitatively confirm that contact time is the most important parameter for optimizing Pb (II) adsorption performance.

5.6.1.2. Joint Plot Analysis

The joint plot analysis is a powerful way to visually represent the relationship between variables. This type of chart shows the relationship between variables with the scatter plot in the center, while the individual distribution characteristics of each variable are combined with histograms or KDE (Kernel Density Estimation) curves at the edges and displayed in a single image. The analyzed experimental data set investigates the relationship between concentration (Ct) and three parameters: reaction time (t), temperature (T) and adsorbent mass (m). The common diagrams used in the examples focus specifically on the relationship between reaction time and concentration. The colors in the figures represent the common data set in green, the test data set in blue and the training data set in orange.

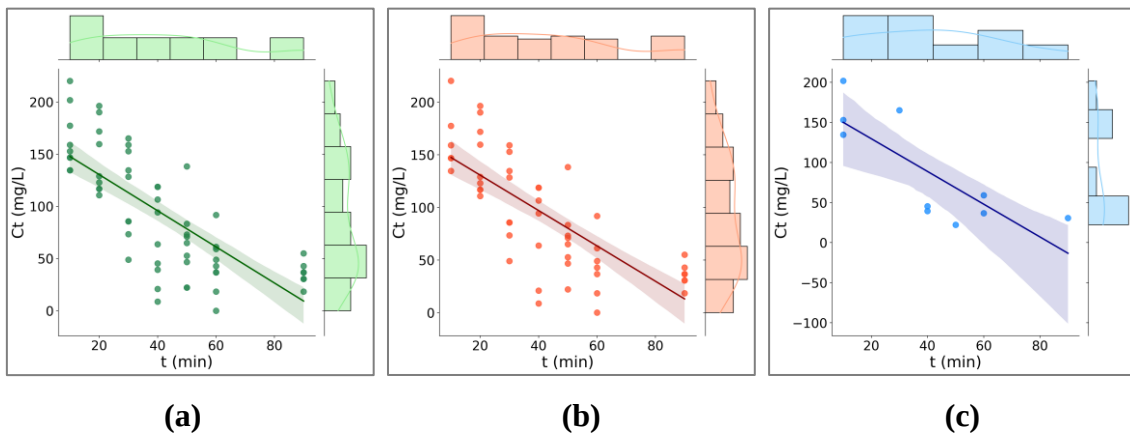


Figure 5.17: The relationship between concentration (Ct) and reaction time (t): (a) All Dataset, (b) Training, (c) Test

In all graphs, the concentration values (Ct) are between 18.3 mg/L and 220.1 mg/L, and the data set is divided into training (n=30, 75%) and test (n=10, 25%) groups accordingly. The training and test subgroups have very similar concentration ranges (18.3-220.1 mg/L in training and 22.1-201.8 mg/L in test) and show similar multimodal distributions. Clear peaks around 25-50 mg/L and 100-160 mg/L were observed in both data sets.

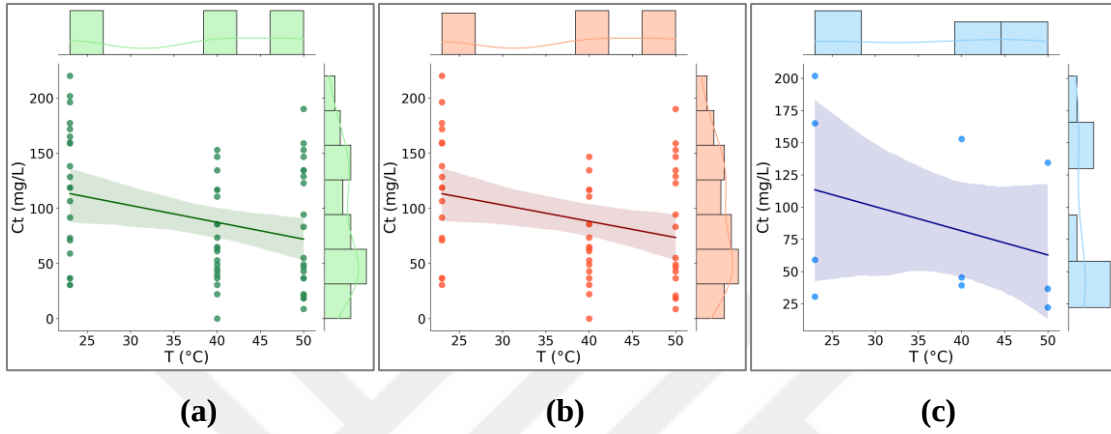


Figure 5.18:The relationship between concentration (Ct) and temperature (T): (a) All Dataset, (b) Training, (c) Test

Two important experimental parameters, reaction time (10-90 min) and temperature (23°C, 40°C and 50°C), are closely related to concentration in all data sets. In the time-based analysis, the regression slopes are approximately -1.37 mg/L/min (± 0.31) for the training data and -1.52 mg/L/°C for the test data. These consistent slope values confirm the representativeness of the split data set despite the different sample sizes. The colors used in the graphs (green for the combined data, blue for the test data) illustrate the statistical similarities between the two groups. In particular, the clear overlap of the confidence intervals (colored shaded areas) and the proximity of the trend lines indicate that the data groups are statistically similar and that a successful separation was achieved. However, the wider confidence interval and the steeper regression slope of the data in the test group are to be expected due to the smaller amount of data.

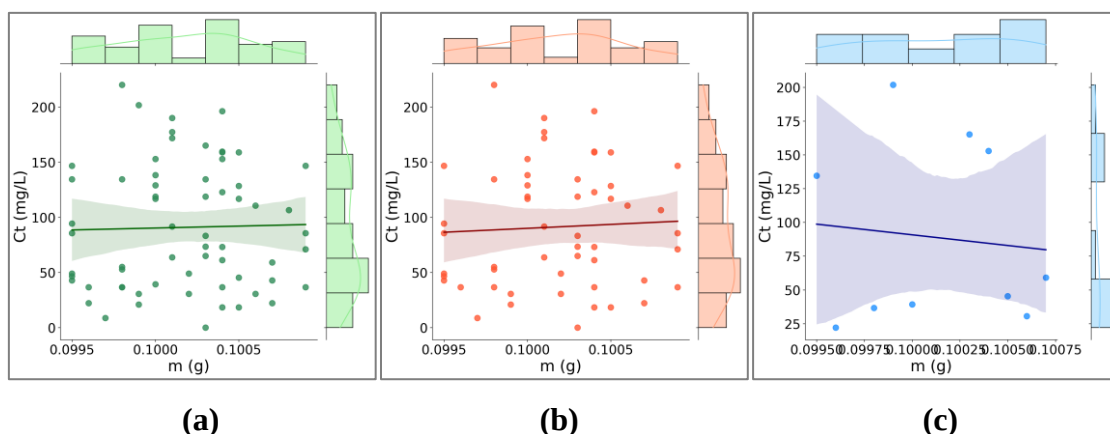


Figure 5.19: The relationship between concentration (C_t) and adsorbent mass (m): (a) All Dataset, (b) Training, (c) Test

For adsorption mass (between 0.0995-0.1009 g, less than 1.5 % change), inconsistent trends and low coefficients of determination (R^2 approx. 0.07-0.11) were observed. The plots obtained from the joint plot analysis show that the data set is randomly but homogeneously partitioned and that this partitioning allows early detection of problems such as data leakage or overfitting.

5.6.2. ANFIS Model

In modeling complex systems such as adsorption processes, classical methods may be inadequate, especially in the analysis of multi-parameter and nonlinear relationships. Therefore, the Adaptive Network-Based Fuzzy Inference System (ANFIS), which combines the strengths of artificial neural networks and fuzzy logic, is one of the widely preferred methods for effective and accurate modeling of the adsorption mechanism. The ANFIS model is of great importance in heavy metal removal studies as it is able to predict the impacts of the parameters within the system with high accuracy and reliability.

In this study, the ANFIS model was created to predict the adsorption process of Pb(II) ions with AL@ZIF-8 composite hydrogels more accurately and to provide a comprehensive analysis of the experimental data. For the modeling study, randomly divided training ($n=53$) and test ($n=10$) data sets were used in the MATLAB environment. Thanks to this approach, the learning and generalization capacity of the ANFIS model created was evaluated and the prediction accuracy and stability of the model were

demonstrated through numerical and graphical analyzes. The diagrams and evaluations presented in the following sections show the success of the ANFIS model in detail.

In the contour plot created for the training data (Figure 5.20(b)), it is observed that the predicted density is distributed along the perfect prediction line (red dashed line) in the range of 0-200 mg/L with high correlation ($R^2 > 0.99$ for training) and the density is between 3.0-4.5 especially in the concentration ranges of 35-50 mg/L and 100-150 mg/L.

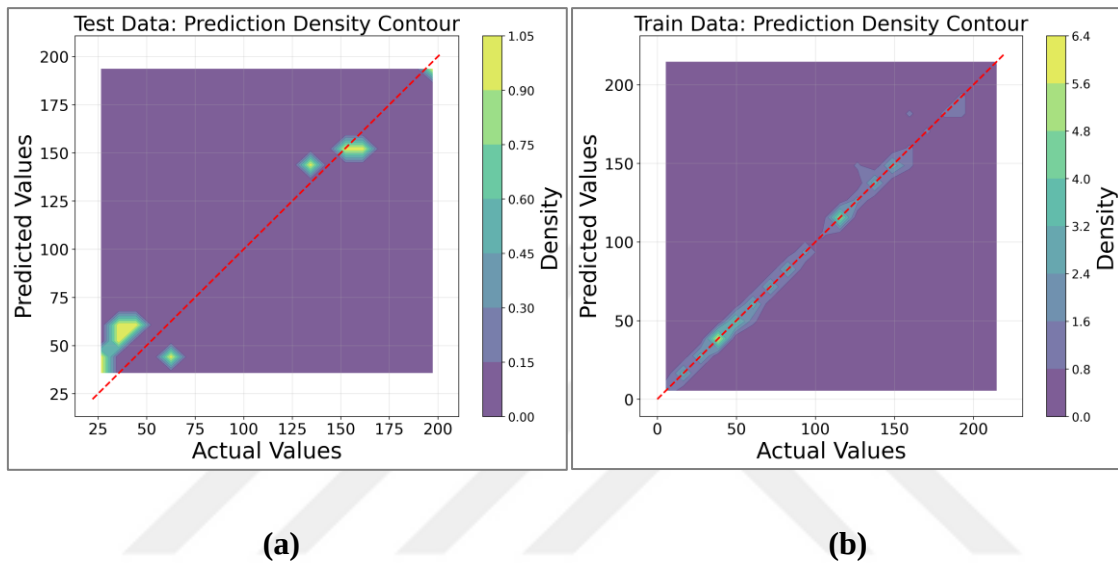
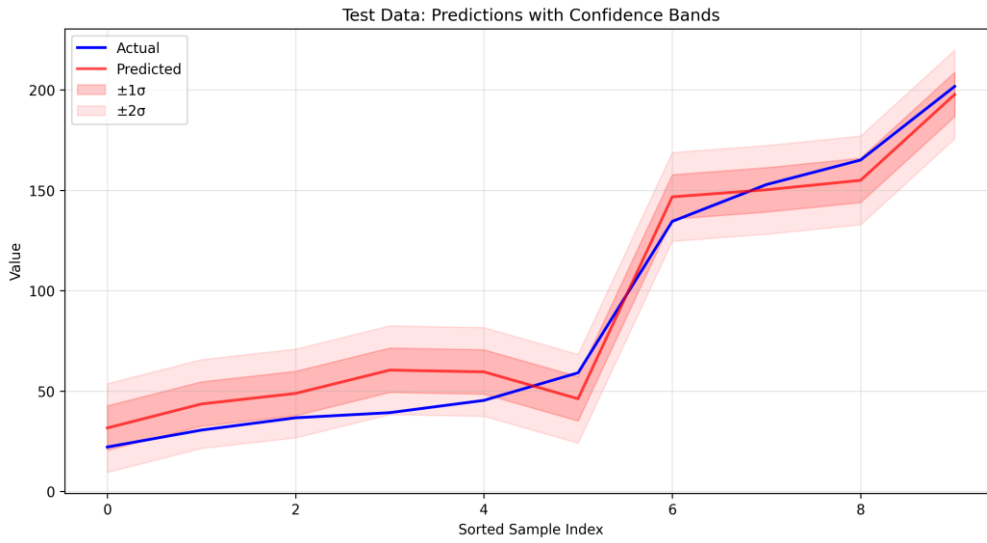
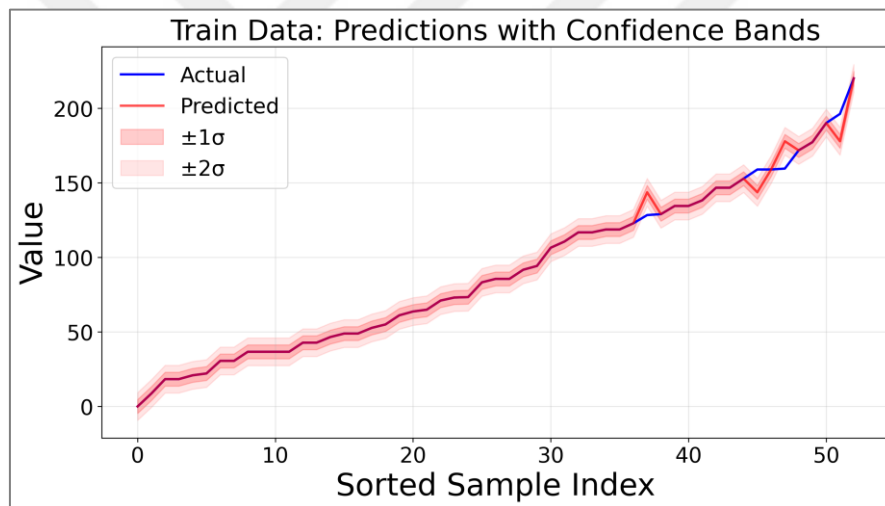


Figure 5.20: Prediction Density Contour: (a) Test Data, (b) Training Data

When the performance in the test data (Figure 5.20(a)) is examined ($R^2 > 0.96$), it is seen that the Pb(II) removal efficiency of the AL@ZIF-8 adsorbent material is concentrated in three different concentration regions (35-60 mg/L, ~45 mg/L and 140-155 mg/L) and the predicted density reaches the levels of 0.75-1.05 at these points. The model provides highly accurate predictions at specific concentration values where AL@ZIF-8 interacts and successfully characterizes the effectiveness of the adsorbent material, especially at low (35-60 mg/L) and high (145-155 mg/L) removal concentrations. The ANFIS hybrid structure was able to effectively model the complex adsorption mechanism of AL@ZIF-8 by means of fuzzy rules.



(a)



(b)

Figure 5.21: Predictions with Confidence Bands: (a) Test Data, (b) Training Data

In the confidence bands plot, particularly for tiny index values (between 0-4), the test results show notable differences between the actual values (blue line) and the anticipated values (red line) (Figure 5.21(a)). Low values are often overestimated by the model. The model predicts more accurately after the fifth index. However, there are a lot more data points (about 50 samples) in the training set (Figure 5.21(b)). The model matches the training data well, and predictions are significantly closer to the actual values. The

model's trust in the training data is demonstrated by the reduced confidence intervals ($\pm 1\sigma$ and $\pm 2\sigma$).

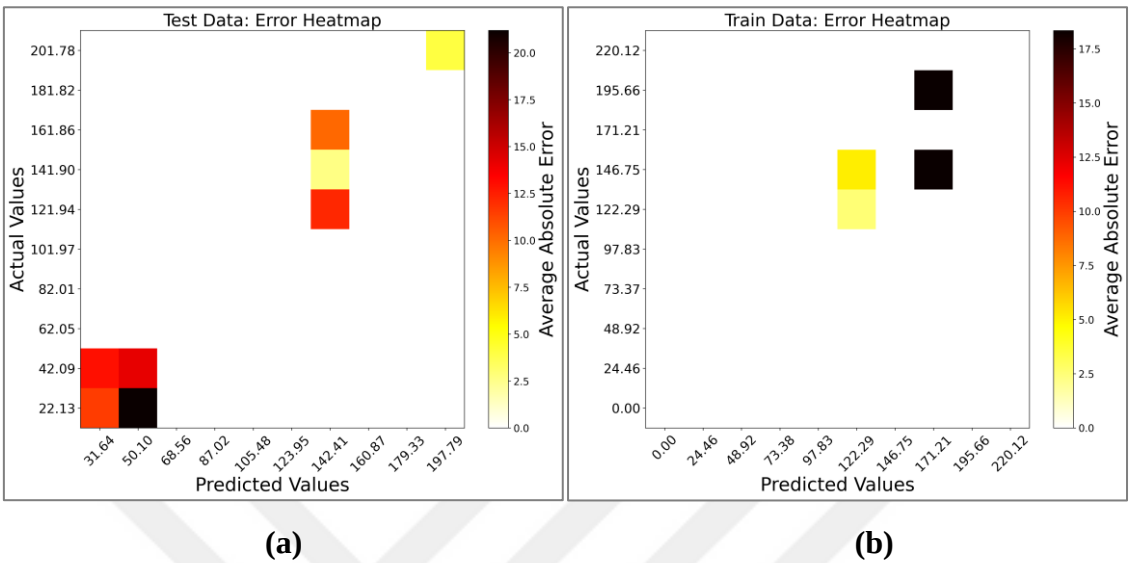


Figure 5.22:Error Heatmap: (a) Test Data, (b) Training Data

In the error heatmap plot, the highest mistake rates are displayed in the darkest regions (black/dark red) of the test error heatmap plot (Figure 5.22.(a)). Low projected values (50.10) and low true values (22.13) exhibit high mistakes. Errors are also present at high numbers (between 160 and 200). Significant errors are visible at higher values (range 140-220) in the training error heatmap display, Figure (5.22.(b)), although there are fewer problem zones overall. In the medium range (100-140), error rates are lower. In a nutshell, both images use a color scale to display the absolute error between the true and anticipated numbers. Higher mistake rates are shown by darker colors.

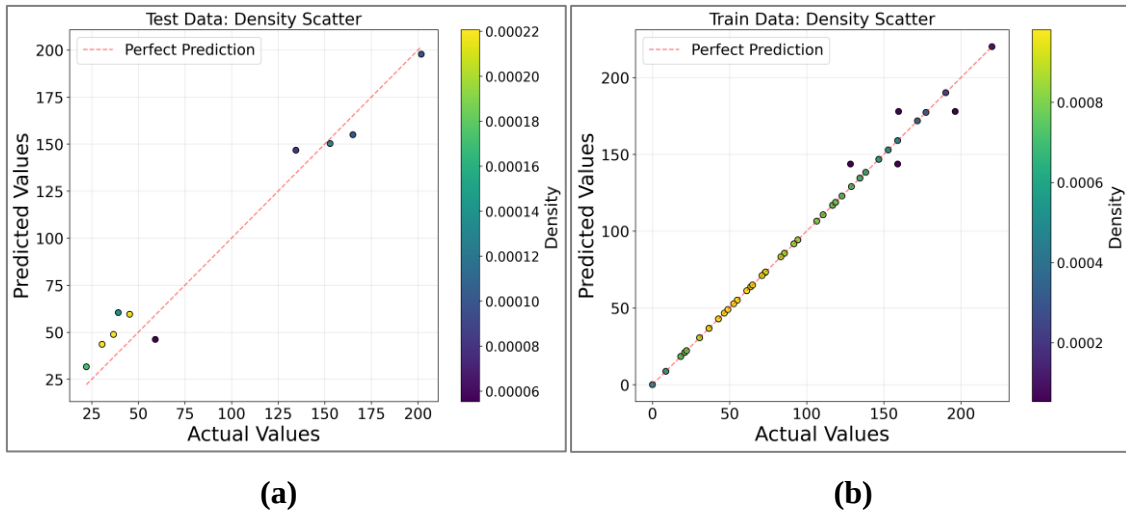


Figure 5.23:Density Scatter: (a) Test Data, (b) Training Data

In the density scatter plot, the points in the test data (Figure 5.23.(a)) deviate more from the ideal line, and the model consistently overpredicts, particularly at low values (between 20 and 50). The majority of the points in the training data have an almost perfect fit and are quite near to the ideal line. The training data plot (Figure 5.23.(b)) has more points and a higher density than the test data plot, which has a lot fewer points. The test data's maximum density is approximately 0.00022, whereas the training data's is approximately 0.0010. In summary, the link between the actual and anticipated values is depicted in both images. The ideal predictions are represented by the red dashed line ($y=x$). The density is shown by the colors of the dots.

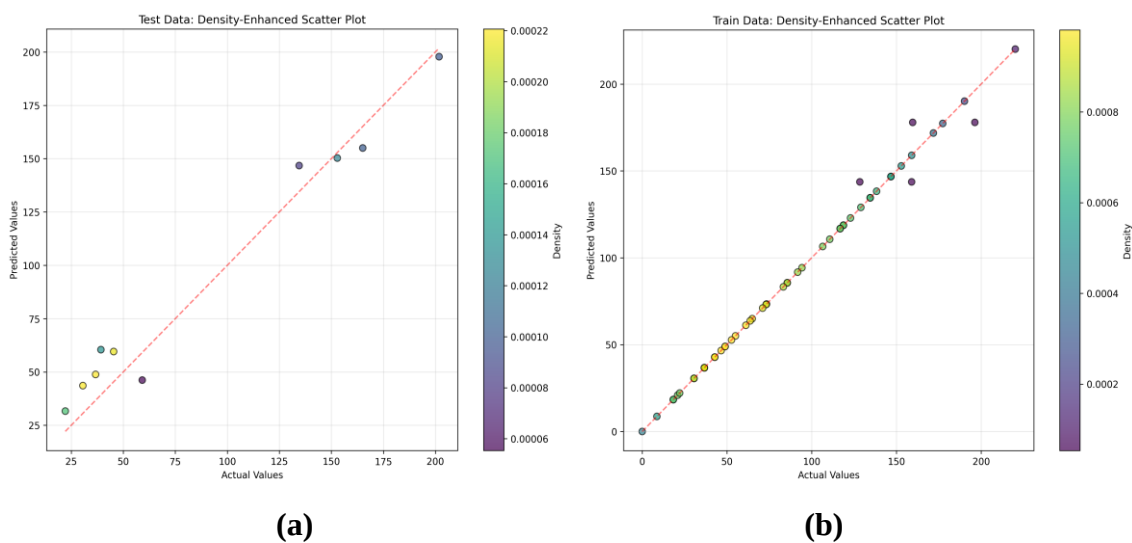


Figure 5.24:Density-Enhanced Scatter: (a) Test Data, (b) Training Data

In the density-enhanced scatter plot, the training data's (Figure 5.24.(b)) value ranges are more uniformly distributed, whereas the test data's (Figure 5.24.(a)) ranges are wider. The training data has more uniformly distributed mistakes than the test data, which contains substantial negative errors (-10 to -20) in the low value range (22-58). The training data includes data in all ranges, however the test data seldom has any data in the middle value range (58-93). While the training data includes positive errors in the highest value range (176-220), the test data shows significant positive errors in the high value range (129-165). Compared to the training data (-15 to +15), the test data's errors (-20 to +10) are more uneven. The training data's medians are closer to zero than the test data's, which has a neutral median in the high value range and a negative median in the low value area.

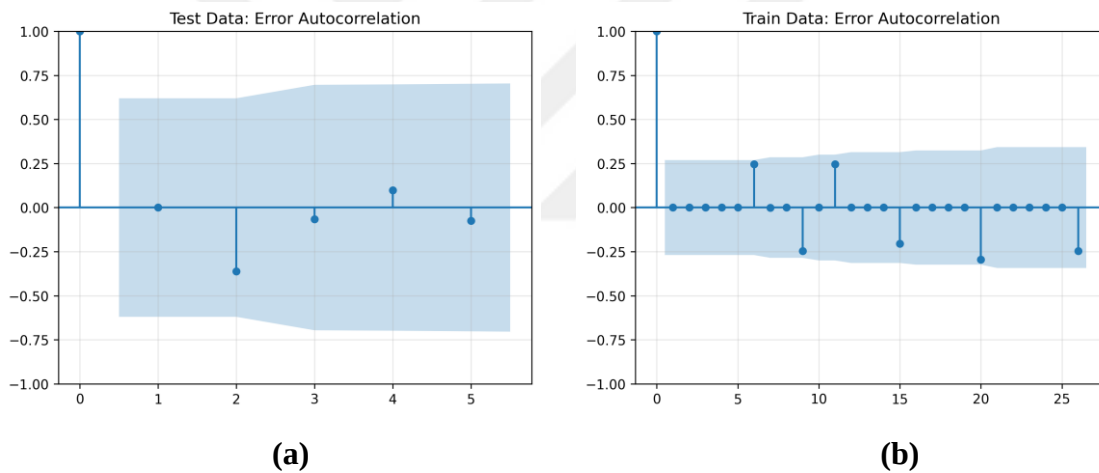


Figure 5.25:Error Autocorrelation: (a) Test Data, (b) Training Data

In the error autocorrelation plot, there are less lags in the test data compared to up to 25 lags in the training data (Figure 5.25.(b)). At lag=0, both plots display a perfect positive correlation (1.0), as would be predicted. At lag=2, the test data, (Figure 5.25.(a)), exhibits a large negative correlation (-0.35), while at lag=4, there is a minor positive correlation. The substantial negative correlations may be seen in the training data at lag=10, 15, 20, and 25, and substantial positive correlations at lag=5 and lag=8. Because the training data has a lower confidence interval (blue shaded region) than the test data, the training data

is larger. There is a periodic pattern in the training data with intervals of roughly five units, but there is no discernible periodic structure in the test data.



6. CONCLUSIONS AND FUTURE WORK

In this thesis, the potential of hydrogel–metal–organic framework (MOF) composites, namely AL@ZIF-8 composite hydrogel containing ZIF-8, as an environmentally friendly and efficient adsorbent in combating heavy metal pollution, in removing Pb(II) ions was investigated in detail. In the research, the limitations of traditional adsorbents were tried to be overcome, the biocompatibility of alginate-based hydrogels and the interaction of a large number of carboxyl groups with metal ions, combined with the high surface area and porosity of ZIF-8, revealed the synergistic effect of both components. Experimental studies made it possible to evaluate the adsorption kinetics, thermodynamic properties and adsorption capacity under different ZIF-8 loading rates (2%, 4% and 6%), temperature conditions (room temperature, 40°C, 50°C) and initial Pb(II) concentrations (400, 450 and 500 mg/L). Experimental results showed that especially at low ZIF-8 ratios (e.g. 2%), adsorption occurs significantly by physical mechanism as well as intraparticle diffusion effects. However, it was observed that the adsorption mechanism shifted towards chemical adsorption with increasing temperature and initial concentration. Especially at 4% ZIF-8 ratio, adsorption kinetic models (pseudo-second order) presented high correlation coefficients (R^2 value above 0.98), revealing that the adsorption of Pb(II) ions became dominant with chemical reaction mechanisms such as valence forces and electron exchange. This indicates that optimum adsorption performance can be achieved at 4% ZIF-8 loading ratio and medium temperature conditions such as 40°C.

Thermodynamic analyses revealed that the adsorption of the system showed endothermic properties with increasing temperature, and that the adsorption capacity and kinetic constants varied depending on the experimental conditions. Especially at low ZIF-8 ratios, the temperature increase positively affected the adsorption rate and capacity, while at high ZIF-8 ratios it exhibited a complex behavior, causing the relative contribution of diffusion mechanisms to increase in some cases. Thus, it was determined that both surface chemistry and mass transfer mechanisms contributed equally to the adsorption process under certain experimental conditions.

In addition, the artificial intelligence-based ANFIS (Adaptive Neuro-Fuzzy Inference System) model used in this thesis gave very successful results in terms of analyzing experimental data and estimating adsorption performance. The ANFIS model was able to

predict changes in adsorption capacity with variables such as temperature, adsorbent dose, contact time and composite ratio as input parameters, and provided high agreement (high R^2 , low RMSE) in model evaluation metrics. Thus, in addition to experimental studies, model-based optimization methods have also proven to be an effective tool in the design of industrial water treatment processes and determination of operating conditions.

The combination of hydrogel and MOF compounds has shown that it provides superior performance in terms of both adsorption capacity and kinetic efficiency in heavy metal removal. This synergistic structure eliminates the limitations of classical adsorbents and offers a sustainable solution proposal in terms of both environmental and economic aspects. The findings show that the AL@ZIF-8 composite hydrogel developed for the removal of Pb(II) ions has significant potential for industrial applications in the future, in addition to providing successful results at the laboratory scale.

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