

**HYBRID ELECTROCOAGULATION/ADSORPTION
SYSTEM FOR THE TREATMENT OF SYNTHETIC
INDUSTRIAL WASTEWATER**

BY

WALEED KHALID ALNOWAISER

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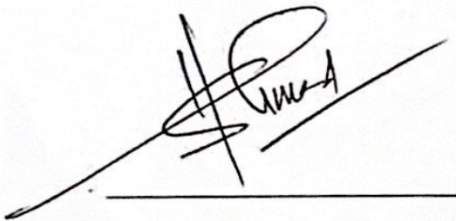
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This thesis, written by **Waleed Khalid Alnowaiser** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY IN CIVIL ENGINEERING**.



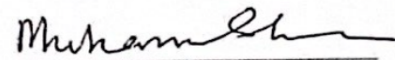
Dr. Shamsad Ahmad
Department Chairman



Dr. Suliman Saleh Al-Homidan
Dean of Graduate Studies

7 May, 2024

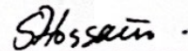
Date



Dr. Muhammad S. Vohra
(Advisor)



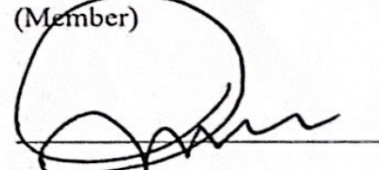
Dr. Mohammad S. Al-Suwaiyan
(Co-Advisor)



Dr. Shakhawat Chowdhury
(Member)



Dr. Sagheer A. Onaizi
(Member)



Dr. Haitham Elnakar
(Member)

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To my Family.

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LIST OF ABBREVIATIONS

RSM: Response Surface Methodology

EC: Electrocoagulation

A: Adsorption

EC/A: Electrocoagulation/Adsorption

AOP: Advanced Oxidation Processes

EO: Electrochemical Oxidation

BDD: Boron Doped Diamond

GAC: Granular Activated Carbon

COD: Chemical Oxygen Demand

TOC: Total Organic Carbon

F: Fenton

PF: Photo-Fenton

AC: Activated Carbon

BBD: Box-Behnken Design

ANOVA: Analysis of Variance

EC/EF: Electrocoagulation/Electrofiltration

POPs: Persistent Organic Pollutants

HA: Humic Acid

TDS: Total Dissolved Solids

GO: Graphene Oxide

ZIFs: Zeolitic Imidazolate Frameworks

ZIF-7: Zeolitic Imidazolate Framework-7

MOFs: Metal-Organic Frameworks

XRD: X-ray Diffraction

FTIR: Fourier Transform Infrared

AAS: Atomic Adsorption Spectrometer

FC-RSM: Face-Centered Response Surface Methodology

DOE: Design of Experiment

CCD: Central Composite Design

ML: Machine Learning

ANN: Artificial Neural Network

XGBoost: eXtreme Gradient Boosting

ATSDR: Agency for Toxic Chemicals and Disease Registry

2FI: Two-Factor Interaction

ReLU: Rectified Linear Unit

]

ABSTRACT

Full Name : Waleed Khalid Alnowaiser
Thesis Title : Hybrid Electrocoagulation/Adsorption System for The Treatment of Synthetic Industrial Wastewater
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The increasing prevalence of water pollution, specifically from heavy metals such as lead (Pb(II)), necessitates advanced solutions for environmental and public health protection. This comprehensive research undertakes two distinct yet interconnected studies focusing on the innovative use of a graphene oxide/zeolitic imidazolate framework-7 (GO@ZIF-7) nanocomposite for Pb(II) remediation. Initially, the research introduces the novel synthesis of the GO@ZIF-7 nanocomposite, leveraging its unique adsorptive properties for Pb(II) removal from aqueous solutions. This nanocomposite exhibited an extraordinary Pb(II) adsorption capacity of approximately 5,000 mg/g, dramatically outperforming the capacities of pristine ZIF-7 and GO, which were around 500 and 600 mg/g, respectively. Optimization through Response Surface Methodology (RSM) highlighted the pivotal influence of solution pH and adsorbent dosage on removal efficiency, achieving up to 95% Pb(II) removal under optimal conditions (50 mg/L initial Pb(II) concentration, 0.6 g/L adsorbent dosage, and solution pH of 6), with significant adsorption performance even at challenging conditions (higher initial Pb(II) concentration of 150 mg/L and lower adsorbent dosage of 0.2 g/L). Expanding upon this foundation, the subsequent study explored a hybrid electrocoagulation/adsorption (EC/A) system integrating aluminum electrodes with the GO@ZIF-7 nanocomposite for enhanced Pb(II) removal efficiency.

This novel EC/A system achieved near-complete Pb(II) removal, with the study meticulously optimizing the process through RSM and analyzing the impacts of four primary variables, including current density and GO@ZIF-7 dosage. The effectiveness of the hybrid system was statistically validated, offering a robust model for Pb(II) removal. Additionally, this investigation assessed the feasibility of employing machine learning models—artificial neural network (ANN), eXtreme Gradient Boosting (XGBoost), and Random Forest Regression—to predict Pb(II) removal efficiency, further underscoring the system's innovative approach. Together, these studies not only demonstrate the exceptional potential of the GO@ZIF-7 nanocomposite for Pb(II) removal, both as a standalone adsorbent and within a hybrid EC/A system, but also the practical viability of integrating advanced statistical and machine learning tools for optimizing and predicting water treatment processes. The outcomes present progress in addressing water pollution through the application of nanocomposite materials and cutting-edge technology, paving the way for sustainable and efficient water purification solutions.

ملخص الرسالة

الاسم الكامل: وليد خالد النويصر

عنوان الرسالة: نظام تخثير كهربائي/امتصاص سطحي هجين لمعالجة مياه صناعية ملوثة

التخصص: الهندسة المدنية

تاريخ الدرجة العلمية: ابريل ٢٠٢٤

تؤدي زيادة انتشار تلوث المياه، وخاصة من المعادن الثقيلة مثل الرصاص ($Pb(II)$)، إلى الحاجة إلى حلول متقدمة لحماية البيئة والصحة العامة. تقدم هذه الرسالة بحثين منفصلين لكن مرتبطين لمحاولة استخدام مركب نانوي جديد مبتكر من أكسيد الغرافين (Graphene Oxide) وإطار العمل الزيوليتي للإيمدوزيلايت (zeolitic imidazolate framework-7) تحت المسمى ($GO@ZIF-7$ nanocomposite) للاستفادة من خصائص المركبين في معالجة المياه الملوثة بالرصاص. في الجزء الأول من الرسالة أظهر المركب النانوي المستخدم قدرة استثنائية على امتصاص الرصاص من المياه الملوثة تصل إلى 5000 mg/g متفوقة بذلك على أداء المركبين بشكل منفصل حيث كانت قدرة المركبين للامتصاص في حدود $500 - 600\text{ mg/g}$. تم استخدام منهجية سطح الاستجابة (Response Surface Methodology) أو (RSM) اختصاراً لمعرفة تأثير العوامل المختلفة مثل حموضة المياه المستخدمة (solution pH) والجرعة المستخدمة من المركب النانوي (adsorbent dosage) بالإضافة إلى تركيز الرصاص في المياه المستخدمة (initial $Pb(II)$ concentration) على قدرة المركب النانوي على معالجة المياه الملوثة بالرصاص والتي وصلت إلى 95% في الظروف المثالية التالية: تركيز الرصاص بالمياه الملوثة المستخدمة 50 mg/L ، جرعة مستخدمة من المركب النانوي تقدر بحوالي 0.6 g/L ، وحموضة محلول بدرجة 6. كما أظهر المركب قدرة عالية على معالجة الرصاص في ظروف أحث في ظل تركيز عالي للرصاص يصل إلى 150 mg/L وباستخدام جرعة 0.2 g/L من المركب النانوي. بتوسيع مجال استخدام المركب النانوي ($GO@ZIF-7$) في الجزء الثاني من الرسالة، تم استكشاف استخدام المركب النانوي ضمن نظام هجين يعتمد على المركب النانوي كعنصر لامتصاص الرصاص السطحي إلى جانب استخدام قطبي ألومنيوم (Al electrodes) لغرض التخثير الكهربائي (Electrocoagulation) للحصول على نتائج معالجة أعلى للمياه الملوثة. أظهر النظام المركب الذي تم إطلاق مسمى (Novel Al-Electrodes/ $GO@ZIF-7$ Hybrid) (Electrocoagulation/Adsorption System) عليه قدرة شبيهة كاملة على معالجة الرصاص من المياه الملوثة. تم استخدام

منهجية سطح الاستجابة (RSM) في هذه الرسالة أيضًا لمعرفة أثر عوامل مختلفة مثل كثافة التيار الكهربائي (current density) وجرعة المركب النانوي المستخدمة (adsorbent dosage) إلى جانب عوامل أخرى للحصول على معادلة رياضية يمكن الاعتماد عليها للتنبؤ نسبة معالجة الرصاص بالمياه الملوثة وفق العوامل المختلفة. بالإضافة إلى ذلك تمت دراسة إمكانية استخدام نماذج تعلم آلي مختلفة (machine learning models) تتضمن الشبكات العصبية الاصطناعية (artificial neural network)، طريقة eXtreme Gradient Boosting (XGBoost)، وطريقة Random Forest Regression لمحاولة تنبؤ قدرة النظام الهجين على معالجة الرصاص من المياه الملوثة ولمحاولة زيادة القدرة على فهم طريقة عمل النظام الهجين. أظهرت الرسالة قدرة المركب النانوي (GO@ZIF-7) العالية على معالجة الرصاص من المياه الملوثة سواء كعنصر منفرد باستخدام الامتصاص السطحي (GO@ZIF-7 adsorption) أو كعنصر مساعد كما في حالة النظام الهجين (Al-Electrodes/GO@ZIF-7 Hybrid Electrocoagulation/Adsorption System). كما أظهرت كذلك نجاح استخدام منهجيات وأدوات التنبؤ المستخدمة (RSM) ونماذج التعلم الاصطناعي (machine learning models) في القدرة على التنبؤ بفعالية المركب النانوي والنظام الهجين في معالجة المياه الملوثة. تمهد نتائج الرسالة بشكل عام الطريق لمزيد من استخدامات المركبات النانوية والأنظمة الهجينة كحلول عملية فعالة لمعالجة المياه الملوثة.

CHAPTER 1

INTRODUCTION

Industrial activities worldwide produce amounts of wastewater that contain a variety of pollutants, such as remnants of reactive dye chemicals that are hard to break down, and high levels of Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) [1]. Global regulations require treating this wastewater to eliminate color and lower pollutant levels before releasing it into the environment. Recent environmental rules have prompted the development of treatment methods to meet discharge standards [2]. Traditional physical and chemical treatments like adsorption [3], coagulation and flocculation [4], ion exchange [5], membrane filtration [6], precipitation [7], and oxidation [8] often struggle to degrade pollutants. Biological treatments are not as effective against the properties of wastewater especially at elevated contaminant concentrations [9]. In times electrochemical methods like electrocoagulation (EC), electrooxidation, and electroflotation have emerged as ways to purify industrial wastewater [10]. The combination of these technologies has shown results in treating types of wastewater; hybrid systems combining electrocoagulation/adsorption (EC/A) hold potential for different uses. This discussion examines EC/A systems with a focus on removing heavy metals while highlighting the advantages of integrating EC with adsorption. It discusses enhancements in water quality, cost efficiency, reduction in waste, and the attainment of high-quality effluents, for discharge.

At times the combined EC/A method has been receiving attention for its potential, in treating water offering benefits in removing pollutants while saving energy and costs. Despite its promise, there are still challenges to overcome in refining and bringing this technology to the market [11]. More research is required to determine its efficacy against a variety of pollutants, and heavy metals when mixed with other substances. It is necessary to explore ways to decrease wear and improve the efficiency of the process potentially through designing specialized electrodes. Evaluating energy efficiency and creating models for the process are steps, towards making it commercially viable. These efforts should involve conducting pilot-scale experiments and analyzing operations to prepare for introducing the technology into the market.

1.1 Research objectives

The review of existing literature highlights a significant field of study on the treatment of heavy metals from wastewater, with a particular focus on adsorption and EC technologies. However, despite the extensive studies, there remains a notable gap in understanding the combined integration of the two systems. The primary objective of this research is to evaluate the effectiveness of a hybrid EC/A system in treating synthetic wastewater. The detailed objectives of this study are as follows:

- Investigate the effectiveness of the hybrid EC/A system for treating inorganic pollutants, including heavy metals from synthetic wastewater.

- Study the effect of different operational factors on the performance of the hybrid EC/A system, which could reveal insights into optimizing treatment processes for better efficiency and lower costs.
- Investigate the impact of the use of modified adsorbents on the hybrid EC/A system's performance. This could lead to improvements in pollutant removal capabilities, potentially making the process more effective against a wider range of contaminants.
- To further enhance the understanding and application of this hybrid EC/A system, by developing both adsorption models and optimization models based on the Response Surface Method (RSM). These models could provide a theoretical foundation for predicting system performance and facilitating the optimization of process parameters, thereby accelerating the advancement and application of the hybrid EC/A technology in wastewater treatment.

1.2 Significance of the research

In times Saudi Arabia has seen an increase, in its population and industrial development resulting in a rise in different types of industrial wastewater. This growth is particularly noticeable in industries like oil production, textiles, paper manufacturing, petrochemicals, pharmaceuticals, and food processing all contributing to an amount of wastewater being produced. The need to find methods for treating this wastewater has become crucial to lessen the environmental effects of these pollutants. EC is recognized as a method for treating wastewater due to its various advantages over traditional techniques. Moreover,

adsorption is another used method for removing both inorganic pollutants from industrial waste streams. Despite their effectiveness on their own studies suggest that combining EC and adsorption methods for wastewater treatment has not been extensively explored. This study aims to investigate the implementation of an EC/A system. By achieving levels of removal efficiency at lower operational costs such a system could greatly improve the reusability of industrial wastewater while reducing the release of harmful substances, into the environment.]

[CHAPTER 2]

[LITERATURE REVIEW

Water scarcity is a pressing global issue, exacerbated by the contamination of freshwater resources through industrial and agricultural activities. A significant body of research highlights the alarming rate at which untreated wastewater, containing diverse toxic chemicals, is discharged into the environment, posing serious risks to human health and aquatic ecosystems [12, 13]. The resilience of these pollutants, due to their resistance to degradation, underscores the urgent need for effective wastewater treatment methods.

EC, a process that removes contaminants from wastewater by applying an electric current, has emerged as a promising solution owing to its simplicity, low energy consumption, and efficacy in extracting various pollutants [14]. However, the process faces challenges such as electrode passivation and sludge production. Adsorption, another key technique, employs physicochemical interactions to transfer pollutants from the liquid phase to a solid medium, known for its adaptability and high removal efficiency [15]. Despite its advantages, the cost and performance limitations in certain scenarios have prompted the exploration of hybrid methods combining EC and adsorption to enhance treatment efficiency and overcome individual drawbacks.

The pioneering study by Linares-Hernández et al. [16] on the hybrid EC/adsorption method marked a significant advancement, demonstrating substantially improved removal efficiencies for color and turbidity in mixed industrial wastewater treatment. This

integrated approach not only mitigates the limitations associated with each method but also enhances overall performance through synergistic effects.

This review aims to critically examine the removal efficiency of the combined EC/adsorption system in wastewater treatment, filling a notable gap in the literature by comparing its efficacy across different operational conditions and process designs. By providing a comprehensive analysis of existing studies and identifying areas for future research, this work seeks to establish a foundation for the operational feasibility and optimization of the integrated EC/adsorption (EC/A) approach in addressing contemporary wastewater treatment challenges.

2.1 Adsorption of heavy metals and other pollutants from wastewater

Heavy industrialization generates major economic benefits, but industrial plants have to find optimal ways of dealing with some of the byproducts of the manufacturing process, including heavy metals. These components are known to have significant negative effects on the environment and human health and governments have legislated strict laws that require companies or individuals to develop a sound strategy for the removal of heavy metals. When they enter water, these contaminants take various forms, including hydroxide complexes, anions, or cations [17]. Researchers have proposed several approaches for the removal of poisonous industrial waste from water, including electrochemical method, membrane filtration, and adsorption.

Among the listed approaches, researchers have significantly analyzed the use of carbon-based materials. These adsorbent materials are made from non metallic solids, either in

powdered form or as a bulk substance, with carbon being the main component [18]. Carbon in these compounds, as Duan et al. [18] continue to observe, is made up of carbon nanotubes (CNTs), graphene substances, and activated carbon and biochar, among other elements. The application of carbon-based adsorbents is favored because of several advantages. Firstly, researchers note that these types of adsorbents, apart from exhibiting good thermal stability, are also known to have enormous surface area and high mechanical strength [19]. Elsewhere, other studies have shown that carbon-based adsorbents have not only controllable morphology but also high adsorption capacity [20].

Research into adsorption techniques is conducted as part of efforts to improve water quality. In existing work, Duan et al. [18] note that researchers propose several carbonaceous compounds and their derivatives. At the same time, researchers also suggest a number of ways these compounds can be deployed for the removal of impurities, which mainly comprise heavy metal ions. Among the approaches that are proposed are magnetization, oxidization, functional group grafting techniques, and inorganic substances compositing [21]. Elsewhere, researchers analyzed whether different kinds of carbon-based materials, such as CNTs, among others, could be modified; however, these assessments do not set clear guidelines for the modification process, which makes their applicability challenging [22]. Since proposed modification methods in existing studies are almost identical, the question that remains concerns whether systematic analysis of the regeneration strategy for separating heavy metals from aqueous solutions can lead to a more optimized approach.

The two most applied adsorption models include the kinetic models and the adsorption isotherms. The underlying assumption behind the adsorption isotherm technique is that certain relationships can develop between an adsorbate and an unadsorbed adsorbate under certain temperature conditions on the adsorbent's water surface [18].

Various theories have been put forward regarding the adsorption of heavy metals on carbon-based materials. These methods encompass the physical process of adsorption, interactions due to electrostatic forces, the formation of surface complexes, ion exchange, and the process of precipitation or co-precipitation [21]. With physical adsorption, the process involves diffusing and depositing heavy metal ions in the adsorbent material's pores. To increase the surface area for the adsorption of heavy metals, the process requires enlarged micro-pores and mesoporous. With electrostatic interaction, on the other hand, the reaction conveys positive charges on the surface of the adsorbent, resulting in an electro-charged electrostatic attraction, which enhances adsorption [18]. Various techniques used in the adsorption of heavy metals seek to exploit both the chemical and physical properties of the metals and the carbon adsorbents.

The deleterious effects of industrial waste on individuals' health and the environment also come in the form of chemical discharges from the textile and printing industries. Methyl blue (MB) dye is among the most harmful of these waste products; hence, the removal of this substance, which usually seeps into the ecosystem, is prioritized. MB has applied industrial use in coloring cotton, silk, paper, hair, and wool, but the compound is connected to several ailments, including eye, respiratory, and digestive defects [23]. In light of the

link between MB and these ailments, it is critical for concerned industries to find optimal ways for the treatment of the compound from the ecosystem.

Carbon-based adsorption of MB seeks to exploit certain features. Other than the large surface area and high porosity associated with carbon, the separation of MB from water also benefits from the existence of functional groups, for example, the aromatic ring on the surface of the carbon ion [24]. The molecular structure of an MB's cation contains six carbon aromatic rings, sulfur, and nitrogen. This structure influences the interaction of MB with the surface of the carbon molecule. Particularly, researchers note that the adsorption process occurs via electrostatic interaction that involves attraction between adsorbent and oppositely charged ions [23]. The process also involves the creation of a hydrogen bond, acting as the electron donor receptor, and the forces of dispersion between MB molecules and the functional groups of the carbon surfaces. To improve the surface functionality of the adsorbent, the process employs thermal activation, which is performed through high temperature annealing under N₂ flow. Apart from improving the quantity of carboxyl groups, the process generates greater porosity and surface area. To raise the surface functionality of the carbon, some researchers propose the formation of composites through the chemical activation of compounds that contain preferred functional groups.

The surface functionality of carbon is a critical aspect of MB adsorption. In one study, researchers added –NH₂ groups to the carbon surface by treating biomass carbon material using propylene diamine, ethylene diamine, aniline, and ethylene amine [25]. Functional groups, including –COOH and –OH, interact with heavy metal ions or complexes, like lead hydroxide, to facilitate the enrichment from aqueous solutions [18]. Other researchers

added -NH and -SH functional groups to the nano-carbon by reacting cysteamine with carboxylic groups on the surface of the nano-carbon [26]. Overall, researchers have ascertained that the formation of activated carbon composites generates a carbon-based adsorbent with increased concentrations of -NH_2 , -C=O , and -OH functional groups, which are known to increase the rate of MB adsorption.

After establishing the properties of carbon or carbon composites that make the compound ideal for MB adsorption, the question that remains concerns the source of the adsorption agent. Santoso et al. [23] postulated that the most extensive renewable carbon sources comprise biomass and its waste. Particularly, biomass sources vary from plants to animal waste. Activated carbon in these sources has to be synthesized, and the process begins with pre-treatment of the biomass source. The goal of the initial step is to remove any impurities from the source. Such pre-treatment is usually done by washing and drying the biomass to rid it of contaminants that reduce the purity of the carbon. The biomass is also ground and sieved, which reduces the size of the carbon precursor [23]. In the next phase, the biomass is annealed at moderate to high temperatures under inert atmospheric conditions, which carbonizes the compound. In the final step, the carbon is activated, which enhances its surface functionality. Carbon from biomass has to be prepared through a series of sequential steps before the compound can be used as an adsorbent.

For optimal MB adsorption, a carbon-based compound needs to exhibit certain properties. Studies argue that carbon that is generated from different types of biomasses has varying properties when activated [23]. In a related study, researchers established that the type of chemicals and gas employed in the activation phase determined the pore structure,

functionality, and surface area of the resulting compound, which ultimately defined the adsorption capacity of the adsorbent [27]. Altenor et al. [28] generated activated carbon from vetiver roots. The study employed H_3PO_4 to improve the sizes of the carbon pores, which optimized the compound's MB adsorption capacity. Different types of biomasses produce activated carbon with varying properties and researchers have sought ways to increase the adsorption capacity of the resulting compound.

2.2 Hybrid EC/A systems

Integrating various wastewater treatment methods is imperative for addressing the complex composition of industrial effluents. This approach combines chemical, physical, and biological processes to optimize contaminant removal efficiency. Recent studies have explored diverse combinations, such as biological degradation with photocatalysis, EC with electrochemical oxidation, advanced oxidation processes (AOP) with membrane bioreactors, and coagulation-flocculation and fenton oxidation for textile wastewater management [29]. Specifically, the integration of EC and adsorption techniques has garnered attention for its potential to reduce operational costs and improve treatment efficacy, especially in developing countries [30, 31]. This review critically examines the hybrid EC/A method, focusing on its application across varied operational parameters and its impact on contaminant removal efficiency.

The literature underscores the growing body of evidence supporting the hybrid EC/A approach, particularly in textile industry wastewater treatment. As an example, GilPavas et al. [32] combined EC, electrochemical oxidation (EO), and adsorption in treating textile

effluents. An iron (Fe) anode and a cathode made from Boron-doped diamond were employed for EC processes, while electrode polarities were reversed for EO procedures. Granular activated carbon (GAC) was used as the adsorbent in these processes. This multifaceted strategy achieved complete color removal and substantial reductions in COD and total organic carbon (TOC). Importantly, the acute toxicity of the effluent was significantly mitigated only with the incorporation of adsorption. Another study by GilPavas et al. [31] investigated the efficacy of combining EC with Fenton (F) and photo-Fenton (PF) processes, followed by activated carbon (AC) adsorption. Their findings highlighted that while F/PF processes outperformed EC in removing certain compounds, they fell short in reducing water toxicity, underscoring the indispensable role of adsorption in enhancing effluent quality.

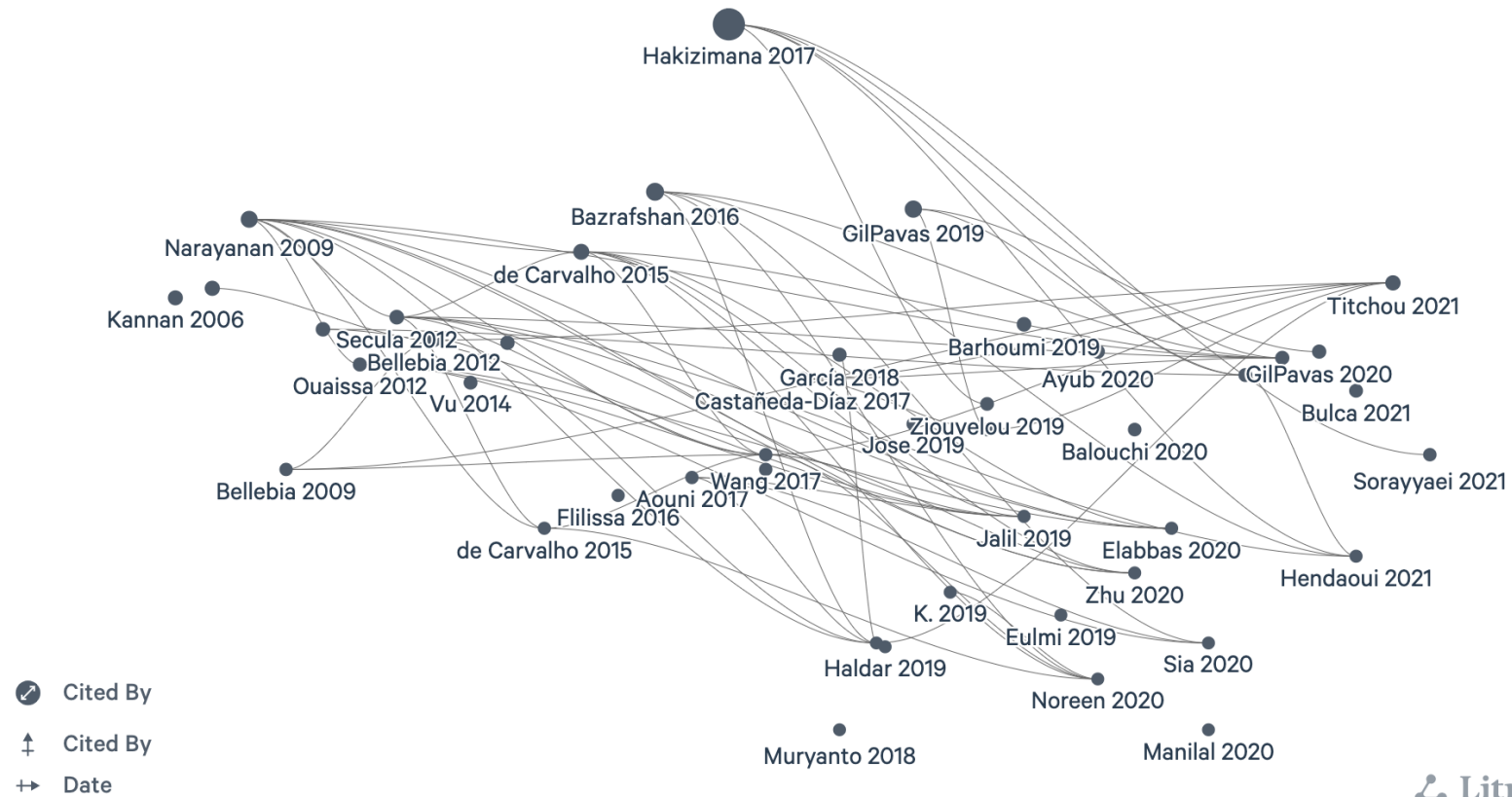
This review methodically analyzes the effect of key operational factors as pH level, current density, and adsorbent dosage on the hybrid method's performance. By covering recent advancements and identifying gaps in current literature, it aims to contribute to the optimization of the hybrid EC/A systems for optimal treatment of industrial wastewater. The concluding section will distill these insights, offering a critical evaluation of the method's viability and outlining future research directions to further refine this promising treatment strategy. Figure 1 shows a network diagram visualizing the evolution of research on hybrid EC/A systems, generated using Litmaps. Nodes represent individual studies, arranged from left to right to reflect their chronological publication order, highlighting the development of the field over time. Edges indicate citation relationships, with a noticeable increase in cross-disciplinary references in recent years.

2.2.1 Hybrid EC/A systems literature visualization

The Litmaps visualization diagram presented in Figure 1 presents a network of the covered scholarly articles in this literature review connected through citation relationships, as indicated by the lines, and ordered from left to right based on their publication year. The labels on each node denote the lead author and year of publication. There are several distinct clusters of articles that appear to be more densely interconnected, suggesting these works share a common research theme or methodology. For example, articles by Bazrafshan et al. [33] and Hakizimana et al. [34] form a tight cluster, indicating a specific subtopic or a continuation of research themes over time. The time span of the research is from 2006 (Kannan et al. [35]) to date, showing an active field of study over the last 18 years. The latest articles, such as those published in 2021 by Titchou et al. [36] and Sorayyaee et al. [12], and in 2022 by Hendaoui et al. [37], may point to the most recent research directions in the field. The size of the nodes implies the relative importance and the citation count of the articles, with larger nodes like Hakizimana et al. [34] being more influential within the reviewed literature. The map's structure suggests a dynamic field with a healthy exchange of ideas and building upon previous work, as seen in the citation connections. The Litmaps visualization map presented in Figure 2 effectively outlines a bibliometric network of the covered scholarly articles in this review with a focus on their content similarity. It delineates their interconnections through both citations and content similarities. The varying node sizes suggest differential citation frequencies or intrinsic significance within the academic network. The presence of dense clusters, such as those around Noreen et al. [38], Barhoumi et al. [39], and Hakizimana et al. [34], implies that these articles are closely related. Many connections indicate high interconnections between

certain nodes, suggesting these works are highly influential or foundational within this field of literature.

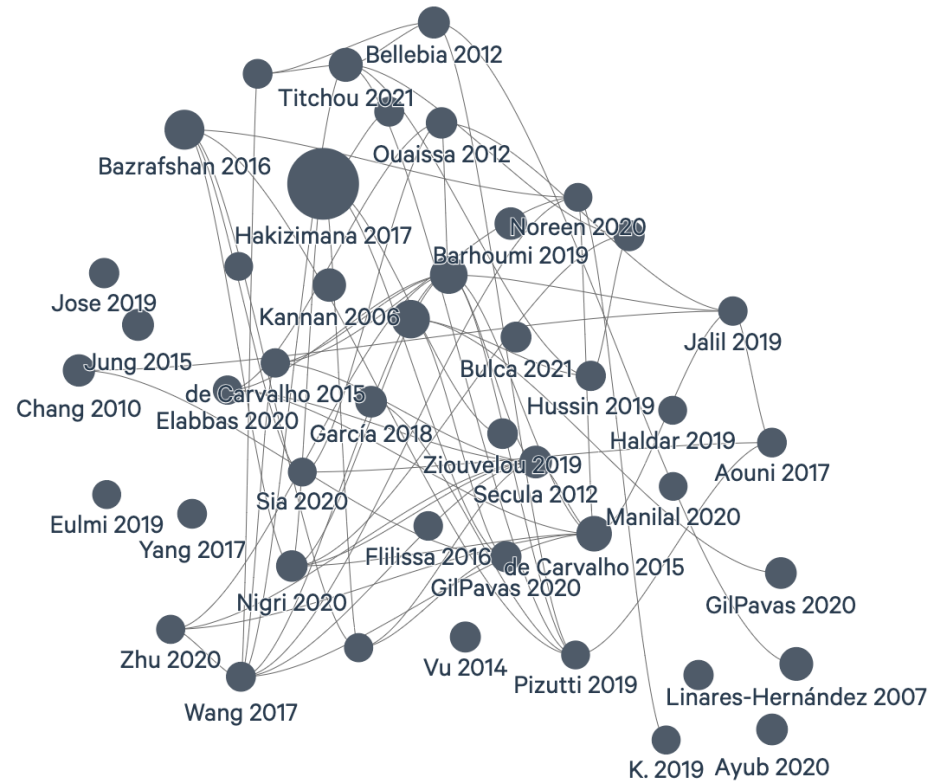
● Articles



Litmaps

[Figure 1: Network diagram of the scholarly articles covered on hybrid EC/A systems arranged from left to right based on the date of publication (Litmaps)]

● Articles



↗ Cited By

↔ Content Similarity

 Litmaps

[Figure 2: Network diagram of the scholarly articles covered on hybrid EC/A systems arranged based on content similarity (Litmaps)]

2.3 Operational parameters in hybrid EC/A systems

Understanding the operational dynamics of hybrid EC/A systems is pivotal for optimizing wastewater treatment processes. This section delves into the significance of the operational setup—specifically, the choice between sequential and simultaneous integration of EC and adsorption—and its impact on treatment efficacy.

Sequential and simultaneous operational designs represent two primary approaches in the integration of EC and adsorption. Sequential systems, where EC is followed by adsorption, have been widely investigated in studies such as those by Hendaoui et al. [37], Alnawab and Ridha [40], and Vinothkumar et al. [41], among others. This approach allows for the targeted removal of contaminants through EC before further purification via adsorption. Conversely, simultaneous operations, as explored by Jung et al. [42], de Carvalho et al. [43], and a host of other researchers, integrate EC and adsorption concurrently, aiming to leverage the synergistic effects of both processes in real time.

Research into simultaneous hybrid systems has highlighted several operational advantages, including lower current density requirements and reduced contact times, without compromising removal efficiency. The integration of adsorbents directly into the EC process has proven to enhance the removal of contaminants at significantly lower current densities and within shorter time frames. This efficiency gain is attributed to the immediate availability of adsorbent surfaces for contaminant capture, which may also introduce beneficial secondary effects such as improved electrochemical reactions and pollutant adsorption capacities. Despite these advantages, variations in electrode material, adsorbent type, reactor design, and electrolyte composition across studies suggest that the optimal operational parameters are highly context-dependent.

Notably, the introduction of adsorbents during the EC process has not only improved efficiency but also led to positive, albeit unintended, effects. These include enhanced electrode longevity, reduced sludge production, and potentially lower operational costs. However, the variability in system design and operational conditions across studies underscores the necessity for a tailored approach when implementing hybrid EC/A systems in industrial applications.

This analysis emphasizes the critical role of operational parameters and system design in determining the efficacy of hybrid EC/A methods for wastewater treatment. By comparing the sequential and simultaneous approaches, it becomes evident that while both have their merits, the choice of method should be informed by specific treatment goals, contaminant characteristics, and logistical considerations. Future research should aim to further elucidate the mechanisms underlying the observed efficiencies and explore the scalability of these systems for widespread industrial use.

Table 1: Hybrid EC/A systems in the literature

Wastewater Used	Main Aim	Treatment Technique	Statistical Analysis	Optimization	RSM	Modeling	Notes	Ref.
Industrial textile wastewater	Evaluation of the improved treatment of indigo polluted industrial textile wastewater	Sequential EC and adsorption with activated carbon	A 4-factor Box-Behnken experimental design (BBD) was employed. The data collected for each response variable were analyzed and modeled using a quadratic model of the independent variables. This analysis was conducted through multivariate linear regression analysis utilizing the R programming language.	Nonlinear programming was utilized to identify the optimal conditions for process variables based on the quadratic models that were derived	RSM plots were illustrated			[44]
Synthetic dye solution	Optimization and modelling using RSM methodology for MB dye treatment	Hybrid EC/hazelnut shell (HNS) adsorption system	A non-linear regression approach employed to fit the second order model into the structure of quadratic polynomial equation	BBD was used for factors optimaization			Economic and technical analysis	[45]
Pb(II) removal from aqueous solution	Pb(II) removal from aqueous solution	Hybrid solar EC and adsorption processes	Statistical analysis was performed to achieve well-fitted regression models		RSM employed to assess the results of various process parameters	RSM based on CCD was employed to examine the results of different independent variables		[13]
Real cotton textile wastewater	Color and COD removal from real cotton textile wastewater	Fluidized metal impregnated GAC in three dimensional EC system	For analyzing variance (ANOVA) and creating mathematical regression models to examine the interactions between independent and response variables, as well as plotting response surfaces, Design-Expert software version 6 (Stat-Ease, Inc., USA) and SAS software version 9.1 (SAS Institute) were utilized. Further ANOVA tests were conducted to validate the appropriateness and effectiveness of the chosen models. The comprehensive results from ANOVA highlighted that the selected quadratic models, developed within the designated design range using Response Surface Methodology (RSM) with a Central Composite Design (CCD), are highly capable of predicting optimal conditions and evaluating the interaction effects of the independent variables.					[42]
Distillery effluent	Comparison of treatment potential	Comparing EC with and without activated carbon made from areca catechu nut						[35]
Textile industry wastewater	Optimization and toxicity assessment	Successive EC, electrochemical oxidation, and adsorption treatment		Operational conditions were optimized using BBD. RSM and nonlinear optimization algorithm were applied focusing on the efficiency of organic matter degradation				[32]
Paper industry wastewater	High rate humic acid elimination from real wastewater from cellulose and paper industry	Hybrid EC/A using GAC					Treatment cost calculations	[39]
Greywater	Treatment of greywater	Hybrid electrochemical-granular activated carbon system	linear regression first-order decay model fit to the removal efficiency data					[46]

Wastewater Used	Main Aim	Treatment Technique	Statistical Analysis	Optimization	RSM	Modeling	Notes	Ref.
Remnant obtained from chemical retting of coconut fiber	Improvement of water quality	Electrocoagulation and activated carbon treatment					Cost analysis	[47]
Textile wastewater treatment	Wastewater treatment and toxicity assessment	A hybrid EC H ₂ O ₂ /Fe ²⁺ /UV and adsorption using activated carbon		Three level BBD and optimized using RSM				[31]
Real textile wastewater	Performance investigation of the hybrid method	hybrid treatment using adsorption or catalytic wet air oxidation after EC					Kinetic modelling	[29]
Acid dye from aqueous solutions	Acid dye treatment from and kinetics and electrical operating costs calculations	Electrocoagulation/GAC adsorption coupling					Kinetics studies. Electrical operating costs calculations and unit energy demand	[14]
Effluent from an industrial wastewater treatment plant of an oil refinery	Organic compounds, calcium, and strontium treatment	Simultaneous electrocoagulation and adsorption					Adsorption kinetics studies with detailed results	[48]
Peat obtained from Northern Finland has been used in the preparation of an aqueous solution containing humic material	Treatment of total organic carbon from peat solution	Hybrid EC/A system					Anode loss calculations	[49]
Reactive black dye synthetic wastewater	Treatment of Reactive Black 5	Hybrid EC/GAC adsorption with the use of microwave regeneration technique					Regeneration of GAC	[50]
Synthetic effluents	Improvement in the elimination of chromium from synthetic wastewater	Use of adsorption using granular activated carbon (GAC) for the enhancement of removal of chromium from synthetic wastewater by electrocoagulation						[30]
Synthetic dye contaminated wastewater	Treatment of color from acidic and reactive dye wastewater	Al electrodes and GAC adsorbent						[51]
Palm oil mill effluent	Treatment using hybrid EC/A process	Hybrid EC/A process						[52]
Synthetic dye contaminated wastewater	Eliminate anionic and cationic dyes from water solutions using photovoltaic (PV) energy	Hybrid EC/A process				The outcomes of the kinetic EC and the fixed-bed adsorption processes were effectively characterized by a first-	The experimental results were adjusted to the Bohart-Adams model using Origin 8.0 software	[15]

Wastewater Used	Main Aim	Treatment Technique	Statistical Analysis	Optimization	RSM	Modeling	Notes	Ref.
						order model and a Bohart-Adams model		
Tannery wastewater	Treatment of tannery wastewater using hybrid EC/A system	Electrocoagulation and adsorption						[53]
Synthetic fluoride solution	Fluoride removal	Electrocoagulation-adsorption process						[54]
Real textile wastewater	Investigate the viability of processing real collected textile wastewater	The approach combines coagulation (utilizing PAC as the coagulant), EC (employing Al), and adsorption (using ash derived from pistachio nut shells)						[33]
Wastewater from industrial dairy	Evaluation of EC and adsorption using activated carbon treatment used separately or coupled	Electrocoagulation and activated carbon adsorption techniques used separately or coupled					Cost analysis	[55]
Real wastewater from a local municipal wastewater treatment plant	Treatment of micropollutants from municipal wastewater	The process involves graphene adsorption with a hybrid electrocoagulation/electrofiltration (EC/EF) method						[56]
Raw textile industry wastewater	Feasibility evaluation	Combined electrocoagulation (EC)/adsorption process						[57]
Methylene blue (MB) dye stock solution	Removal of methylene blue	Electrocoagulation and adsorption					Adsorption isotherm studies	[40]
Real car wash wastewater	Treatment with equilibrium and kinetic studies	EC treatment followed by adsorption and simultaneous EC/A were assessed					Equilibrium isotherms and adsorption kinetics with statistical evaluation	[58]
Urban wastewater effluent	Characteristics of a hybrid EC and EF treatment system	Electrocoagulation–electroflotation process						[59]
Synthetic dye solution	Removal of eosin yellow and nigrosin dyes	EC coupled with adsorption						[41]
Synthetic dye solution	Removal of methylene blue in aqueous solution	electrocoagulation (EC)/micro-crystalline cellulosic (MCC) adsorption combined process					Kinetic study	[38]
Synthetic dye solution	Removal of Acid Black 1 and Basic	EC/Moringa oleifera seeds (MOS) adsorption hybrid process by using Al and						[60]

Wastewater Used	Main Aim	Treatment Technique	Statistical Analysis	Optimization	RSM	Modeling	Notes	Ref.
	Red 2 from aqueous solutions	stainless-steel electrodes using batch reactor						
Synthetic solution	Cetylpyridinium (CP ⁺) removal	EC, phosphate-assisted EC, and adsorption on electrogenerated adsorbents					Adsorption kinetics and isotherm studies	[61]
Synthetic solution	Removal of malachite green	EC/peanut shell (PS) adsorption hybrid treatment technique					Unit energy and electrode material consumption calculations	[62]
Synthetic solution	Removal of persistent organic pollutants (POPs)	Review Paper					Graphical abstract.	[36]
Tanning wastewater	Chromium removal	Eggshell adsorption process coupled with electrocoagulation					Energy consumption calculations	[63]
Real wastewater from electroplating industry	Different heavy metals treatment	Hybrid EC and adsorption treatment						[64]
Synthetic wastewater containing EBT	Eriochrome black T (EBT) removal	Hybrid treatment process using EC and adsorption					Kinetic modeling	[65]
Synthetic groundwater solutions containing different initial nitrate concentrations	Groundwater denitrification (nitrate-contaminated groundwater)	Hybrid EC/A system						[66]
Cardboard paper mill effluents	Treatment of COD and turbidity	Al and Fe electrodes EC followed by adsorption using GAC						[67]
Beverage industry wastewater	Removal of TSS and COD	A combination of EC and adsorption						[68]
Synthetic dye solution	Treatment of Methylene Blue (MB)	EC/banana peel (BP) adsorption hybrid system						[43]
Synthetic solution	Removal of phenol	GAC and EC						[69]
UASB effluent	COD, BOD, turbidity, and phosphorus removal	Hybrid EC followed by adsorption system		Electrocoagulation stage was optimized using response surface method				[70]
Real groundwater	Defluoridation of groundwater	EC as a pretreatment for groundwater followed by adsorption using activated alumina						[71]

2.3.1 Current density in hybrid EC/A systems

Current density stands as a pivotal operational parameter in EC, uniquely positioned as the directly controllable factor influencing the efficiency of cathodic and anodic reactions and the overall chemical rate of the process. According to Barrera-Díaz et al. [72], the application of Faraday's law within EC frameworks provides a quantitative basis for understanding the connection between current density and the dissolution rate of metal electrodes. The law's formula, $n = (it)/(zF)$, where n represents the moles of metal dissolved, i the current in amperes, F the Faraday constant ($96,500 \text{ C mol}^{-1}$), and t the time in seconds with z denoting the cation charge ($2+$ for Fe and $3+$ for Al), facilitates the calculation of electrochemically produced Fe and Al ions' mass.

However, deviations from Faraday's predictions, termed superfaradic efficiency, indicate that the concentration of Fe or Al ions may surpass theoretical expectations. This phenomenon is attributed to the complex interplay of electrochemical and chemical processes, including the simultaneous evolution of H_2 and dissolution of Al or Fe at the cathode, alongside variations in pH levels across the anode surface due to electrochemical water oxidation and reduction [72]. Manilal and Solomon [73] observed that experimental anode dissolution rates could reach 105% to 190% of theoretical values under super faradic conditions, highlighting the potential to optimize EC by adjusting current density and process duration more efficiently.

The effectiveness of EC is influenced by multiple factors, involving operational conditions, characteristics of the feed, and the configuration of the reactor and electrodes. For instance, current density not only dictates the rate of H_2 evolution near the cathode and the generation of coagulants from the anode as per Faraday's law but also affects the agglomeration of

coagulated particles and the formation of hydrolyzed metal species, which are further modulated by water pH [34]. The pH level plays a critical role in determining the coagulation mechanism through the production of hydrolyzed metal ions, influencing the efficacy of EC alongside other operational mechanisms.

This review narrows its focus to critically evaluating the effect of current density and water pH within the context of combined EC/A systems. It explores how factors such as electrode configuration (e.g., monopolar in series, parallel, or bipolar arrangements), inter-electrode spacing, reactor design, and water conductivity serve as guiding principles for optimizing EC processes [34]. By dissecting the nuances of these operational parameters, the review aims to shed light on their synergistic impact on enhancing the treatment capabilities of hybrid EC/A systems. The coupling of EC with adsorption, particularly using low-cost adsorbents, has demonstrated significant efficacy in removing synthetic dyes from wastewater, a critical concern for environmental sustainability. This section reviews several key studies that explore this hybrid approach, highlighting the innovative use of natural materials as adsorbents and the varied experimental setups and outcomes observed.

Alnawab and Ridha [40], and Zhu et al. [45] employed pomegranate peels, zizith's leaves, and hazelnut shells, respectively, achieving removal efficiencies exceeding 93% for methylene blue. These studies underscore the possible use of agricultural waste as an effective adsorbent when integrated with EC, showcasing an impressive removal rate of up to 99% through the utilization of hazelnut shells. Different EC configurations were employed, showcasing the process's flexibility with various electrode materials: Alnawab and Ridha [40] utilized iron electrodes, whereas Zhu et al. [45] selected an aluminum anode and stainless-steel cathode.

Similarly, de Carvalho et al. [43] and Nooren et al. [38] experimented with banana peels and microcrystalline cellulose, respectively, as adsorbents for methylene blue removal, both achieving around 99% efficiency. These studies not only confirm the high potential of bio-based adsorbents but also highlight the hybrid method's ability to reduce operational demands, such as current density and contact time, enhancing the process's overall efficiency. Vinothkumar et al. [41] expanded the spectrum of treatable dyes to include eosin yellow and nigrosine, utilizing GAC for post-treatment adsorption. Their findings revealed a significant reduction in dye concentrations, with the integrated approach markedly improving eosin yellow removal and completely eliminating nigrosine dye. This suggests that the choice of adsorbent plays a crucial role in the hybrid method's success, with GAC proving particularly effective. Wang et al. [62] further validated the efficacy of combining EC with adsorption using peanut shells to enhance malachite green removal, achieving a 98% efficiency. This study, along with those by Sorayyaei et al. [12] and GilPavas and Correa-Sanchez [44], which explored the treatment of methyl orange and indigo dyes, respectively, underscores the versatility and effectiveness of the EC/A approach across a wide range of dye pollutants and operational conditions. Lastly, Secula et al. [14] and de Carvalho et al. [60] focused on the removal of acid dyes, utilizing activated carbon and *Moringa oleifera* seeds as adsorbents. Both studies achieved high removal efficiencies, around 99% for the acidic dyes, further demonstrating the hybrid approach's ability to meet stringent environmental regulations through reduced operational requirements.

These studies collectively highlight the hybrid EC/A method's potential to address the pressing issue of dye pollution in wastewater. By leveraging low-cost, often bio-based,

adsorbents, this approach not only enhances dye removal efficiencies but also offers a sustainable and economically viable solution for wastewater treatment. The varied experimental designs and outcomes emphasize the method's adaptability and the significant role of adsorbent selection in optimizing treatment processes.

2.3.2 Inter-electrode distance in hybrid EC/A systems

The inter-electrode distance within EC setups shows a critical role in determining the efficiency and effectiveness of the treatment process. As outlined by Hakizimana et al. [34], the configuration of electrodes—whether arranged in monopolar series, monopolar parallel, or bipolar series—alongside the inter-electrode distance, significantly influences the EC process dynamics. These variables directly impact the electrical field distribution, current density, and consequently, the rate of electrochemical reactions occurring within the reactor. An optimal inter-electrode distance is crucial for balancing energy consumption with treatment efficacy. A shorter distance between electrodes typically results in a stronger electric field, which can enhance coagulant generation and pollutant removal efficiency. However, it also rises the energy consumption and the risk of electrode passivation due to accelerated anode dissolution. Conversely, a larger electrode gap may reduce energy costs and slow down electrode wear but at the expense of reduced treatment efficiency due to a weaker electric field and lower reaction rates. The choice of electrode arrangement and the precise setting of inter-electrode distance must, therefore, be carefully considered. These decisions are influenced by factors including the specific contaminants being treated, the desired treatment capacity, and the overall design of the EC reactor.

Water conductivity further modulates these effects, as it affects the resistance of the solution and, thereby, the efficiency of current transfer between electrodes.

Incorporating insights from studies like that of Hakizimana et al. [34], this review highlights the importance of inter-electrode distance as a determinant of EC performance. By adjusting this parameter, practitioners can optimize the balance between operational cost and treatment effectiveness, tailoring the EC process to meet specific water or wastewater treatment objectives.

2.3.3 Solution pH in hybrid EC/A systems

The initial pH of the electrolyte emerges as a critical determinant in the effectiveness of combined EC and adsorption processes. The solubility of numerous contaminants, and consequently their amenability to EC and adsorption, is markedly influenced by the pH of the solution. Furthermore, initiating the EC/A treatment can lead to changes in the initial pH, potentially increasing or decreasing, thereby impacting the efficiency of the integrated method. The optimal pH range—whether acidic, basic, or neutral—depends on a complex interplay of factors including the electrode material, adsorbent type, and the specific contaminants targeted.

Research findings on the effect of solution pH on the removal efficiency of hybrid EC/A methods present a diverse picture. Studies such as those conducted by Hendaoui et al. [37] and Noreen et al. [38] report enhanced removal efficiencies under basic pH conditions. This suggests that certain contaminants or treatment configurations may benefit from a

higher pH, possibly due to the increased formation of hydroxide complexes that facilitate coagulation and subsequent adsorption.

Conversely, investigations by Alnawab and Ridha [40], GilPavas and Correa-Sanchez [44], and Secula et al. [14] have illustrated a preference for acidic conditions in improving the hybrid technique's efficiency. This could be attributed to the enhanced dissolution of metal ions from the electrodes under acidic conditions, improving the coagulation process and potentially increasing adsorption sites on the adsorbent material.

Interestingly, de Carvalho et al. [43] and Sorayyaei et al. [12] found that neutral pH levels were most conducive to achieving high removal efficiencies. This neutrality may offer a balanced environment that supports both the electrochemical reactions of EC and the physicochemical interactions of adsorption without favoring the dissolution or precipitation of contaminants excessively. Vinothkumar et al. [41] reported high removal efficiencies across both acidic and basic pH ranges, highlighting the possibility of tailoring the EC/A process to work efficiently across a broad pH spectrum. This adaptability underscores the importance of understanding the detailed characteristics of the wastewater being treated and the necessity of optimizing the initial pH to match the treatment objectives. These studies collectively underscore the nuanced role of solution pH in the efficacy of EC/A processes. Adjusting the pH to suit the specific conditions of the treatment can significantly enhance contaminant removal efficiency, pointing to the need for careful consideration of initial pH values in the design and optimization of hybrid EC/A systems.

2.3.4 Contact time in hybrid EC/A systems

Contact time, alongside current density, is a critical factor in the optimization of EC processes, especially when coupled with adsorption. The integration of adsorption into EC not only enhances removal efficiency but also affects the operational dynamics, including the reduction of required contact times. This synergy allows for efficient contaminant removal at lower current densities and within shorter operational durations, underscoring the method's effectiveness and potential for cost savings.

The introduction of adsorbents directly into the EC process has been shown to yield significant advantages, including the achievement of higher removal efficiencies within reduced contact times. This observation suggests that adsorbents play a vital role in facilitating faster contaminant capture, thereby expediting the purification process. Despite variations in electrode materials, adsorbent types, reactor designs, and electrolyte compositions, the consistent outcome across studies is the beneficial impact of adsorption on the efficiency and speed of EC treatments. Barhoumi et al. [39] explored the treatment of a real wastewater from paper industry, employing a hybrid EC/adsorption approach with aluminum electrodes and GAC for adsorption. Their findings revealed a remarkable 99.11% removal efficiency for Humic acid (HA) without incurring significant cost increases. Importantly, this study highlighted the method's ability to reduce both contact time and energy consumption, demonstrating the efficiency of the integrated approach.

Similarly, Jose et al. [47] investigated the treatment of coconut retting wastewater, using iron electrodes for EC and AC for adsorption. The hybrid method proved exceptionally effective, achieving significant reductions in total dissolved solids (TDS), TOC, COD, and color. Notably, reductions of 92.8% for COD, 56% for TOC, and 99% for TDS were

recorded, alongside the attainment of an acceptable LC_{50} value, indicating the treated water's safety for disposal. These studies affirm the broad applicability and effectiveness of the hybrid EC/A method, particularly in reducing operational contact time while maintaining or enhancing contaminant removal efficiency. The integrated approach not only promises environmental benefits but also operational efficiencies, making it a compelling option for wastewater treatment across various industries.

2.3.5 Adsorbent dosage in hybrid EC/A systems

Adsorbent dosage is a vital factor for the effectiveness of contaminant removal within the combined EC/A technique. As the dosage increases, so does the surface area available for adsorption, theoretically enhancing the process's capacity to remove contaminants. However, the dynamics of adsorbent concentration vary, especially in batch systems where the adsorbent concentration can fluctuate, potentially affecting the overall efficiency of contaminant removal. In contrast, fixed-bed systems offer a more stable environment for adsorption, making them potentially more effective for wastewater treatment applications. Despite these variations, an increase in adsorbent dose is feasible and often beneficial in both system types. A comprehensive review of the literature reveals a consistent pattern: the majority of studies report an improvement in the removal efficiency with an increase in the adsorbent dosage. This trend is evidenced by research from Hendaoui et al. [37], Alnawab and Ridha [40], de Carvalho et al. [43], Noreen et al. [38], and many others, who observed a positive correlation between higher adsorbent dosages and enhanced process efficiency. This relationship underscores the importance of optimizing adsorbent dosage to achieve maximal contaminant removal, particularly in the context of the hybrid EC/A

method. Interestingly, a deviation from this trend was noted in the study by Sorayyaei et al. [12], which reported a decline in contaminant removal efficiency with an increased adsorbent dose. This exception highlights that while generally beneficial, the impact of increased adsorbent dosage on treatment efficiency may be contingent on specific factors such as the nature of the contaminant, the type of adsorbents used, and the particularities of the wastewater being treated.

The prevailing evidence supports the notion that carefully calibrated increases in adsorbent dosage can significantly enhance the efficacy of combined EC/A processes. However, the nuanced outcomes observed across different studies suggest that the optimal adsorbent dosage must be determined based on a comprehensive understanding of the system's specific operational conditions and requirements. This tailored approach ensures that the integrated treatment method achieves its full potential in removing contaminants from wastewater, providing a versatile and effective solution for wastewater management.

2.4 Conclusion

The discharge of wastewater from diverse industrial and domestic sources poses a significant threat to ecological sustainability. Addressing this challenge requires effective treatment strategies that can tackle a wide array of contaminants. This review has systematically examined the efficacy of integrating EC with adsorption techniques, highlighting its application across various industrial sectors including textile, tannery, jewelry, dairy, and in the treatment of laboratory-synthesized solutions. The findings underscore the superior contaminant removal capabilities of the hybrid method compared to either EC or adsorption used in isolation. Key pollutants including lead (Pb), copper

(Cu), zinc (Zn), chromium (Cr), COD, BOD, TDS, total suspended solids (TSS), fats, and various micro-pollutants have been effectively reduced using this combined approach. Notably, the concurrent application of EC and adsorption processes has demonstrated not only enhanced efficiency in contaminant removal but also significant reductions in energy consumption and operational costs. This synergistic effect positions the integrated method as a promising, cost-effective solution for wastewater treatment within industrial contexts. The evidence presented in this review suggests that the hybrid EC/A technique holds considerable potential for improving wastewater management practices. By offering a versatile and efficient approach to removing a broad spectrum of contaminants, it contributes to the development of sustainable treatment technologies. Future studies should concentrate on optimizing the operational parameters of this integrated method, exploring its applicability to a wider range of pollutants and wastewater types, and evaluating its performance in larger-scale industrial applications. The goal is to fully realize the environmental and economic benefits of this innovative treatment strategy, thereby contributing to the preservation of water resources and the protection of the environment.

CHAPTER 3

Synthesis and Application of Novel GO@ZIF-7 Nanocomposite for the Removal of Lead from Aqueous Solutions

3.1 Abstract

Water pollution is a growing environmental problem with negative impacts on the ecosystem and the public health. Lead is one of the highly toxic water pollutants, requiring effective elimination from contaminated waters. In this study, a novel graphene oxide/zeolitic imidazolate framework-7 (abbreviated as GO@ZIF-7) nanocomposite has been synthesized and utilized for the adsorptive removal of lead from aqueous solutions. Despite the low level of GO in the nanocomposite, the nanocomposite extremely outperformed its parental materials (GO and ZIF-7) with a lead adsorption capacity approaching 5,000 mg/g relative to about 500 and 600 mg/g obtained using ZIF-7 and GO, respectively. The adsorptive removal of lead using this nanocomposite was also optimized using the Response Surface Methodology (RSM) and the optimization results revealed a greater role of aqueous pH and the adsorbent dosage in achieving higher lead removal. Typically, higher lead adsorption was noted at pH 6, most likely, resulting from a greater interaction between the cationic lead species and the adsorbent surface due to comparatively less presence of the cationic H^+ ions. Furthermore, a greater removal at higher adsorbent dosage is also attributed to higher availability of surface sites for lead adsorption. Lead adsorption was also noted to follow the Freundlich adsorption isotherm

trend, suggesting a multi-layer adsorption of lead onto the adsorbent surface. This is consistent with the above-mentioned higher lead uptake capacity by the GO@ZIF-7 nanocomposite as compared to the unmodified GO and ZIF-7. The outcomes of this study reveal the high commercial potential of the GO@ZIF-7 nanocomposite in successfully treating waters contaminated with lead.

Keywords: Adsorptive removal of lead (Pb); Zeolitic imidazole frameworks (ZIFs); ZIF-7; Graphene oxide (GO); GO@ZIF-7 nanocomposite; Response Surface Methodology (RSM)

3.2 Introduction

Metal organic frameworks (MOFs) are a type of crystalline organic and inorganic hybrid compounds formed by linking the metal clusters or ions with organic linkers [74]. These MOFs are currently attracting much attention for their potential applications to remove organic and inorganic contaminants from wastewater because of their significantly higher adsorption capacity compared to conventional adsorbents. MOFs offer the possibility of tuning their characteristics to meet the requirements of certain applications; this flexibility is usually lacking in the previously used microporous and mesoporous materials. Therefore, MOFs have been used for a variety of applications including gas separation, energy storage, and catalysis [75]. Although there are numerous MOFs with different structures and chemical compositions that can be potentially synthesized, the synthesis of

MOFs with high thermal and chemical stability for industrial implementation is still a challenge [76].

Unlike MOFs, zeolitic imidazolate frameworks (ZIFs), a new class of MOFs, usually possess higher thermal and chemical stability [77, 78]. Various ZIFs can be formed when Zn or Co atoms is linked to the N atom of a suitable imidazolate ligand. ZIFs have emerged as a new type of highly porous materials that combine the advantages of zeolites and conventional MOFs. Accordingly, ZIFs have been synthesized and applied in energy storage [79, 80], gas separation [81, 82, 83], gas storage [84], photocatalysis [85], food safety electrochemiluminescence sensors [86], and catalytic studies [87], with relatively a smaller number of studies focusing on their application for organic and inorganic pollutants removal from wastewaters. Nonetheless, even these relatively smaller number of studies focusing on ZIFs application in wastewater treatment are mainly using ZIF-8 and ZIF-67 [88]. As detailed by Xiao et al. [89] in their recent review, there is a lack of studies on utilizing ZIF-7 for any of the above-mentioned applications, including the adsorptive removal of pollutants from contaminated aqueous solutions. Thus, this study focuses on the application of ZIF-7 and its nanocomposite with graphene oxide (i.e., GO@ZIF-7) for the adsorptive removal of lead from aqueous solutions.

Lead, which is harmful to living organisms, is widely distributed in the environment including the lead-contaminated wastewaters. Pb is a very toxic heavy metal that can have serious effects on water quality. It can contaminate both groundwater and surface waters through the discharge of lead-contaminated streams from various industrial activities. Pb contamination can also harm aquatic life since it is toxic to a variety of aquatic species and can cause reproductive problems in these species and even their death [90]. It can also

accumulate in the food chain and become harmful to animals and humans consuming such lead-contaminated food.

It should be noticed that the long-term exposure to low levels of lead in drinking water can also cause chronic health problems, including developmental delays in children, hypertension, and cognitive decline in adults [91], among others. Hence, the key aim of this study is to synthesize a novel GO@ZIF-7 nanocomposite by combining ZIF-7 with GO and to investigate its efficiency in removing lead from synthetic wastewater samples. The adsorption performance of the nanocomposite towards will be also benchmarked to those of the pristine GO and ZIF-7. The RSM modelling will be used to optimize the Pb removal through the variations of some key adsorption parameters (i.e., pH, adsorbent dosage, and Pb concentration). The kinetics and the isotherm of Pb adsorption onto GO@ZIF-7 nanocomposite will be also investigated. To the best of our knowledge, this is the first study on the application of ZIF-7 for the adsorptive removal of Pb from contaminated water samples. Additionally, there are no published studies so far, to the best of our knowledge, on the synthesis and the application of GO@ZIF-7 nanocomposite for the adsorptive removal of any water pollutant. The utilization of GO@ZIF-7 nanocomposite for any other applications is also still greatly lacking in the published literature, to the best of our knowledge, highlighting the novelty and the significance of this study.

3.3 Materials and methods

3.3.1 Materials

Benzimidazole, zinc nitrate hexahydrate, graphite powder, potassium permanganate (KMnO_4), sulfuric acid, phosphoric acid, hydrogen peroxide, and HPLC grade methanol were purchased from Sigma-Aldrich while $\text{Pb}(\text{NO}_3)_2$ was obtained from BDH Chemicals. All chemicals/materials utilized in this study were of analytical grade purity or higher, and used as received without treatment.

3.3.2 Synthesis of GO

GO was prepared according to the improved Hummers method [92]. Briefly, 360 mL H_2SO_4 and 40 mL H_3PO_4 ($\text{H}_2\text{SO}_4\text{:H}_3\text{PO}_4$ volumetric ratio = 9:1) were carefully mixed in a flask. To regulate the temperature, the flask was placed in an ice bath. Then, 3 g of graphite powder was added to the above mixture, followed by the slow addition of 18 g KMnO_4 while continuously stirring. The reaction mixture was then transferred to a warm water bath and stirred for 12 h at 50 °C. After that, the reaction mixture was poured into about 400 g of crushed ice, followed by the slow addition of H_2O_2 (~ 5 mL) until the mixture color turned a dark yellow. Then, the mixture was stirred continuously for 12 h at room temperature. The mixture was, then, washed consecutively with distilled water and HCl (10 vol%) solution three times each, and the solid was recovered after each wash cycle by centrifugation at 8000 rpm. After this step, GO was further rinsed several times with copious amounts of distilled water to completely remove the residual acid. Finally, the obtained GO was dried at 50 °C and ground to produce fine powders.

3.3.3 Synthesis of ZIF-7

The preparation of ZIF-7 was according to the protocol reported by Yaghi group [93], with some modifications. In this preparation, 5.94 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to 40 mL HPLC grade methanol. In a separate beaker, 9.44 g benzimidazole was added to 40 mL HPLC grade methanol. The two solutions were then stirred at room temperature until the solid materials were completely dissolved. After that, the zinc solution was poured quickly into the benzimidazole solution while stirring for 1 h at room temperature. The mixture was then transferred into a Teflon-lined autoclave reactor and kept in an oven at 130 °C for 24 h. Then, the autoclave reactor was removed from the oven and left to cool down naturally. Following that, the formed ZIF-7 powder was purified via several washes with HPLC grade methanol; the solid ZIF-7 material was recovered after each wash using centrifugation at 6000 rpm. The purified ZIF-7 was then dried at 50 °C. The dried ZIF-7 powder was ground to obtain a fine powder. The ZIF-7 powder was stored in tightly closed containers until use.

3.3.4 Synthesis of GO@ZIF-7 nanocomposite

To prepare GO@ZIF-7 nanocomposite, 5.94 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to 40 mL HPLC grade methanol, followed by stirring until the zinc salt was completely dissolved. Then, 0.25 g GO was added to the above zinc solution and stirred at room temperature for 5 min to disperse GO. After that, the GO dispersion was sonicated at 50% amplitude for 30 min using a probe sonicator. The remaining preparation steps are similar to those used to prepare ZIF-7.

3.3.5 Characterization of GO, ZIF-7, and GO@ZIF-7 nanocomposite

X-ray diffraction (XRD) patterns of GO, ZIF-7, and GO@ZIF-7 nanocomposite were obtained in the range of 5-60° (step width: 0.03°, scan rate: 5.00°/min) using an X-ray diffractometer (MiniFlex 300/600, Rigaku). Additionally, Fourier transform infrared (FTIR) spectra of the synthesized GO, ZIF-7, and GO@ZIF-7 nanocomposite were recorded using an FTIR spectrometer (Nicolet RaptIR FRIR Microscope, Thermo Fisher Scientific) in the range of 400–4000 cm⁻¹.

3.3.6 Adsorption experiments

A stock solution of lead with a concentration of 1000 mg/L was prepared by dissolving lead nitrate Pb(NO₃)₂ in distilled water. This stock solution was then used to prepare other lead solutions. The initial pH of each respective solution was adjusted using 0.1 M HNO₃ or 0.1 M NaOH solution before each adsorption experiment.

All adsorption experiments were carried out in capped 100-mL conical flasks containing 25 mL of lead solutions (50, 100, and 150 mg/L), with varying pH (2, 4, and 6), and GO@ZIF-7 dosages (200, 400, and 600 mg/L). The respective flasks were, then, placed on a speed controlled magnetic stirrer at a fixed speed of 250 rpm for 24 h. The residual lead concentration after each experiment was determined using a flame atomic absorption spectrometer (AAS, PerkinElmer). The samples were filtered using 0.2 µm filter (Whatmann) before subjecting them to analysis. The instrument accuracy was periodically checked using standard metal solutions.

3.3.7 Benchmarking the performance of GO@ZIF-7 to its precursors

Before conducting the optimization of lead removal from contaminated water samples using RSM, the adsorption performance of GO@ZIF-7 was compared to those of GO and ZIF-7. In these experiments, the adsorbent dosage, sample volume, adsorption time, and shaking speed were fixed at 100 mg/L, 100 mL, 24 h, and 250 rpm, respectively. Two lead concentrations (100 and 500 mg/L) were prepared using distilled water and utilized in these experiments to measure the lead uptake capacity by the above 3 adsorbents. The uptake capacity (q_e) was calculated using the following equation:

$$q_e = \frac{(C_i - C_f)V}{m} \quad (3.1)$$

Where C_i and C_f are, respectively, the initial and final (after 24 h) lead concentrations, V is the sample volume, and m is the adsorbent mass.

3.3.8 Response surface methodology (RSM) modeling

The initial lead concentration, adsorbent dosage, and pH of the solution were selected as the factors for the RSM modeling. Each factor unit and respective levels are shown in Table 2. The RSM design used in the current study is a randomized three numeric factors face-centered (FC-RSM) design with three levels for each numeric factor and five center points per block, along with the lead removal efficiency (%) as the response. Table 3 shows the full FC-RSM design of the experiments.

Table 2: FC-RSM factors and levels

Factors	Levels		
A = pH	2	4	6
B = Initial lead concentration (mg/L)	50	100	150
C = Adsorbent dosage (mg/L)	200	400	600

Table 3: Full FC-RSM design of experiments along with the obtained lead removal parentage at each experimental condition

Exp. No.	A	B	C	Lead removal (%)
1	4	100	400	82.2
2	4	100	200	42.2
3	2	50	200	39.3
4	4	50	400	56.4
5	6	100	400	84.0
6	2	100	400	24.8
7	6	50	200	82.9
8	2	150	200	31.7
9	2	150	600	39.7
10	6	150	600	93.4
11	4	100	600	87.0
12	2	50	600	48.5
13	6	150	200	83.4

14	4	150	400	84.6
15	6	50	600	94.8

3.4 Results and Discussion

3.4.1 Characterizations

Figure 3 shows the XRD patterns of ZIF-7, GO, and the GO@ZIF-7 nanocomposite. The diffraction peaks of ZIF-7 appearing at 2θ of 9.12, 16.0, 16.68, 17.52, 19.98, 21.6, 23.1, 27.39, 31.59, 33.54, 35.43, and 37.8° are in line with those observed for ZIF-7 prepared using diethylformamide [94], ammonia atmosphere [95], water/ethanol mixture [96], and N,N-dimethylformamide [97] as the synthesis medium. The sharp and intense characteristic diffraction peak at 9.12° is indicative of the formation of microporous ZIF-7 [96]. Based on the synthesis conditions and medium, ZIF-7 might exist as phase I, II, or III. The diffraction peaks of ZIF-7 shown in Figure 3 indicate the formation of ZIF-7 phase III. The above cited references also reported the formation of ZIF-7 phase III. This ZIF-7 phase has a (4,4) square planar with a rigid structure formed via the coordination of benzimidazolate tetrahedra with quadruply linked corner-shared networks of Zn(II) [98]. Although ZIF-7 III phase is the densest among other ZIF-7 phases (and also many other ZIFs), it is the most stable phase of ZIF-7 [98].

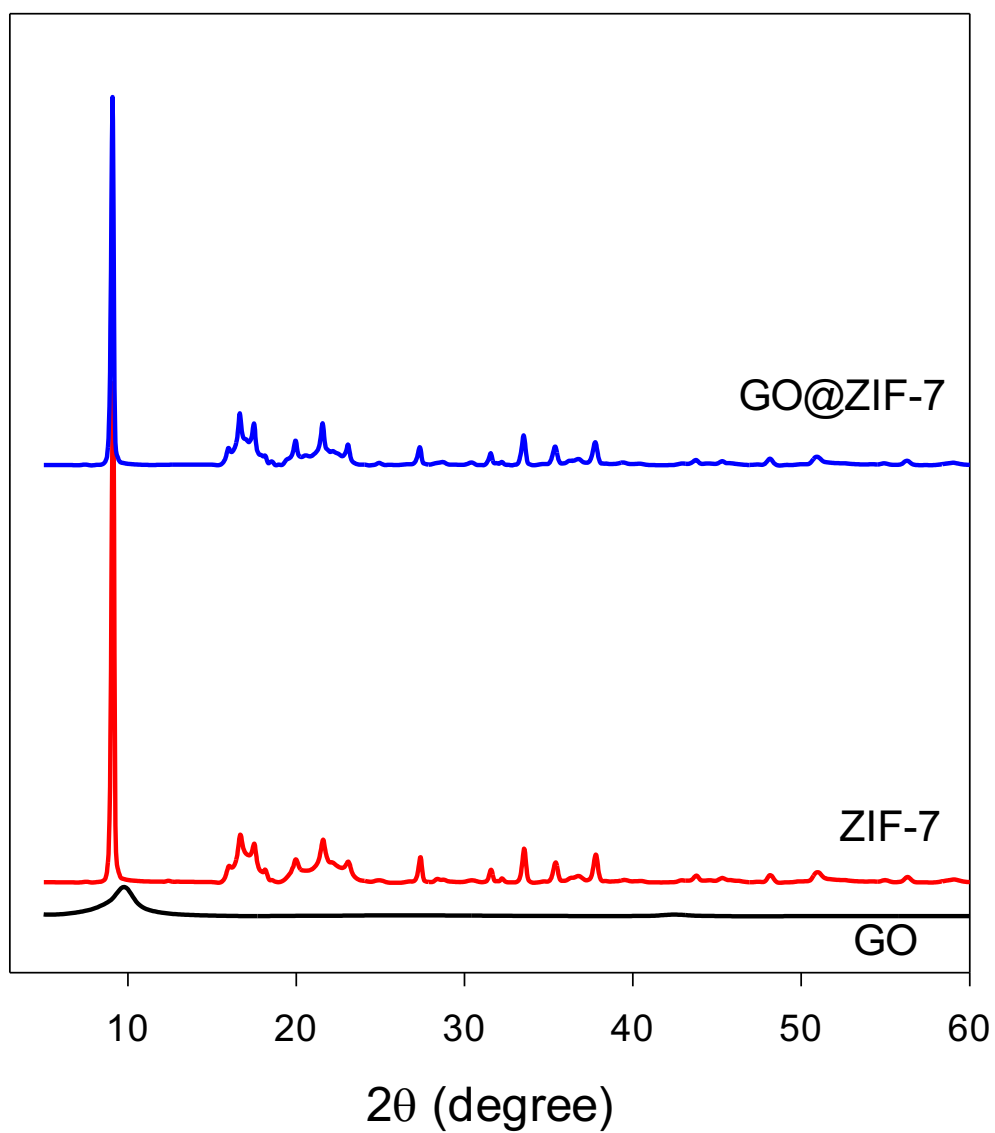


Figure 3: XRD patterns of GO, ZIF-7, and GO@ZIF-7 nanocomposite

Figure 3 also shows the XRD diffraction pattern of GO, which reveals a single minor diffraction peak at 9.8° . This GO diffraction pattern is in line with the relevant literature on GO prepared using the improved Hummers method [92, 99, 100]. Additionally, Figure 3 displays the XRD pattern of the GO@ZIF-7 nanocomposite. According to the data presented in this figure, the XRD patterns of ZIF-7 and GO@ZIF-7 nanocomposite are similar. This similarity is justified by the low intensity of the GO diffraction peak at 9.8° , which is about 5% of the intensity of the ZIF-7 peak appearing at a close proximity (i.e., at 2θ angle of 9.12°). The close proximity of the minor GO and the intense ZIF-7 diffraction peaks could result in concealing the diffraction peak of GO by that of ZIF-7. Additionally, the low level of GO in the GO@ZIF-7 nanocomposite (about 1.63 % of the mass of the ZIF-7 precursors in the synthesis solution) is another plausible reason for the similarity of the XRD diffraction patterns of ZIF-7 and GO@ZIF-7 nanocomposite.

The FTIR spectra of GO, ZIF-7, and the GO@ZIF-7 nanocomposite are shown in Figure 4. As displayed in Figure 4, GO spectra have a wide and intense absorption peak at around 3417 cm^{-1} , which corresponds to the O–H stretching vibration due to the presence of water moisture and/or the KBr deliquescence [101, 102]. The minor peaks at 2936 and 2855 cm^{-1} are attributed to the bending vibration of the C–H bond in the GO framework [103, 104]. Additionally, the peak at 1730 cm^{-1} corresponds to the C=O stretching vibration while the relatively intense peak at 1636 cm^{-1} is related to the skeletal vibration of the sp^2 hybridized carbons in the graphitic structure [105, 106]. Furthermore, the absorption peaks at 1385 and 1060 cm^{-1} correspond to the bending of the alcohol bond (O–H) and the C–H stretching vibrations, respectively.

Figure 4 also displays the FTIR spectra of ZIF-7 and GO@ZIF-7 nanocomposite. The ZIF-7 spectra shown in Figure 4 are comparable to those reported by Davoodian et al. [107], Zhao et al. [108], and Li et al. [109]. Additionally, the FTIR spectra of ZIF-7 and GO@ZIF-7 nanocomposite are comparable, most likely due to the low level of GO in the nanocomposite as stated earlier. Nonetheless, despite the low GO level in the nanocomposite, the inclusion of GO in the ZIF-7 framework resulted in a significant increase in lead adsorption as will be presented and discussed subsequently. The FTIR spectra of ZIF-7 and GO@ZIF-7 nanocomposite shown in Figure 4 display several absorption peaks. The peaks appearing at around 2700–3100 cm^{-1} might be attributed to the O–H stretching vibration of the residual alcohol used in the synthesis and purification. The absorption peaks at 1700–2000 cm^{-1} could be assigned to the bending vibration

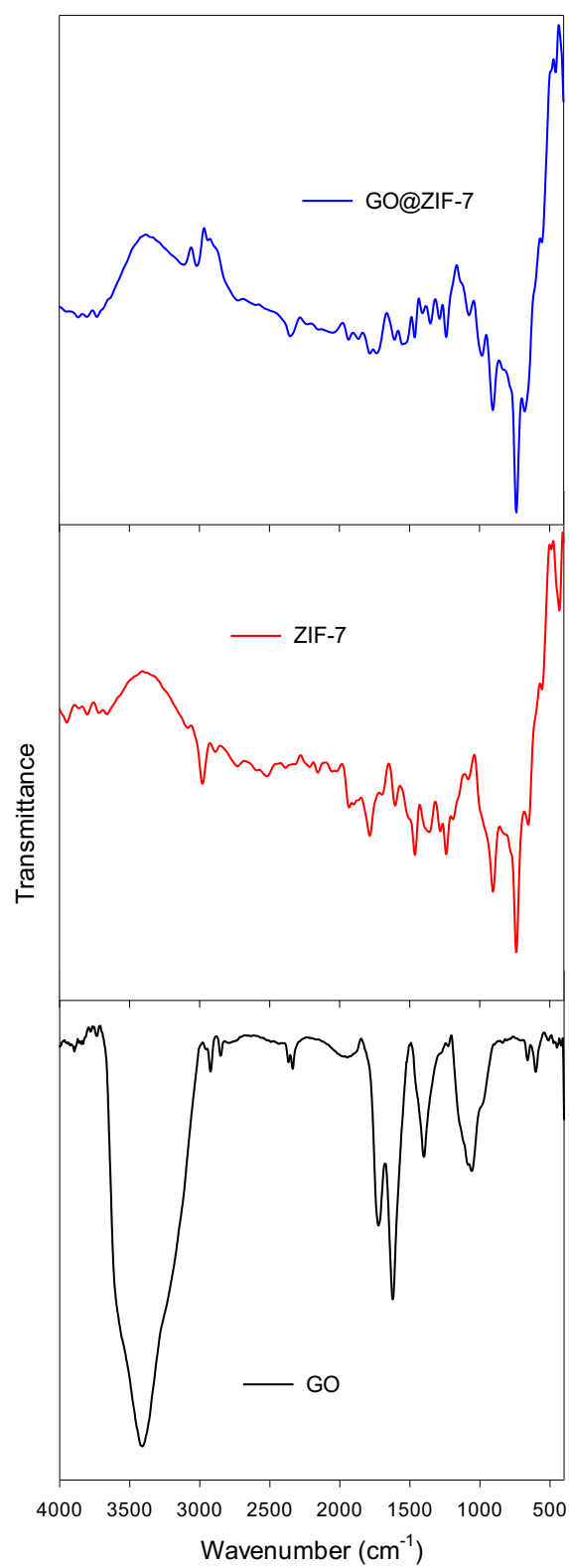


Figure 4: The FTIR spectra of GO, ZIF-7, and GO@ZIF-7 nanocomposite

of the C–H bond in the benzyl ring of the organic linker (i.e., benzimidazole) while the absorption peaks at 1500–1700 cm^{-1} can be ascribed to the C=C stretching of the aromatic ring of the benzimidazole [110]. The peaks at 1300–1365 cm^{-1} might be attributed to the C–N stretching while the peak appearing at around 1240 cm^{-1} stems from the C–C stretching. The absorption peaks at ~1100–1200 and ~740–900 cm^{-1} can be attributed to the in-plane and out-of-plane bending vibrations of the C–H bond, respectively. The peak appearing at around 1080 might be related to the C–C–C trigonal bending of the organic linker. Additionally, the peaks appearing at ~450–550 cm^{-1} can be ascribed to the C–C–C out-of-plane bending vibration while the one at ~650 cm^{-1} is related to the C–C–C in-plane bending vibration. The peak centered at around ~430 is due to the stretching vibration of the formed Zn–N bond between the organic linker and the Zn atom.

3.4.2 Lead uptake capacities by GO@ZIF-7, ZIF-7, and GO

The adsorption of lead on GO, ZIF-7, and GO@ZIF-7 nanocomposite from two different initial lead concentrations (i.e., 100 and 500 mg/L) is shown in Figure 5. As displayed in this figure, the adsorption capacity of lead on the GO@ZIF-7 nanocomposite is 941 mg/g when the adsorption took place from 100 mg/L lead solution. This lead uptake capacity by the GO@ZIF-7 nanocomposite is about 4-fold higher than its adsorption on the parental materials (i.e., GO and ZIF-7) of the nanocomposite. Increasing the initial lead concentration to 500 mg/L resulted in a huge boost in lead adsorption capacity by the GO@ZIF-7 nanocomposite, reaching 4695 mg/g, which is almost 10 times higher than its adsorption capacity on the pristines GO and ZIF-7. These results demonstrate the superiority of the GO@ZIF-7 nanocomposite relative to GO and ZIF-7 as well as many

other materials reported in the literature as shown in Table 4. Accordingly, lead removal optimization study using RSM was conducted using the GO@ZIF-7 nanocomposite as the most effective adsorbent.

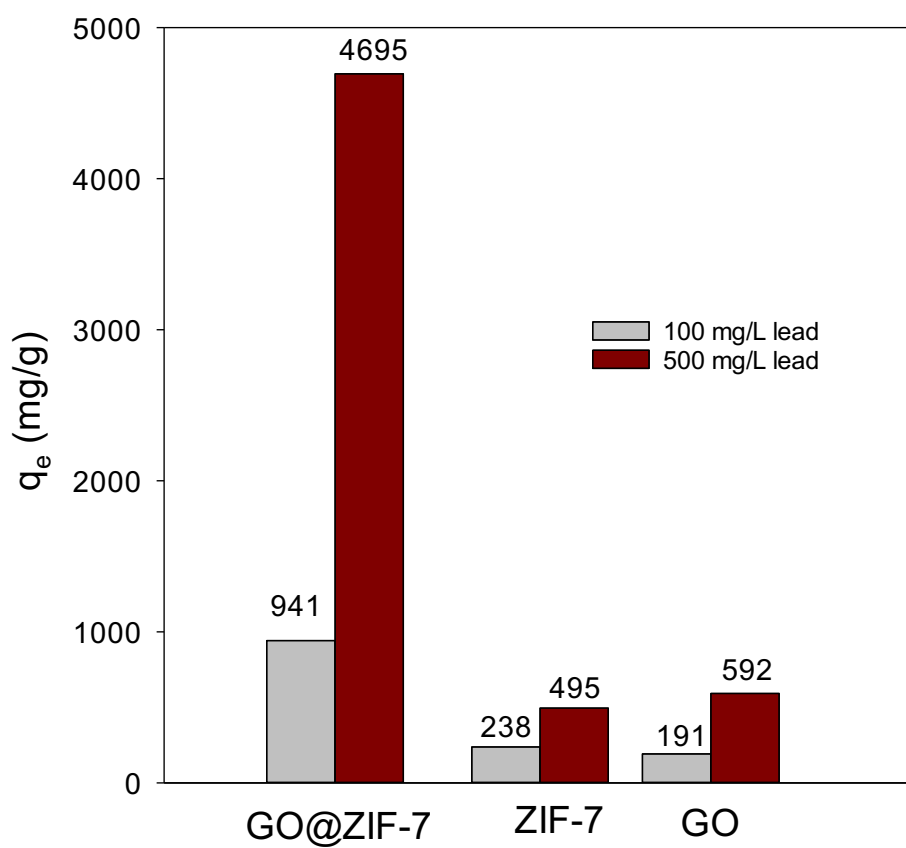


Figure 5: Benchmarking the lead uptake capacity by the GO@ZIF-7 nanocomposite to its uptake capacity by the unmodified GO and ZIF-7 materials

Table 4: Comparison of lead uptake capacity obtained using the GO@ZIF-7 nanocomposite to its uptake capacity by other adsorbents as reported in the relevant literature

Adsorbent	Lead adsorption capacity (mg/g)	Ref.
GO@ZIF-7	4695	This study
Sulfur modified biochar	421.8	[111]
Novel hybrid polymer	349.5	[112]
Sulphydryl modified attapulgite	65.6	[113]
ZIF-8	1119.8	[114]
ZIF-67	1348.4	
Mercaptoethanol modified silica	10.4	[115]
Mercapto functionalized palygorskite	66.3	[116]
Amino functionalized palygorskite	74.6	
Thiol-functionalized MOF	312.5	[117]
Unmodified MOF-5	211	
Post-synthetically modified UiO-66-NH ₂	232	[118]
Aluminum based magnetic framework composites	492.4	[119]
Self-assembled flower-like TiO ₂ on exfoliated graphite oxide	45.0	[120]
	65.6	
Chitosan and cellulose based novel recyclable fibrous composite modified adsorbent	144.9	[121]
Nanostructured magnesium oxide coated magnetite cluster composite	238	[122]
Few-layered graphene oxide	1850	[123]
Functionalized graphene	406.6	[124]

ZIF-8	1780.9	[125]
ZIF-67	1978.6	
Activated carbon derived from waste coconut buttons	94.3	[126]
pH-sensitive polymer hydrogels	117.9	[127]
Untreated olive tree pruning	13	[128]
Chemically treated OTP	15.4	
HNO ₃ -OTP	14.1	
NaOH-OTP	16.0	
Untreated peach palm waste	43.3	[129]
NaOH treated peach palm waste	65.3	
NaOH/citric acid treated peach palm waste	36.1	
Thiol/amine bifunctionalized nanoparticles	110.1	[130]
Commercial activated carbon	60.7	[131]
Commercial granular activated carbon (GAC)	43.1	[132]
Powdered activated carbon	46	[133]

3.4.3 Lead removal & response surface methodology (RSM) modeling

The lead removal results under a varying set of process conditions are given in Table 3. Despite the relatively high lead concentration (50-150 mg/L) and relatively low adsorbent dosage (0.2-0.6 g/L), lead removal can be as high as ~95% (see Table 3). Nonetheless, it is evident that at acidic pH (e.g., pH 2), lead removal is generally low. This is noted even at lower lead concentration of 50 mg/L in spite of using a higher adsorbent dosage of 600 mg/L. At low pH, lead will be mostly present in the cationic form. Furthermore, the H⁺ ions will also be dominant at pH 2. This will, consequently, create competition between

lead species and protons for adsorbing at the available adsorption sites, resulting in lower lead removal at the acidic pH values (Table 3). Hence lower lead removal at pH 2 (even at 50 mg/L lead and using higher adsorbent dose of 600 mg/L) can be attributed to competition between the cationic lead and cation H^+ species for the available adsorption sites. Nevertheless, at pH 6, a significant lead removal is noted (even for initial lead concentration of 150 mg/L) using 600 mg/L adsorbent dose.

It should also be noted that the upper pH limit of 6 was considered to prevent/minimize lead precipitation. Also, in general an increase in the adsorbent amount causes enhanced process efficiency, whereas the initial lead concentration shows minimal effect on its removal (under a specific set of conditions). This indicates that the mass transfer of lead from the bulk aqueous to the solid surface is enhanced at its higher concentration. Nevertheless, a decrease in adsorbent does reduced lead removal due to the decrease in the available of adsorption sites. Hence, mass transfer from the bulk liquid to the adsorbent surface, availability of sufficient uncovered adsorption sites, and diffusion of lead species to respective adsorption sites play important roles in lead removal efficiency. Further to the results presented in Table 3, an effective RSM based model was also explored, and the modeling findings supported the negligible effect of initial lead concentration (factor B) on its removal by the GO@ZIF-7 nanocomposite as given by the equation (3.2):

$$\text{Lead Removal Efficiency} = 64.9947 + 25.465 \times A + 8.381 \times C \quad (3.2)$$

Where A is the solution pH and C is the adsorbent dosage. Several statistical parameters for the respective RSM modeling are given in Tables 5 and 6.

The adequate precision that measures the signal to noise ratio (i.e., the ratio of predicted value to the average of prediction errors) is aimed to be greater than 4, indicating a better statistical fit and suitability of the suggested model. The adequate precision value of 11.28 (see Table 5) for equation (3.1) (i.e., the RSM-based model) does meet the suggested statistical parameters (i.e., adequate precision should be greater than 4). Furthermore, the adjusted and predicted R^2 values with a difference of less than 0.2 are also supportive of the suggested model as given by equation (3.1). It should be noted that unlike the traditional R^2 value, the adjusted R^2 value is enhanced only upon the inclusion of the specific factor(s) and/or combination(s) of factor(s) that improve the model output. Similarly, the predicted R^2 is enhanced with a conformance between the predicted and actual results. Furthermore, the model p -values (see Table 6) of less than 0.05 indicate that the model factors, except for Factor B (i.e., initial lead concentration), are significant. The aqueous pH and adsorbent dosage with p -value of less than 0.05 show their significance. Additionally, the RSM based plot of predicted lead removal versus the actual lead removal (Figure 6) shows an approx. slope of 45° that also tends to support the suggested RSM model. Moreover, Figure 7 shows the normal probability plot of the lead removal residuals also tends to show randomness

and a reasonable scatter, and the linearity of respective normal probability plot also supports the suggested model.

Table 5: FC-RSM model fit statistics

Fit Statistic	FC-RSM Model
R^2	0.8197
Adjusted R^2	0.7706
Predicted R^2	0.7224
Adeq Precision	11.2832

Table 6: ANOVA analysis for FC-RSM model

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	7199.31	3	2399.77	16.67	0.0002
A	6484.66	1	6484.66	45.05	< 0.0001
B	12.23	1	12.23	0.0850	0.7761
C	702.41	1	702.41	4.88	0.0493
Residual	1583.30	11	143.94		
Cor Total	8782.61	14			

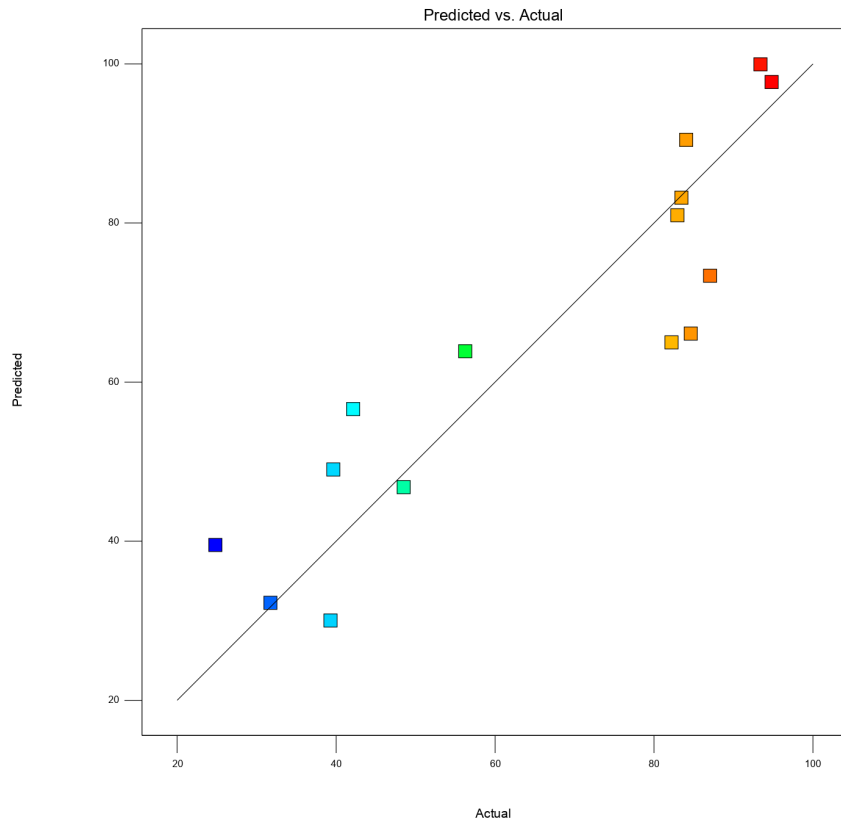


Figure 6: Actual versus predicted obtained from the RSM modelling

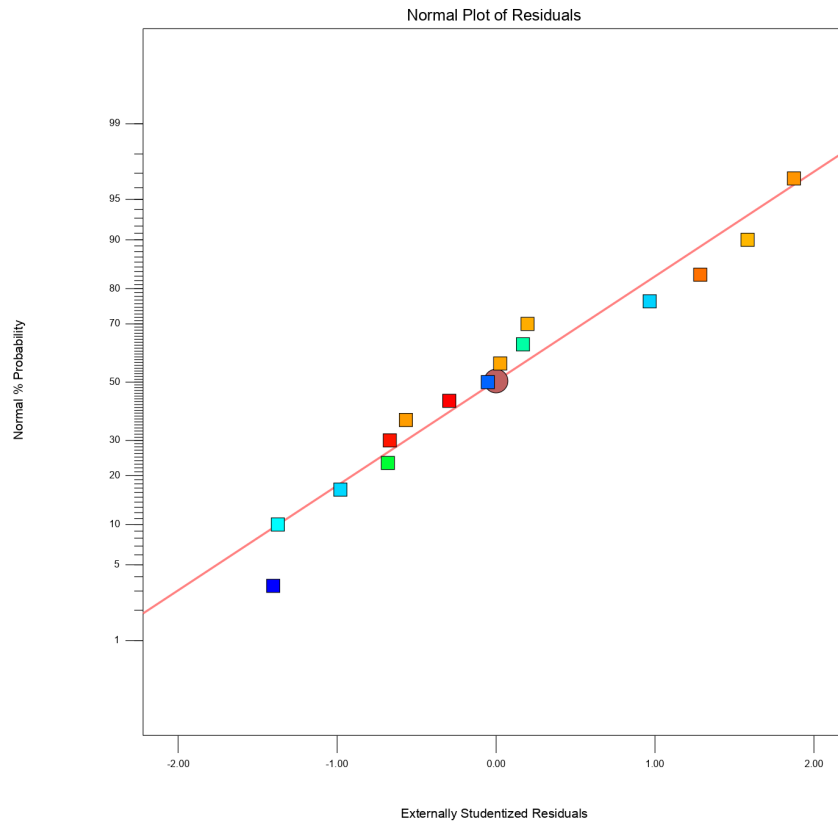


Figure 7: Normal plot of residuals for lead removal efficiency

These observations indirectly indicate that the mass transfer of lead (from the bulk liquid phase to the adsorbent surface) does not control its rate of removal, and rather it is the surface based diffusion and attachment that may be more defining for lead effective adsorption-based removal. This is further supported by the pH effect findings where reduced lead removal was noted at acidic pH values and near complete lead removal transpired at pH 6 along with higher adsorbent dosage. Moreover, Figure 8 that shows the effects of operational parameters on lead removal also confirm the above discussion. Figure 8A shows that the removal efficiency of lead (at an initial fixed lead concentration of 100 mg/L) is enhanced with an increase in pH of the aqueous solution. As the pH goes up, the presence of H^+ cations in the near vicinity of the adsorbent surface (and the surface binding sites) decreases, which in turn allows more lead species to approach the respective surface exchange sites on the adsorbent surface.

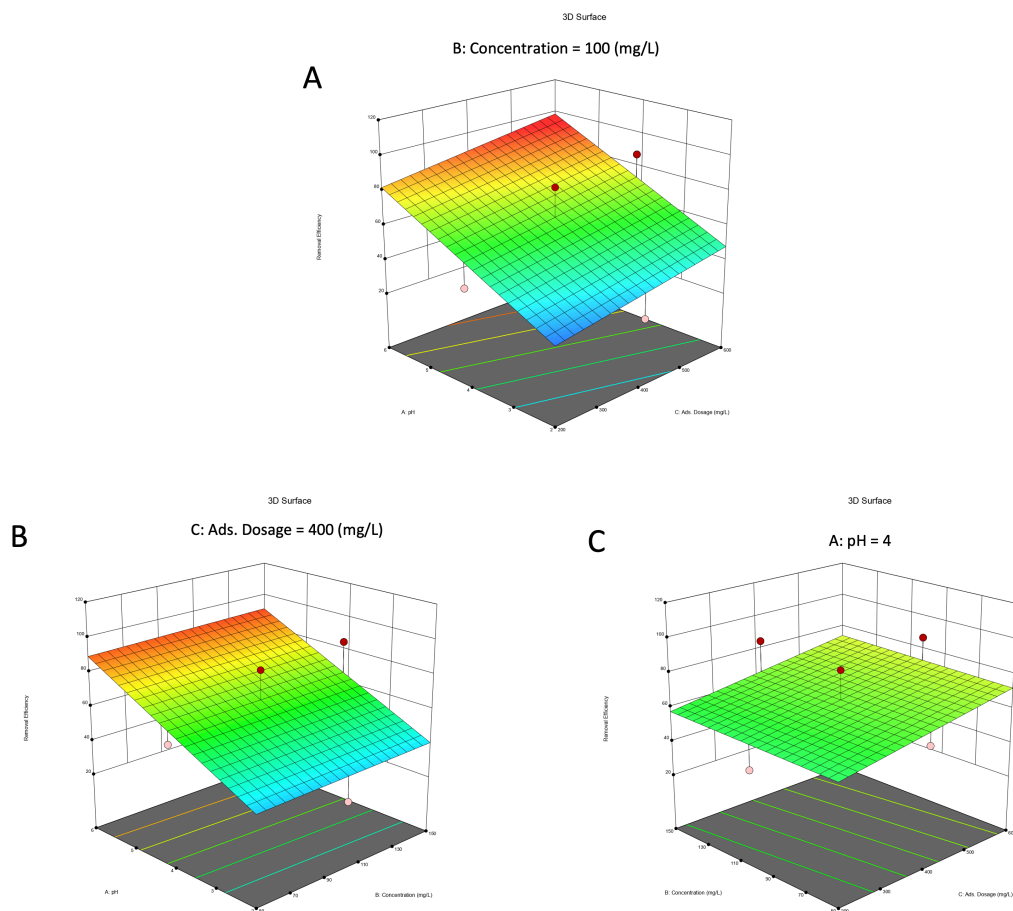


Figure 8: FC-RSM modeling graphs A) pH and adsorbent dosage effects at a fixed initial lead concentration of 100 mg/L, B) pH and initial lead concentration effects at a fixed adsorbent dosage of 400 mg/L, and C) initial lead concentration and adsorbent dosage effects at affixed solution pH of 4

Similar observation was reported elsewhere with highest adsorption noted at pH 7, below which a decrease was noted because of competition between protons and the metal cations for the same surface sites and an increase in the positive charge of the adsorbent, which results in increased electrostatic repulsion between the metal cations and the adsorbent surface [78]. Thus, the solution pH has a significant impact on how well heavy metals are absorbed on a given adsorbent. The functional groups on the adsorbent surface and the metal chemistry in solution, which affect the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate, are related to the pH dependency of metal uptake [78]. Also, Figure 8B shows the combined effect of pH and initial lead concentration on the lead removal efficiency by the GO@ZIF-7 nanocomposite at a fixed adsorbent dosage of 400 mg/L. As seen in this figure, an increase in the initial lead concentration indicates a negative effect on its removal. On the other hand, Figure 8C shows that lead removal efficiency increases with increasing the adsorbent dosage from 200 to 600 mg/L due to the availability of more surface binding sites, resulting in a greater mass transfer of lead species from the bulk liquid to the adsorbent surface. In summary, these results indicate that the GO@ZIF-7 nanocomposite can be effectively used for aqueous phase lead removal with an appropriate adjustment of the process conditions to their respective optimum values, as discussed above.

3.4.4 Equilibrium isotherms

The lead removal data obtained from the adsorption experiments using the GO@ZIF-7 nanocomposite at different initial lead concentrations were also fitted to the Langmuir and Freundlich isotherm models. Equation (3.3) shows the linear form of the Langmuir model,

which takes into account a monolayer coverage of the solid surface at the equilibrium concentrations in the liquid phase at various adsorbent dosages. The respective Langmuir model parameters were calculated using the slope and the intercept of C_e/q_e vs C_e plot as given in Figure 9A. Moreover, the experimental data were also fitted using the linear version of the Freundlich isotherm as given by equation (3.4), where K_f and n are the Freundlich constant and the heterogeneity factor, respectively [78]. The slope and intercept of the plot of $\ln q_e$ against $\ln C_e$, as shown in Figure 9B, were used to calculate the model parameters.

$$(C_e/q_e) = \frac{C_e}{qm} + \frac{1}{b * qm} \quad (3.3)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (3.4)$$

Figure 9B shows that the Freundlich isotherm provides a better fit for lead removal using the GO@ZIF-7 nanocomposite as compared to the Langmuir isotherm (Figure 9 A) with an R^2 equal to 0.96. This also indicates that lead adsorption on the GO@ZIF-7 nanocomposite transpires via a multilayer adsorption pattern. In fact, the results shown earlier in Figure 5 are also supportive of this observation (i.e., lead adsorption onto GO@ZIF-7 follows Freundlich type adsorption isotherm with multilayers). In short, these observations suggest that GO@ZIF-7 nanocomposite is very promising for a possible application in the removal of lead and probably other toxic species from contaminated waters.

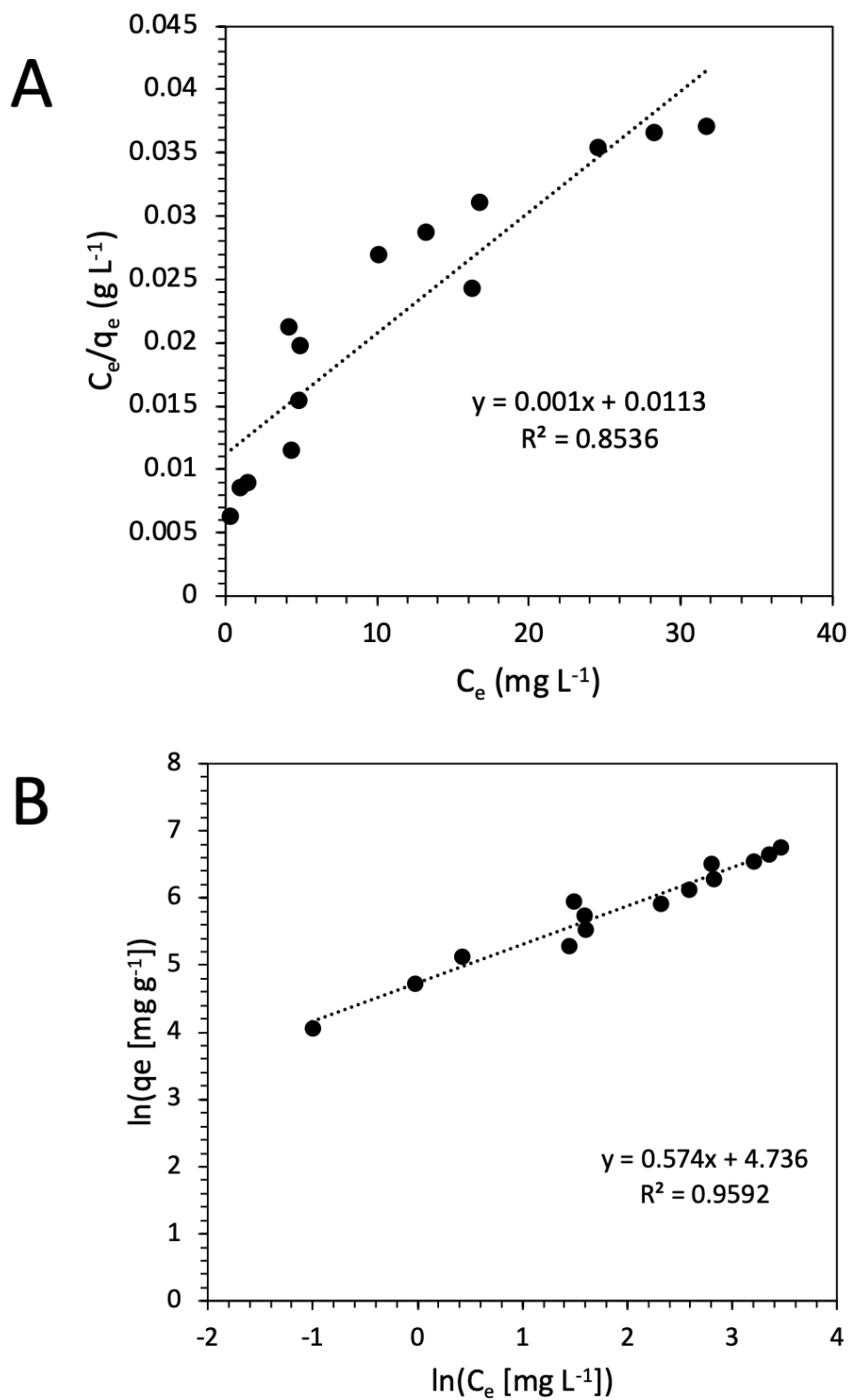


Figure 9: Adsorption isotherm of lead onto the GO@ZIF-7 nanocomposite fitted using (a) the linearized Langmuir model, and (b) the linearized Freundlich model

3.5 Conclusions

The present study synthesized GO@ZIF-7 nanocomposite and successfully used it for the treatment of aqueous phase lead. The FTIR findings showed several surface functional groups that are important for cationic lead species adsorption. The GO@ZIF-7 nanocomposite extremely outperformed its parental materials (GO and ZIF-7) with a lead adsorption capacity approaching 5,000 mg/g relative to about 500 and 600 mg/g obtained using the pristine ZIF-7 and GO, respectively. The study also evaluated the effects of key operational parameters (i.e., pH, initial lead concentration, and adsorbent dosage) on the efficiency of lead removal from aqueous solutions. The adsorptive removal of lead using the GO@ZIF-7 nanocomposite was also optimized using the RSM. The optimization results supported a greater role of aqueous pH and adsorbent dosage in achieving higher lead adsorption. The respective findings demonstrate that the GO@ZIF-7 nanocomposite can effectively treat water streams contaminated with lead under different operating conditions. In terms of adsorption isotherm, the lead adsorption was also noted to follow the Freundlich adsorption isotherm trend, indicating a multilayer adsorption of lead onto the GO@ZIF-7 nanocomposite surface, which is consistent with the observed high lead uptake capacity by the GO@ZIF-7 nanocomposite as compared to the pristine GO and ZIF-7. The results obtained in this work suggest the commercial potential of GO@ZIF-7 nanocomposite as revealed by the very high lead uptake capacity and the successful treatment of lead contaminated water.

CHAPTER 4

Novel Al-Electrodes/GO@ZIF-7 Hybrid

Electrocoagulation/Adsorption System for Efficient Pb(II)

Removal: Experimental and Machine Learning Modeling

Studies

4.1 Abstract

Water pollution resulting from heavy metals including lead [Pb(II)] is a major health concern for humans, animals, and aquatic life. Pb(II) is a highly hazardous contaminant that must be effectively removed from water before reuse or discharge. In this study, a hybrid electrocoagulation/adsorption system (EC/A) using aluminum electrodes integrated with a novel adsorbent GO@ZIF-7 nanocomposite, was studied for aqueous phase Pb(II) removal. The hybrid EC/A system yielded a near complete Pb(II) removal. The system was optimized using the Response Surface Methodology (RSM) based design of experiments (DOE) technique; specifically using the central composite design (CCD) the study analyzed the impacts of four primary process variables (i.e., current density, Pb(II) initial concentration, dosage of GO@ZIF-7 nanocomposite, and conductivity) on the Pb(II) removal. Notably, the findings show the significant role of current density in the Pb(II) removal process, particularly at a current density of 1.5 mA/cm². The above-mentioned

RSM design along with the analysis of variance (ANOVA) based statistical analysis and optimization, confirmed the suitability of the proposed RSM-based equations for Pb(II) removal modeling. Collectively, the findings of this study indicate that the proposed hybrid EC/A system using aluminum electrodes integrated with a novel GO@ZIF-7 nanocomposite has a significant practical viability as suggested by the remarkably high Pb(II) removal efficiency. Furthermore, this study also presents the effectiveness of three advanced machine learning (ML) based models, i.e., artificial neural network (ANN), eXtreme Gradient Boosting (XGBoost), and Random Forest Regression, for predicting the Pb(II) removal using the EC/A process.

Keywords: Pb(II) removal from wastewater; Electrocoagulation (EC); Electrocoagulation/adsorption hybrid system (EC/A); Zeolitic imidazole framework-7 (ZIF-7); Graphene oxide (GO); Response surface methodology (RSM).

4.2 Introduction

Urbanization and the significant increase in population have brought about challenges concerning the safe consumption of the available water resources. The growth in world population and industrial activities has resulted in the production of large quantities of wastewater on a daily basis, highlighting the need for innovative, efficient, and economically feasible methods for treating the respective wastewater streams [134]. Many water pollutants are very hazardous and toxic to humans and the ecosystem. One such toxic pollutant is lead [Pb(II)], which is noted in several wastewater streams [135, 136].

According to the Agency for Toxic Chemicals and Disease Registry (ATSDR), Pb(II) is the second most hazardous species (after arsenic) that warrants attention [137]. Wastewater produced from industries like battery manufacturing, electroplating, and paints & pigments, often contain large amounts of Pb(II). Hussin et al. [13] noted that Pb(II) concentration in wastewater can vary between 1 to 50 mg/L. The consumption of water contaminated with Pb(II) could lead to damage to varying human organs including the brain, liver, and kidneys [13].

Various technologies including ion exchange, ultrafiltration, reverse osmosis, and chemical precipitation have been used for aqueous phase Pb(II) treatment. Nonetheless, the quest for more effective wastewater treatment has led to the exploration of other innovative methods as well, including EC [138], electroflotation [139], electrofenton [140, 141], electrodialysis [142] and electrooxidation [143]. Among these, EC has been effectively used for wastewater treatment [144]. The EC involves in-situ generation of metal coagulants through the oxidation-based dissolution of anode because of current flow through the EC cell. Some common electrode materials used include aluminum (Al) and iron (Fe) [145]. The production of insoluble metal hydroxide flocs effectively removes the target aqueous phase pollutants through adsorption [146].

Recently MOFs have also been used for aquatic pollution control [74, 147] along with various other applications such as gas separation, energy storage, and catalysis [75, 148]. However, the susceptibility of MOFs to water-instability poses a challenge in their use for wastewater treatment [148]. Nonetheless, ZIFs are a class of MOFs that offer better water-stability. Thus, ZIFs have gained considerable attention for wastewater treatment [77, 78].

However, published research on utilizing ZIFs for wastewater treatment is still limited, and mainly focuses on ZIF-8, ZIF-67, and their composites [88, 149, 150]. In addition to the limited number of studies on the application of ZIFs for wastewater treatment (particularly ZIFs other than ZIF-8 and ZIF-67), combined EC-ZIF-based treatment of aqueous heavy metals is not reported, to the best of our knowledge. This combined process is considered to produce a positive synergistic effect for the removal of toxic heavy metal species from respective wastewater streams. Hence, the present work successfully investigated both the synthesis of novel GO@ZIF-7 nanocomposite and its effectiveness in removing aqueous Pb(II) via the combined EC/adsorption process. The efficacy of the EC/GO@ZIF-7 combined process was demonstrated via the successful Pb(II) removal, and the respective outcomes are reported in the sections below.

4.3 Materials and methods

4.3.1 Materials

Sodium chloride (99.8% purity) was purchased from J.T.Baker. Benzimidazole (98% purity), zinc nitrate hexahydrate ($\geq 99.0\%$ purity), graphite powder (99.99% purity), potassium permanganate ($\geq 99.0\%$ purity), sulfuric acid (98.0% purity), phosphoric acid (85%, the rest is water), hydrogen peroxide (30% in water), and HPLC grade methanol ($\geq 99.9\%$ purity) was purchased from Sigma-Aldrich while $\text{Pb}(\text{NO}_3)_2$ (99.5% purity) was obtained from BDH Chemicals. All chemicals/materials utilized in this study were used as received without treatment.

4.3.2 Synthesis of GO

The improved Hummers method described in references [92, 151], was employed to synthesize GO. In this experiment, 360 mL H_2SO_4 and 40 mL H_3PO_4 were mixed in a flask, resulting in a final volume of 400 mL with H_2SO_4 : H_3PO_4 volumetric ratio of 9:1. Subsequently, a quantity of 3 g graphite powder was introduced into the aforementioned mixture, followed by the gradual incorporation of 18 g potassium permanganate (KMnO_4) under constant agitation. During the addition of graphite powder and KMnO_4 , the mixture was kept in an iced water bath to avoid overheating. Subsequently, the reaction mixture was transferred to a water bath kept at 50 °C and stirred for 12 h. Then, the reaction mixture was mixed with approximately 400 g of crushed ice, and then H_2O_2 was gradually introduced until the color of the liquid changed to a dark yellow. Subsequently, the mixture underwent a series of washes using distilled water and a 10 vol% hydrochloric acid (HCl) solution. Following each wash cycle, the solid was recovered using centrifugation at a speed of 8000 rpm. Finally, GO was washed multiple times with a large amount of distilled water in order to thoroughly eliminate any remaining acid residue before drying it at 50 °C. The produced GO was subjected to grinding to produce fine powders before its utilization for the preparation of GO@ZIF-7 nanocomposite.

4.3.3 Synthesis of GO@ZIF-7 nanocomposite

In order to synthesize the GO@ZIF-7 nanocomposite, a total of 5.94 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was introduced into 40 mL methanol of HPLC grade. The resulting mixture was then subjected to stirring until complete dissolution of the zinc salt was achieved. Subsequently, a quantity of 0.25 g GO was introduced into the aforementioned zinc solution, and it was

agitated at ambient conditions for a duration of 5 min to facilitate the dispersion of GO particles. Then, the dispersion of GO was subjected to sonication at an amplitude of 50% for a duration of 30 min, utilizing a probe sonicator. In parallel, 40 mL HPLC methanol was added to 9.44 g benzimidazole in a separate container and stirred at ambient temperature until the complete benzimidazole dissolution. Subsequently, the above two solutions were mixed and stirred for 1 h at ambient temperature. Then, the reaction mixture was placed in a Teflon-lined autoclave reactor and incubated at 130 °C for a duration of 24 h. To recover and purify the produced GO@ZIF-7 nanocomposite, the reaction mixture was centrifuged and washed several times with HPLC-grade methanol. Subsequently, the GO@ZIF-7 nanocomposite was dried at 50 °C, followed by grinding into fine powder.

4.3.4 Characterization of GO@ZIF-7 nanocomposite

The x-ray diffraction (XRD) pattern of GO@ZIF-7 nanocomposite was acquired within the angular range of 5–60°, with a step width of 0.03° and a scan rate of 5.00°/min, utilizing an X-ray diffractometer (MiniFlex 300/600, Rigaku). Furthermore, the Fourier transform infrared (FTIR) spectra of the synthesized GO@ZIF-7 nanocomposite were obtained using an FTIR spectrometer (Nicolet RaptIR FRIR Microscope, Thermo Fisher Scientific) within the frequency range of 400–4000 cm⁻¹.

4.3.5 Hybrid EC/A system setup

A stock solution of Pb(II) with a concentration of 1000 mg/L was prepared by dissolving lead nitrate (Pb(NO₃)₂) in distilled water. This stock solution was then used to prepare other

Pb(II) solutions. The initial pH of each respective solution was adjusted using 0.1 M HNO₃ or 0.1 M NaOH solution before each experiment. All experiments were carried out in the same experimental setup which is mainly an electrochemical cell that consists of a DC power supply used to control the current density (0.5, 1, and 1.5 mA/cm²), a pair of aluminum electrodes immersed in a glass beaker filled with 1.6 L of Pb(II) solution (50, 100, and 150 mg/L), with varying conductivity (4, 8, and 12 mS/cm), and GO@ZIF-7 dosage (200, 400, and 600 mg/L). Figure 10 presents a schematic diagram of the setup used in the experiments. The residual Pb(II) concentration after each experiment was determined using a flame atomic absorption spectrometer (AAS, PerkinElmer). The samples were filtered using a 0.2 µm filter (Whatman) before subjecting them to analysis. The instrument accuracy was periodically checked using standard metal solutions.

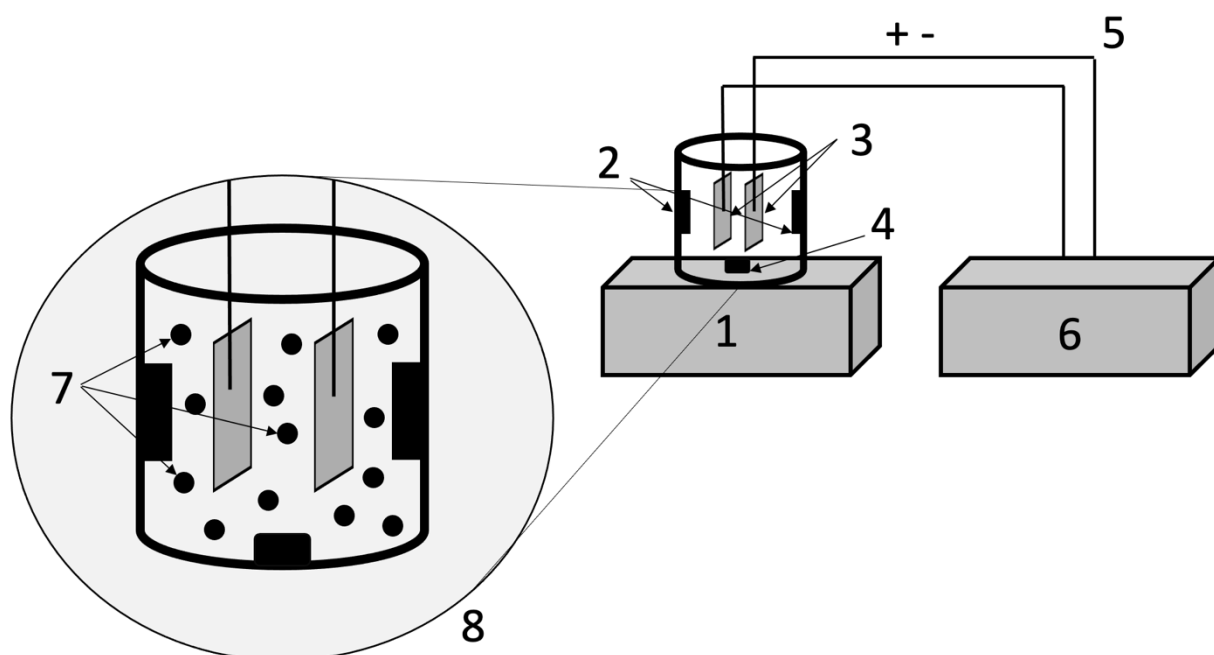


Figure 10: Schematic diagram of the experimental setup (1. magnetic stirrer controller, 2. baffles, 3. aluminum electrodes, 4. magnetic bar, 5. Cables, 6. DC power supply, 7. GO@ZIF-7 adsorbent nanoparticles, 8. magnified display of the electrochemical cell tank)

4.3.6 Aluminum electrodes

All the aluminum electrodes utilized in the experiments were assembled in a workshop located in the AlKhudhria Industrial Area in Dammam. They were secured to their holders with compression screws and have dimensions of 10 x 5 cm².

4.3.7 Response surface methodology (RSM) modeling

Current density, Pb(II) initial concentration, adsorbent dosage, and initial conductivity of the solution were selected as the factors for the RSM modeling. Each factor unit and respective levels are shown in Table 7. The RSM design and all relevant equations and analyses carried out in this study were generated using Stat-Ease software. The RSM-based design of experiments (DOE) as used in the current study was based on the central composite design (CCD) with three levels for each factor, along with the Pb(II) removal efficiency (%) as the response (Table 8). The experimental Pb(II) removal efficiency was calculated using the following equation:

$$Pb(II)Removal (\%) = \frac{(C_i - C_f)}{C_i} \times 100 \quad (4.1)$$

where C_i and C_f denote the initial and final concentrations of Pb(II) (mg/L), respectively.

Table 7: The factors used for the central composite design and respective levels

Factors	Levels		
A = Current density (mA/cm ²)	0.5	1	1.5
B = Pb(II) initial concentration (mg/L)	50	100	150
C = Adsorbent dosage (mg/L)	200	400	600
D = Conductivity (mS/cm)	4	8	12

Table 8: The RSM-based design of experiments along with the respective Pb(II) removals

Exp. No.	A	B	C	D	Pb(II) Removal (%)			
					Sample after (min)			
					15	30	60	90
1	1.5	150	600	12	30.2	72.6	79.9	86.1
2	0.5	50	200	12	32.7	68.2	74.9	85.2
3	1	100	400	16	41.8	76.0	82.8	88.5
4	0.5	150	200	12	31.8	71.2	74.4	84.6
5	1	100	0	8	29.4	45.8	63.8	74.1
6	0	100	400	8	18.9	22.2	24.5	25.8
7	0.5	150	200	4	29.1	66.1	69.4	80.5
8	1.5	50	600	12	32.8	69.2	78.0	87.3

9	2	100	400	8	26.6	66.0	77.3	80.1
10	1	100	400	0	20.6	23.1	25.2	27.1
11	1	0	400	8	0.00	0.00	0.00	0.00
12	0.5	150	600	4	31.5	68.9	81.3	85.1
13	1.5	50	200	12	23.2	59.4	64.7	75.9
14	1.5	150	600	4	28.8	61.3	73.3	75.5
15	1.5	150	200	12	28.4	52.9	62.6	68.7
16	1	200	400	8	32.3	67.2	73.8	79.1
17	1	100	400	8	40.2	57.8	71.2	83.5
18	0.5	50	600	12	43.8	71.7	91.3	98.4
19	0.5	150	600	12	36.5	77.8	87.7	91.3
20	1.5	150	200	4	27.3	70.9	79.1	82.9
21	1	100	800	8	44.2	65.6	72.9	80.4
22	1.5	50	600	4	34.3	69.4	85.6	88.2
23	0.5	50	200	4	36.1	72.8	81.3	87.0
24	1.5	50	200	4	30.9	68.6	73.6	82.3
25	0.5	50	600	4	35.7	74.1	82.7	87.5

4.3.8 Machine learning (ML) modeling

For the machine learning (ML) based modeling, the initial steps focused on processing the data, including encoding of the specific categorical values. This process ensured that the data was refined and structured appropriately, laying the foundation for accurate analysis and modeling. The prepared data was then visualized through various charts and graphical representations, which helped to identify patterns, trends, and relationships within the dataset. All analyses were performed using Python. The core of the analysis involved training three different predictive machine learning models, i.e., the Artificial Neural Network (ANN), eXtreme Gradient Boosting (Xgboost), and Random Forest Regression. Each model was trained rigorously to capture the respective variations, followed by models' performance evaluations to assess their predictive capabilities.

4.4 Results and discussion

4.4.1 Characterizations

The XRD patterns of GO, ZIF-7, and the GO@ZIF-7 nanocomposite are depicted in Figure 11. The diffraction peaks of ZIF-7 observed at 2θ values of 9.12, 16.0, 16.68, 17.52, 19.98, 21.6, 23.1, 27.39, 31.59, 33.54, 35.43, and 37.8° are consistent with those reported for ZIF-7 synthesized using diethylformamide [94], ammonia atmosphere [95], water/ethanol mixture [96], and N,N-dimethylformamide [97] as the synthesis medium. The presence of a distinct and prominent diffraction peak at an angle of 9.12° suggests a microporous ZIF-

7 structure; ZIF-7 can potentially exist in phases I, II, or III depending on the synthesis conditions and media, and the diffraction peaks shown in Figure 11 suggest the phase III crystalline form for the synthesized ZIF-7 [96]. This ZIF-7 phase exhibits a square planar structure with a (4,4) configuration. Such a structure is generated by the coordination of benzimidazolate tetrahedra with quadruply connected corner-shared networks of Zn(II) [98]. The ZIF-7 III phase is the densest among all other phases of ZIF-7 and many other ZIFs. Additionally, it is the most stable phase of ZIF-7 [98].

Figure 11 also displays the XRD diffraction pattern of GO, indicating a solitary weak diffraction peak at 9.8° . The GO diffraction pattern aligns with the pertinent literature on GO synthesized using the improved Hummers method [92, 99, 100]. Furthermore, Figure 11 illustrates the XRD pattern of the GO@ZIF-7 nanocomposite. Based on the data depicted in this figure, the XRD patterns of both ZIF-7 and GO@ZIF-7 nanocomposite exhibit similarities. The similarity is supported by the weak intensity of the GO diffraction peak at 9.8° , which is approximately 5% of the intensity of the ZIF-7 peak observed at a nearby angle of 9.12° . The close proximity of the small GO and the intense ZIF-7 diffraction peaks may lead to the obscuration of the GO diffraction peak by that of ZIF-7. Furthermore, the relatively small amount of GO present in the GO@ZIF-7 nanocomposite (about 1.63% of the total mass of the ZIF-7 precursors in the synthesis solution) is another possible explanation for the similarities observed in the XRD patterns of ZIF-7 and GO@ZIF-7 nanocomposite.

Figure 12 displays the FTIR spectra of GO, ZIF-7, and the GO@ZIF-7 nanocomposite. The respective GO spectra exhibit a broad and strong absorption peak at around 3417 cm^{-1} . This peak originates from the stretching vibration of O-H bonds, which is a result of the

presence of water moisture and/or the deliquescence of KBr [101, 102]. The small peaks located at 2936 and 2855 cm^{-1} are ascribed to the bending vibration of the C-H bond within the GO framework [152, 153]. The peak at 1730 cm^{-1} corresponds to the stretching vibration of the C=O bond, whereas the rather high peak at 1636 cm^{-1} is associated with the vibration of the sp^2 hybridized carbons in the graphitic structure [105, 106]. Additionally, the absorption peaks at 1385 and 1060 cm^{-1} correspond to the bending of the alcohol bond (O-H) and the stretching vibrations of the C-H bond, respectively.

Additionally, Figure 12 also showcases the FTIR spectra of both ZIF-7 and the GO@ZIF-7 nanocomposite. The spectra of ZIF-7 depicted in Figure 12 are similar to those documented by Davoodian et al. [107], Zhao et al. [108], and Li et al. [109]. Furthermore, the FTIR spectra of ZIF-7 and GO@ZIF-7 nanocomposite exhibit similarities, possibly attributed to the low concentration of GO present in the nanocomposite, as previously mentioned. However, despite the low GO level in the nanocomposite, the incorporation of GO into the ZIF-7 framework led to a substantial enhancement in Pb(II) adsorption according to a preliminary study. Figure 12 also exhibits many other peaks for ZIF-7 and GO@ZIF-7 within 2700–3100 cm^{-1} that are likely caused by the stretching vibration of the O-H bonds in the remaining alcohol present after the synthesis and purification processes. Furthermore, the peaks observed within 1700–2000 cm^{-1} can be attributed to the bending vibration of the C–H bond in the benzyl ring of the organic linker, specifically benzimidazole. On the other hand, the absorption peaks detected within 1500–1700 cm^{-1} can be attributed to C=C bond stretching in the benzimidazole aromatic ring [110]. The peaks observed within 1300–1365 cm^{-1} are likely caused by the stretching of the C–N

bonds, while the peak observed at 430 cm^{-1} suggests the stretching vibration of the Zn–N bond formed between the organic linker and the Zn atom.

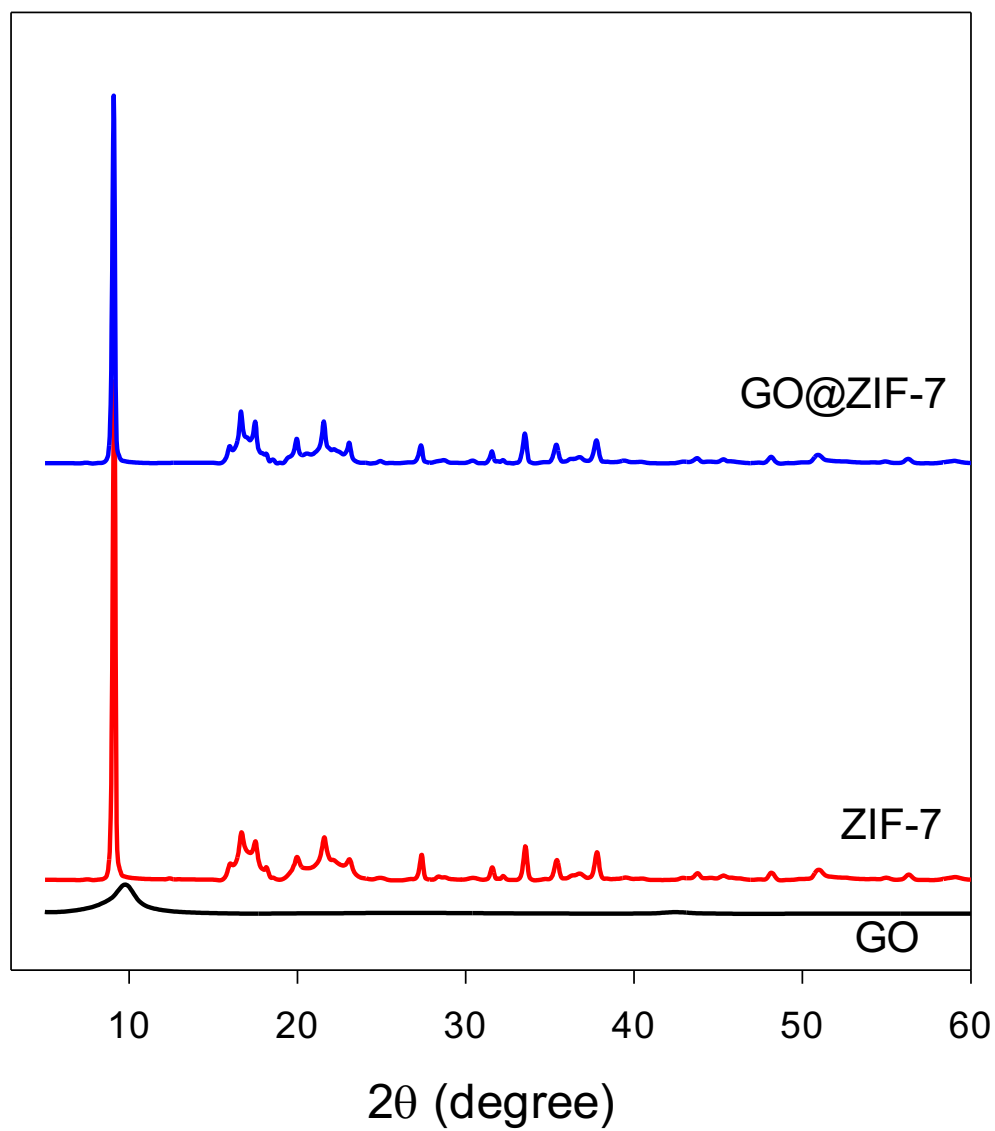


Figure 11: The XRD patterns of GO, ZIF-7, and GO@ZIF-7 nanocomposite

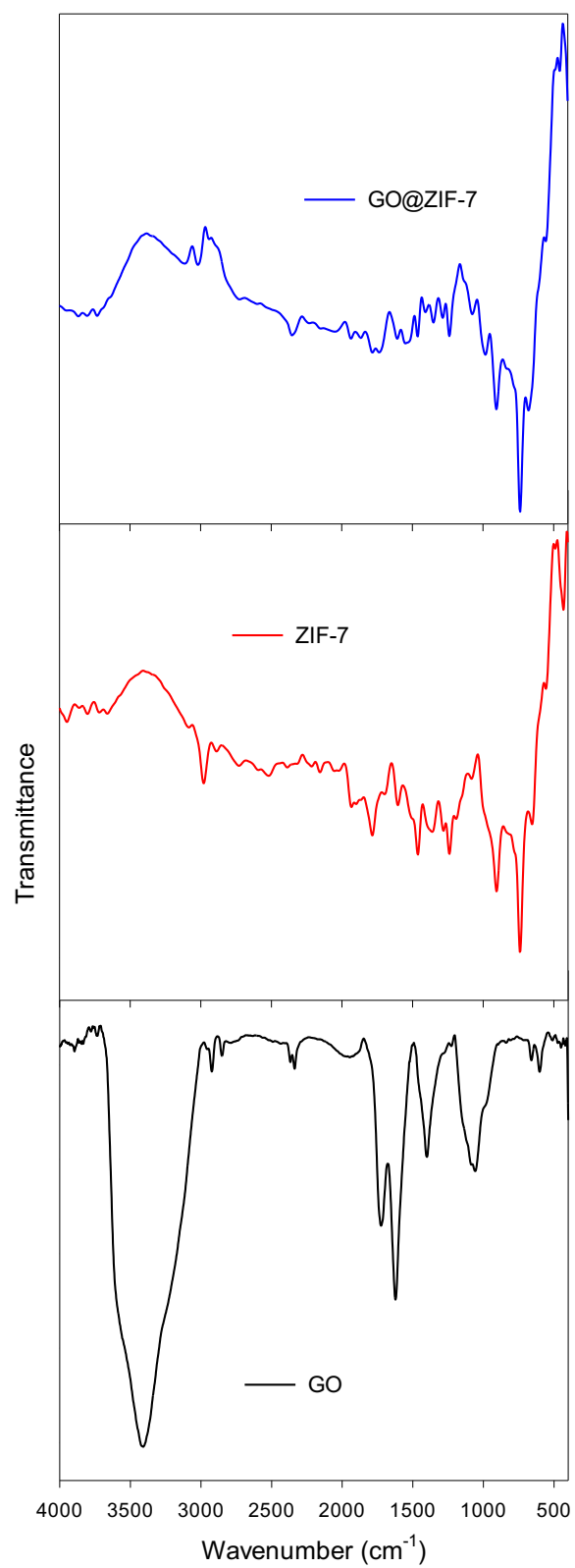


Figure 12: The FTIR spectra of GO, ZIF-7, and GO@ZIF-7 nanocomposite

4.4.2 Performance of the hybrid EC/A system compared to its components

A preliminary study was conducted to investigate and benchmark the performance of the hybrid EC/A system to its components; EC alone and adsorption using GO@ZIF-7 nanocomposite alone. The removal of Pb(II) from the aqueous solution using the three techniques is presented in Figure 13. Comparing these wastewater treatment systems for their efficiency in removing Pb(II) from aqueous solutions reveals noticeable differences between the standalone systems and the developed hybrid EC/A system. The standalone adsorption system showed a maximum removal efficiency of 67% and the standalone EC system showed a removal efficiency of 41% after 90 min of contact time. In contrast, the hybrid EC/A system developed herein has shown remarkable effectiveness, with a Pb(II) removal reaching 87% after 90 min of treatment. This significant improvement in performance not only demonstrates the successful interaction of the combined treatment techniques (i.e., EC and adsorption) but also positions the hybrid system as a more reliable and effective solution for treating Pb(II) polluted wastewater. Furthermore, the proposed hybrid EC/A system typically shows a better treatment efficiency (Table 9) most likely due to the use of novel and highly effective adsorbent (i.e., GO@ZIF-7 nanocomposite). Nevertheless, one exception using combined solar EC and adsorption process for Pb(II) removal is noted [13], which potentially results from a higher adsorbent dosage of 2.50 g/L compared to the 0.6 g/L utilized in the present study. Table 9 also provides an overview of factors studied in the literature that influence the performance of different hybrid EC/A systems. It presents the optimum values for each parameter for treating different water contaminants. Each factor listed in Table 9 not only has an impact on the system performance but also reveals potential positive or negative interactions, between the system

parameters. Additionally, the studies listed in Table 9 reveal how operational parameters are interconnected. As demonstrated in this table, the connection between parameters depends on the nature of the studied pollutant. Accordingly, the key parameters affecting Pb(II) removal (i.e., those listed in Table 9) from aqueous solutions were optimized using RSM. This analysis identified the factors that are most influential on Pb(II) removal by the proposed hybrid EC/A system.

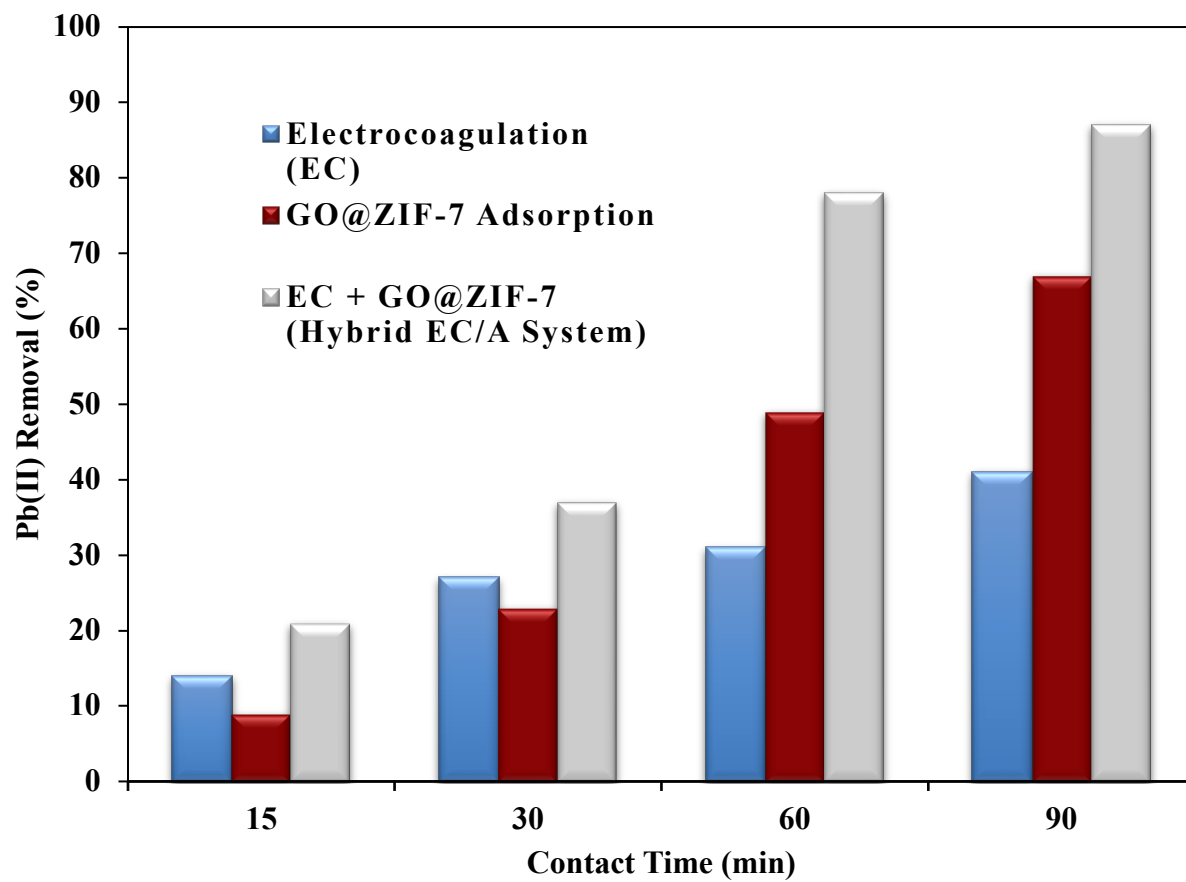


Figure 13: Pb(II) removal (%) vs. contact time (min) for EC, GO@ZIF-7 adsorption, and the hybrid EC + GO@ZIF-7 system (hybrid EC/A system)

Table 9: Optimal EC-based treatment conditions and pollutant removal efficiencies

Wastewater Used	Treatment Technique	Optimal Treatment Conditions				Maximum Removal	Ref.
		pH	Current density	Adsorbent dosage	Others		
Synthetic Pb(II) contaminated wastewater	Hybrid EC/A using aluminum electrodes and GO@ZIF-7 adsorbent	6	0.5 mA/cm ²	600 mg/l	Time 90 min	98%	This work
Industrial textile wastewater	Sequential EC-activated carbon adsorption	5.4	14 mA/cm ²		Time 11 min Conductivity 2 mS/cm ²	Color 95% COD 63% TOC 51%	[44]
Wastewater contaminated with dye	EC/hazelnut shell (HNS) adsorption hybrid process		2.6 mA/cm ²	6 g/L	Time 17.75 min	Methylene blue dye 99.45%	[45]
Wastewater contaminated with Pb(II)	Hybrid solar EC/A treatment process	6.01		2.50 g/L	Initial concentration 15.00 mg/L	Pb(II) 99.88%	[13]
Real cotton textile wastewater	Fluidized metal-impregnated GAC carbon in three-dimensional EC system	6.72		47.7 g/L	Time 72 min	Decolorization 99.13 ± 0.21% COD 97.01 ± 0.18%	[42]
Synthetic wastewater	Hybrid EC/A treatment process					EC/SIAC DOC 77 ± 8% EC/SIAC tTHMs and tDHANs 97 ± 3% EC/GAC DOC 67 ± 14% EC/GAC tTHMs 89 ± 5% tDHANs 75 ± 18%	[154]
Distillery effluent	Hybrid EC/A using activated carbon		182 A/m ²		Time 60 min	Turbidity 99% TDS 72% BOD 89.7% COD 80.1%	[35]
Synthetic wastewater	Continuous-flow EC process	7	3 mA/cm ²		Initial concentration 10 mg/L Time 50 min	Iron 99.9%	[155]

Wastewater Used	Treatment Technique	Optimal Treatment Conditions				Maximum Removal	Ref.
		pH	Current density	Adsorbent dosage	Others		
Synthetic wastewater	EC and microflotation	7	10 mA/cm ²		Time 6 min Air flow rate 2.5 ml/min	Textile dyes 96% (with microbubbles) Textile dyes 70.75% (without microbubbles)	[156]
Real textile industry wastewater	Sequential EC, EO, and adsorption processes	9.3	5 mA/cm ²			Toxicity 100%	[32]
Paper industry wastewater	EC process with adsorption onto GAC	4	1.4 mA/cm ²		Time 10 min Initial concentration 150 mg/L	Humic acid 93%	[39]
Greywater	Hybrid electrochemical-GAC system		15 mA/m ²		Conductivity 1 mS/cm	COD 86.0 ± 6.8% TOC 85.5 ± 1.9% Turbidity 88.6 ± 1.9% Color 100.0 ± 0.0%	[46]
Real wastewater	Hybrid EC/A using activated carbon	7			Time 90 min	Lethal concentration 56%	[47]
Textile wastewater treatment	Hybrid EC/A treatment process	4.3	10 mA/cm ²		Time 60 min	Color 100% COD 76% TOC 78%	[31]
Real textile wastewater	hybrid treatment involving adsorption or catalytic wet air oxidation following EC					TOC 91%	[157]
Synthetic wastewater	Hybrid EC/A using GAC					Indigo carmine 99%	[14]
Real wastewater from oil refinery wastewater treatment plant	Simultaneous EC and adsorption		7.5 mA/cm ²	0.5 g/L	Time 240 min	COD 50% Calcium 88% Strontium 72%	[48]

Wastewater Used	Treatment Technique	Optimal Treatment Conditions				Maximum Removal	Ref.
		pH	Current density	Adsorbent dosage	Others		
Synthetic wastewater	EC combined with adsorption					TOC 95%	[49]
Synthetic wastewater	Combined EC–GAC adsorption–microwave regeneration process			100 g/L	Time 4 h	Reactive black 5 dye 82%	[50]
Synthetic effluents	Hybrid EC/A using GAC	8	26.7 mA/cm ²		Time 100 min Initial chromium concentration 50 ppm	Chromium 97%	[30]
Synthetic effluents	Hybrid EC/A using Al electrodes and GAC			700 mg/L		Reactive dye 100%	[51]
Palm oil mill effluent	EC-adsorption hybrid process					TSS 79% COD 44% Color 89%	[52]
Synthetic wastewater	EC-adsorption processes					Cationic dye 96% Anionic dye 98%	[15]
Tannery wastewater	EC and adsorption					Turbidity 96.1% Chromium (IV) 92% COD 75%	[53]
Synthetic fluoride solution	EC-adsorption process				0.5 g	Fluoride 67.25%	[54]
Real textile wastewater	Hybrid chemical coagulation PAC as coagulant), EC (using Al electrodes), and adsorption process (using pistachio nutshell ash)					COD 98% BOD ₅ 94.2% Dye removal 99.9%	[33]
Wastewater from industrial dairy	EC and activated carbon adsorption techniques used separately or coupled	7.03			Time 15 min	COD >97% BOD ₅ >97% Turbidity >97% TSS >97%	[55]

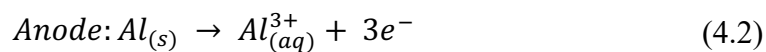
Wastewater Used	Treatment Technique	Optimal Treatment Conditions				Maximum Removal	Ref.
		pH	Current density	Adsorbent dosage	Others		
						Nitrogen >97%	
Real wastewater from a local municipal wastewater treatment plant	Adsorption (using graphene) and simultaneous EC/electrofiltration process					di-n-butyl phthalate (DnBP) $89 \pm 2\%$ di-(2-ethylhexyl) phthalate (DEHP) $85 \pm 3\%$ Acetaminophen (ACE) $99 \pm 2\%$ Caffeine (CAF) $94 \pm 3\%$ Cefalexin (CLX) $100 \pm 0\%$ Sulfamethoxazole (SMX) $98 \pm 2\%$	[56]
Real wastewater from a raw textile industry wastewater	Combined EC/adsorption process		28.57 mA/cm ²	0.75 g/L	Time 120 min	COD 98.33% Turbidity 100% Color 98.37%	[158]
Methylene blue (MB) dye stock solution	EC and adsorption				Time 30 min	Methylene blue dye 96%	[40]
Real car wash wastewater	EC process followed by adsorption and simultaneous EC-adsorption were evaluated			22.5 g/L	Time 60 min	COD 94% Turbidity 98%	[58]
Urban wastewater effluent	EC-electroflotation process		100 A/m ²		Time 10 min	Separation 95%	[59]
Synthetic dye solution	EC coupled with adsorption					Eosin yellow dye 46.69% Nigrosin dye 99%	[41]
Synthetic dye solution	EC/micro-crystalline cellulosic (MCC) adsorption combined process	9	22.15 mA/cm ²	5 g/L	Initial concentration 50 mg/L	Methylene blue dye 98.75%	[38]
Synthetic dye solution	EC/Moringa oleifera seeds (MOS) adsorption coupling process by using Al and stainless steel			0.6 g/L for Acid Black 1		Acid Black 1 99.3% Basic Red 2 94%	[60]

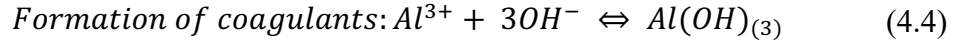
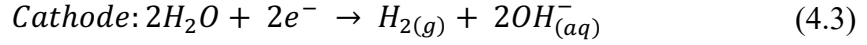
Wastewater Used	Treatment Technique	Optimal Treatment Conditions				Maximum Removal	Ref.
		pH	Current density	Adsorbent dosage	Others		
	electrode in a batch reactor			5 g/L for Basic Red 2			
Synthetic solution	EC, phosphate-assisted EC, and adsorption on electrogenerated adsorbents					Cetylpyridinium 165.3 mg/g	[61]
Synthetic solution	EC/peanut shell (PS) adsorption coupling technique	7	2 mA/cm ²	5 g/L	Initial concentration 50 mg/L	Malachite green dye 98%	[62]
Jewelry industry wastewater	EC, adsorption, and wetland technology					TSS 71% COD 91% Cu 95% CN 96% Oil & grease 71%	[159]
Tanning wastewater	Eggshell adsorption process coupled with EC		200 A/m ²	12 g/L	Time 110 min	Chromium 99%	[63]
Electroplating wastewater	EC and adsorption processes	4		9 g/L	Time 60 min	Chromium (VI) 97% Copper 97.45% Zinc 96%	[64]
Synthetic wastewater containing EBT	Hybrid treatment approach consists of EC and adsorption					Eriochrome black T dye 99.1%	[65]
Synthetic wastewater	Hybrid EC/A treatment reactor		83.33 mA/cm ²			NO ₃ ⁻ -N 96%	[66]
Real wastewater from cardboard paper mill industry	Aluminum and iron electrodes followed by adsorption of treated wastewater on GAC	5.29	4.41 mA/cm ²		Time 10 min	COD 99.93%	[67]
Real wastewater from beverage industry	A combination of EC and adsorption			10 g/L		Color 98.66% COD 92.15% TSS 90.12%	[68]

Wastewater Used	Treatment Technique	Optimal Treatment Conditions				Maximum Removal	Ref.
		pH	Current density	Adsorbent dosage	Others		
Synthetic dye solution	EC/banana peel (BP) adsorption coupling process					Methylene blue dye 99%	[160]
Synthetic solution	GAC and EC		25 ma/cm ²		Time 120 min	Phenol 96%	[161]
UASB effluent	Hybrid EC/A treatment system	6	29.44 A/m ²			COD 100% BOD ₅ 100% Turbidity 96.5% Phosphorus 97.5%	[70]

4.4.3 EC reaction

The processes taking place during EC are influenced by the electrode material, which also determines the types of generated in-situ coagulants. Additionally, the chemical and physical characteristics of the solution being treated, such as its composition, including contaminant concentration and nature, as well as pH and conductivity, play an important role in the process [145]. The electrode employed in this study is aluminum, and the anodic process includes the oxidative dissolution of aluminum into an aqueous solution, as demonstrated in equation (4.2). The reductive dissociation of water occurs in the cathode, as indicated by equation (4.3). Equation (4.4) demonstrates the formation of coagulants [72].





The cathodic reaction shows a role in enhancing the EC process, which helps improve the removal of pollutants. It produces hydroxyl ions (OH^-) which combine with the aluminum ions dissolved in the solution to form insoluble aluminum hydroxides (i.e., coagulants). It should be noted that aluminum hydroxide coagulants $Al(OH)_3$ are effective in the charge neutralization process by compressing the double layer surrounding pollutants, thereby aiding in the formation of aggregates and subsequent precipitation. These coagulants work by adsorbing organic pollutants onto active sites on the adsorbent surfaces [162]. This process is effective in removing various contaminants from wastewater due to the high adsorption capacity of the EC flocs [163] along with possible minor factors such as air flotation [164]. Ion movement in solutions enables current flow between electrodes: oxidation at the anode produces metal ions, while reduction at the cathode generates hydrogen gas and hydroxide ions [165, 166]. Faraday's law links electrical current to metal ion production at the anode, crucial for removing pollutants, with metal ion mass calculable via equation (4.5) [72].

$$m = \Phi \frac{It}{zF} M \quad (4.5)$$

M denotes electrode material mass, and F represents Faraday's constant (96,486C). m is the mass of metal (e.g., aluminum) produced by a current, while "z" indicates electrons transferred per metal atom. Faraday's law applies when all electrons contribute to anode

metal dissolution. The real dissolution process introduces current efficiency or faradaic yield (ϕ), typically <1 , but >1 if chemical and electrochemical oxidation occur [167].

4.4.4 Pb(II) removal and RSM modeling

4.4.4.1 Optimization of the hybrid EC/A system conditions for boosting Pb(II) removal efficiency

Table 8 shows the Pb(II) removals achieved under each experimental condition. The experiments involved employing three levels of four factors as specified in Table 7. The response (i.e., the percentage of Pb(II) removal) was measured at four different time intervals: 15, 30, 60, and 90 min. The respective results suggest that typically the current density (factor A) has an impact on Pb(II) removal. Notably, at the highest level of this factor (i.e., 1.5 mA/cm^2) as in experiments number 1, 8, 13, 14, 15, 20, 22, and 24, Pb(II) removal generally tends to be higher. However, some exceptions are also noted. Additionally, Pb(II) initial concentration (factor B) also appears to play a significant role in its removal; however, it is crucial to consider the overall effect of the combined factors as well. The Pb(II) removal is also influenced by factor C, which refers to the GO@ZIF-7 adsorbent dosage. This emphasizes the importance of using a sufficient quantity of adsorbent to eliminate Pb(II). Based on the obtained results, it is largely observed that higher dosages of GO@ZIF-7 nanocomposite gave a better Pb(II) removal. When considering conductivity impact (factor D), the influence of this factor is relatively subtle. Regardless of the different factors studied, it is evident that as the contact time increases the Pb(II) removal efficiency also increases. Though the effect of the four studied factors is not completely independent, nonetheless, the maximum Pb(II) removal (i.e., 98.4%) was

obtained after a contact time of 90 min when the levels of the factors were set at the values shown in experiment 18 (see Table 8). To get more insights into the effects of the process parameters (i.e., current density, Pb(II) initial concentration, GO@ZIF-7 nanocomposite dosage, and conductivity) on Pb(II) removal, and the interactions among the studied factors, ANOVA analysis was carried out, with the findings detailed in the following section.

4.4.4.2 ANOVA results

The removal efficiency of Pb(II) utilizing the EC/A system was also optimized using ANOVA regression analysis [168]. The ANOVA test results for Pb(II) removal are presented in Table 11 for the respective four models. These results demonstrate an impact ($p < 0.05$) of the examined factors on Pb(II) removal, indicating a level of significance at a 95% confidence level for the computed model. Table 10 showcases the models and their regression coefficients, for the examined responses. Figure 14 which shows actual vs predicted Pb(II) removals typically shows good modeling trends, except for Figure 14D with some outliers. Furthermore, Figure 15 displays the normal probability plots of the four models, also known as the quantile-quantile (Q-Q) plot. This plot is commonly used to assess the normality of residuals in regression analysis. In Figures 15A and 15C, most data points align closely with the line indicating that the residuals are approximately normally distributed. Nevertheless, there is a small deviation around the center, which suggests an outlier or influential data point within the dataset. On the other hand, Figures 15B and 15D generally adhere to the line but exhibit a slight curvature at the lower end. Some data points,

represented by squares and triangles, deviate from the expected pattern, possibly indicating outliers, non-normality, or other complexities in the regression model residuals.

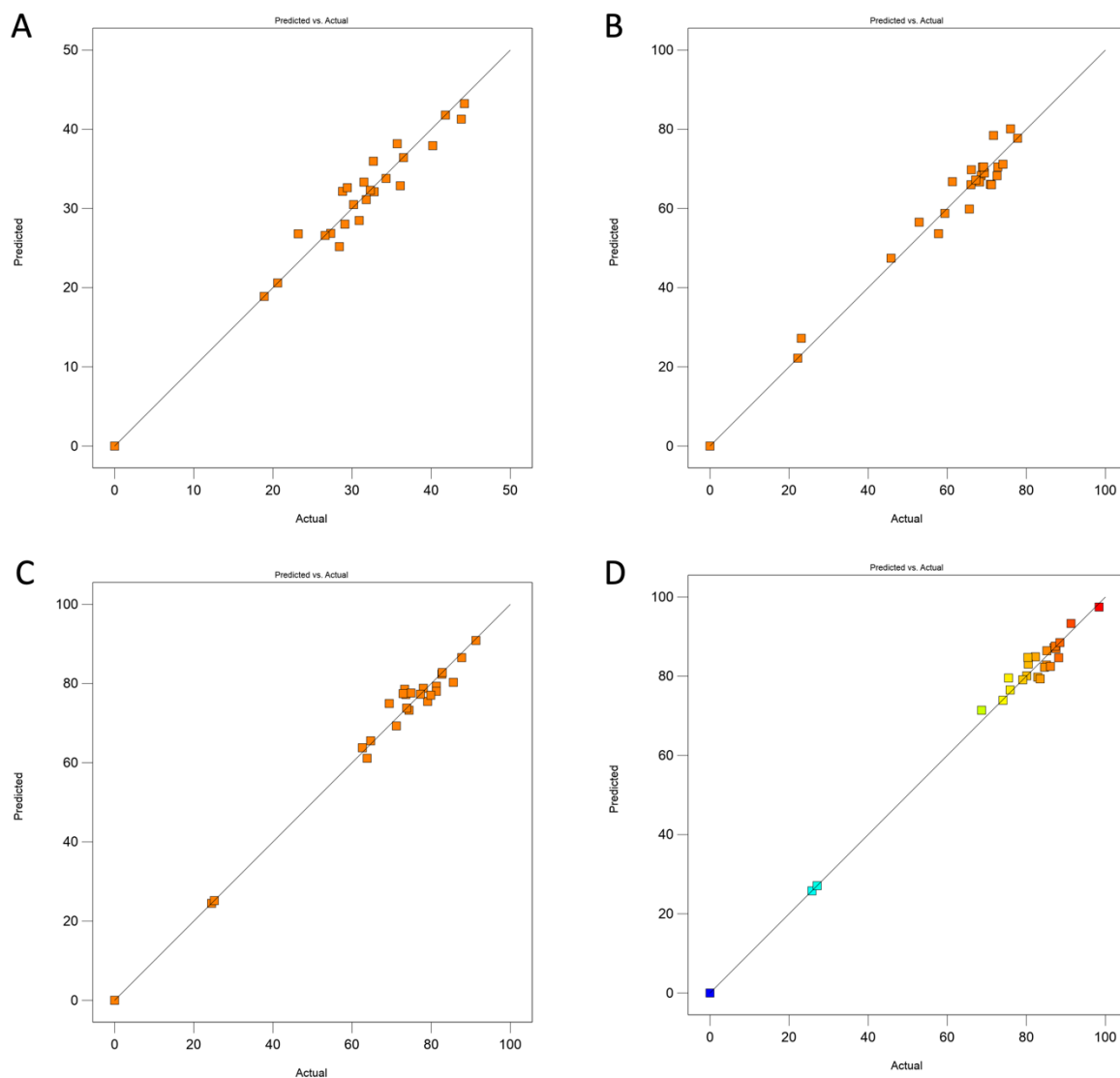


Figure 14: Actual versus predicted Pb(II) removal obtained from the RSM modeling: A) after 15 min, B) after 30 min, C) after 60 min, and D) after 90 min of contact time

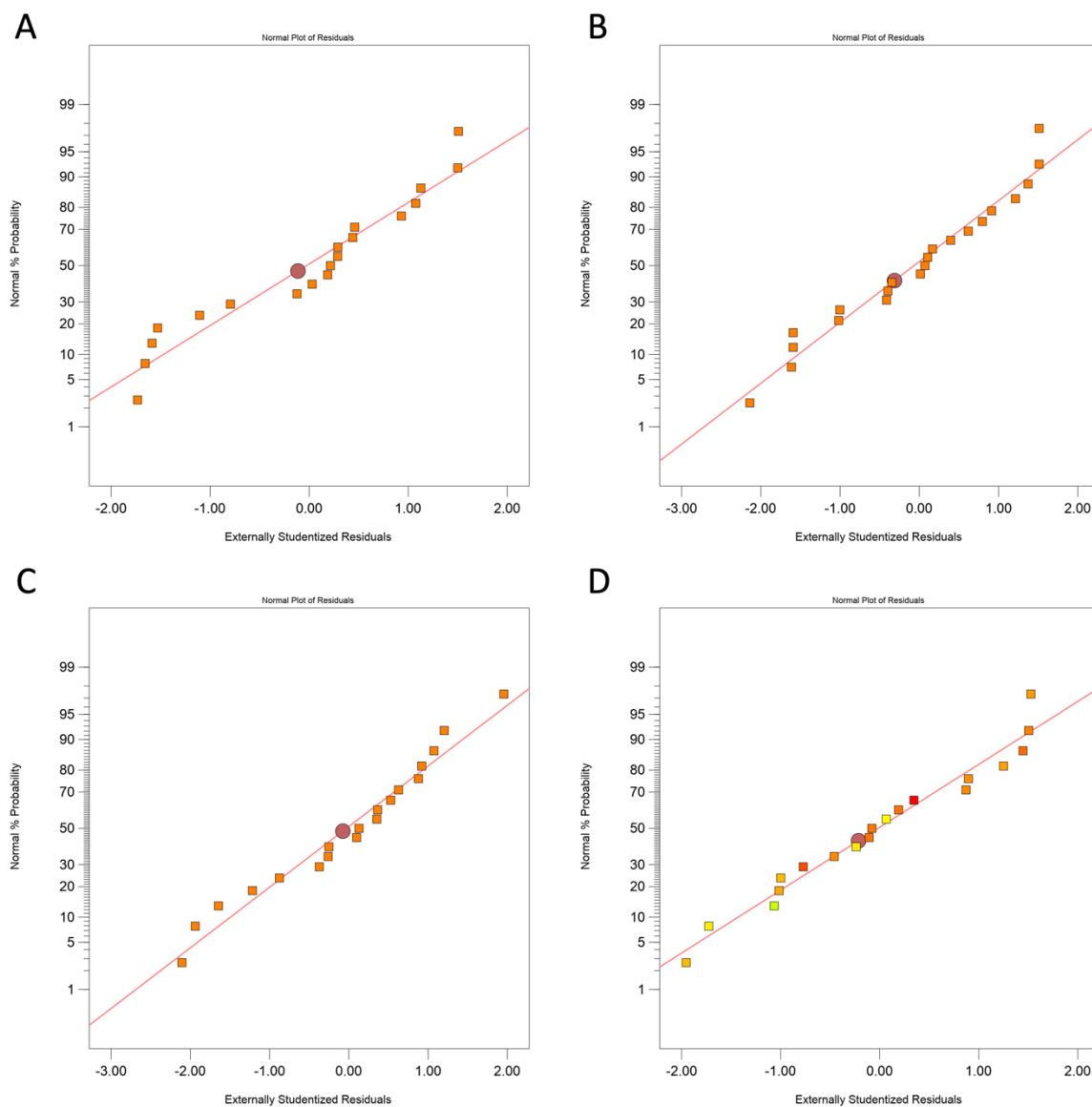


Figure 15: Normal plot of residuals for Pb(II) removal using the EC/A system. A) after 15 min, B) after 30 min, C) after 60 min, and D) after 90 min of contact time

Table 10 presents four mathematical models of the analyzed results and their regression coefficients corresponding to four different contact times: 15, 30, 60, and 90 min, with quadratic models being noteworthy if they have the highest coefficients [169]. These models provide means for predicting Pb(II) removal and highlight the different terms (i.e., factors) affecting such removal. A more comprehensive analysis of their individual performances, using measures like the coefficient of determination (R^2), adjusted R^2 , and adequate precision, reveals some interesting findings. For instance, the model associated with a 15 min contact time has an R^2 value of 95.08%, an adjusted R^2 value of 89.26%, and an adequate precision value of 19.4984. If a mathematical model has an R^2 value of more than 0.75, it is usually considered valid for optimization [170]. The explanatory power of models that use variable reduction to correlate with experimental data decreases the adjusted and predicted R^2 values [171]. During the first 30 min of contact time, the model showcases an R^2 value of 96.78%, an adjusted R^2 value of 92.98%, and an adequate precision value of 21.2745. Moving on to the 60 min model, we observe an improvement, with an R^2 value of 98.37%, an adjusted R^2 value of 96.09%, and an adequate precision value of 27.6351 that ensures reliable accuracy. The last model, which runs for 90 min exhibits impressive statistical measures. Our analysis reveals an R^2 of 99.00%, an adjusted R^2 of 97.61% and, a satisfactory level of precision, as shown by an adequate precision value of 35.3711. Upon examination of the four models' statistics, it becomes evident that all models display impressive R^2 and adjusted R^2 values indicating their ability to effectively fit the data and accurately predict Pb(II) removal efficiency. Significantly, as the duration of interaction increases, there is an obvious improvement in the prediction accuracy of the models. Moreover, an important observation is that each model surpasses

the threshold adequate precision level of 4, highlighting their ability to efficiently navigate the design space. Also, the 90 min model stands out from the group because it has a level of precision making it the most reliable option, for making predictions. In summary, residual plots provide insights into the distribution and predictability of residuals. While there may be some deviations and small abnormalities, the overall assessment suggests that residuals are distributed satisfactorily. The regression models demonstrate an acceptable level of precision within their domains and their accuracy improves with extending contact time. The 90 min model is particularly impressive due to its high level of dependability and prediction capacity as evidenced by its statistical quantities.

Overall, the results obtained from the randomized quadratic response surface central composite design indicate that the hybrid EC/A system used herein is capable of significantly reducing Pb(II) concentration in the treated synthetic wastewater samples. This finding is further supported by the obtained quadratic equations. These equations, shown in Table 10, allow mathematical models to be used for fitting experimental data by including terms that account for factor interactions. These models were developed for each contact time (15, 30, 60, and 90 min) to establish a relationship between observed responses and variables under study. In these models, A is the current density in (mA/cm^2), B stands for the Pb(II) initial concentration (mg/L), C refers to the dosage of the GO@ZIF-7 nanocomposite (mg/L), and D represents conductivity (mS/cm). Figures 14 and 15 show that experimental data align well with the predictions of the models, indicating negligible errors. Table 11 presents the correlations between process variables and response based on ANOVA analysis results. The results of the ANOVA analysis show that there are interactions between variables as indicated by the mean square, F-value, and p-value (Table

11). The effectiveness of removing Pb(II) using the EC/A system is statistically significant at all contact times with all four statistical models showing p-values less than 0.05 [172]. Moreover, the large F-values in these models suggest that the regression model can explain most of the variation in the responses. All four evaluated models have p-values less than 0.0001 further confirming their ability to predict the Pb(II) removal statistically. The presence of acceptable residuals and coefficients of variation indicates that the statistical model is significant. With an adequacy accuracy ratio exceeding four it is suitable for model optimization. Additionally, all the four models exhibit signal-to-noise ratio accuracies ranging from 40.54 to 84.60. The significance of the operational factors and their interactions is presented and discussed in the subsequent section.

Table 10: Regression models for the quadratic response surface central composite design, coefficient of determination, adjusted coefficient of determination, and adequacy precision for the four models used

	Model	R ²	Adjusted R ²	Adeq. Precision
15 min contact time	Removal Efficiency (%) = +37.93 + 1.92A + 8.07B + 2.65C + 5.30D + 0.8062AB - 1.19AD - 3.80A ² - 5.45B ² - 1.68D ² - 9.69A ² B - 4.94A ² D - 4.51AB ² + 5.06A ² B ²	0.9508	0.8926	19.4984
30 min contact time	Removal Efficiency (%) = +53.66 + 10.95A + 16.80B + 3.10C + 13.23D - 0.3813AB - 1.44AD + 2.77CD - 2.39A ² - 5.02B ² - 17.53A ² B - 13.79A ² D - 13.86AB ² + 22.19A ² B ²	0.9678	0.9298	21.2745

60 min contact time	Removal Efficiency (%) = +69.30 + 13.20A + 18.45B + 4.08C + 14.40D + 0.6500 AB - 2.50AD + 2.55CD - 4.60A ² - 8.10B ² - 3.83D ² - 19.97A ² B - 15.20A ² D - 16.09AB ² + 24.71A ² B ²	0.9837	0.9609	27.6351
90 min contact time	Removal Efficiency (%) = +79.33 + 13.57A + 19.77B + 2.70C + 15.35D - 0.2438AB - 1.89AD + 2.82CD - 6.60A ² - 9.95B ² - 5.38D ² - 22.09A ² B - 14.82A ² D - 16.87AB ² + 26.75A ² B ²	0.9900	0.9761	35.3711

Table 11: ANOVA results for Pb(II) removal using the developed EC/A system

	Source	Sum of Squares	df	Mean Square	F-value	p-value	Remark
15 min contact time	Model	1866.09	13	143.55	16.34	< 0.0001	significant
	A	29.65	1	29.65	3.38	0.0933	
	B	521.65	1	521.65	59.4	< 0.0001	significant
	C	169.07	1	169.07	19.25	0.0011	significant
	D	224.72	1	224.72	25.59	0.0004	
	AB	10.4	1	10.4	1.18	0.2998	
	AD	22.8	1	22.8	2.6	0.1354	
	A ²	276.64	1	276.64	31.5	0.0002	significant
	B ²	569.42	1	569.42	64.84	< 0.0001	significant
	D ²	54.41	1	54.41	6.19	0.0301	significant
	A ² B	501.17	1	501.17	57.06	< 0.0001	significant
	A ² D	130.35	1	130.35	14.84	0.0027	significant
	AB ²	108.3	1	108.3	12.33	0.0049	significant
	A ² B ²	144.61	1	144.61	16.47	0.0019	significant

	Residual	96.61	11	8.78			
	Cor Total	1962.69	24				
30 min contact time	Model	8381.94	13	644.76	25.46	< 0.0001	significant
	A	959.22	1	959.22	37.88	< 0.0001	significant
	B	2257.92	1	2257.92	89.17	< 0.0001	significant
	C	231.26	1	231.26	9.13	0.0116	significant
	D	1399.2	1	1399.2	55.26	< 0.0001	significant
	AB	2.33	1	2.33	0.0918	0.7675	
	AD	33.35	1	33.35	1.32	0.2755	
	CD	122.66	1	122.66	4.84	0.05	significant
	A ²	130.56	1	130.56	5.16	0.0442	significant
	B ²	574.86	1	574.86	22.7	0.0006	significant
	A ² B	1639.17	1	1639.17	64.74	< 0.0001	significant
	A ² D	1014.76	1	1014.76	40.08	< 0.0001	significant
	AB ²	1023.98	1	1023.98	40.44	< 0.0001	significant
	A ² B ²	2813.38	1	2813.38	111.11	< 0.0001	significant
	Residual	278.52	11	25.32			
	Cor Total	8660.46	24				
60 min contact time	Model	10885.16	14	777.51	43.13	< 0.0001	significant
	A	1393.92	1	1393.92	77.33	< 0.0001	significant
	B	2723.22	1	2723.22	151.07	< 0.0001	significant

	C	400.17	1	400.17	22.2	0.0008	significant
	D	1658.88	1	1658.8 8	92.03	< 0.0001	significant
	AB	6.76	1	6.76	0.375	0.554	
	AD	100	1	100	5.55	0.0403	significant
	CD	104.04	1	104.04	5.77	0.0372	significant
	A ²	406.27	1	406.27	22.54	0.0008	significant
	B ²	1259.71	1	1259.7 1	69.88	< 0.0001	significant
	D ²	280.91	1	280.91	15.58	0.0027	significant
	A ² B	2128	1	2128	118.05	< 0.0001	significant
	A ² D	1232.21	1	1232.2 1	68.36	< 0.0001	significant
	AB ²	1380.31	1	1380.3 1	76.57	< 0.0001	significant
	A ² B ²	3448.7	1	3448.7	191.32	< 0.0001	significant
	Residual	180.26	10	18.03			
	Cor Total	11065.42	24				
90 min contact time	Model	12583.84	14	898.85	71.02	< 0.0001	significant
	A	1474.24	1	1474.2 4	116.48	< 0.0001	significant
	B	3128.41	1	3128.4 1	247.17	< 0.0001	significant
	C	175.5	1	175.5	13.87	0.004	significant
	D	1884.98	1	1884.9 8	148.93	< 0.0001	significant
	AB	0.9506	1	0.9506	0.0751	0.7896	
	AD	57.38	1	57.38	4.53	0.0591	

	CD	127.13	1	127.13	10.04	0.01	significant
	A ²	835.3	1	835.3	66	< 0.0001	significant
	B ²	1899.26	1	1899.26	150.06	< 0.0001	significant
	D ²	556.42	1	556.42	43.96	< 0.0001	significant
	A ² B	2603.38	1	2603.38	205.69	< 0.0001	significant
	A ² D	1171.18	1	1171.18	92.53	< 0.0001	significant
	AB ²	1517.63	1	1517.63	119.91	< 0.0001	significant
	A ² B ²	4040.19	1	4040.19	319.21	< 0.0001	significant
	Residual	126.57	10	12.66			
	Cor Total	12710.41	24				

4.4.4.3 Effect of operational factors on the Pb(II) removal and their interaction

Pb(II) removal is greatly influenced by current density, Pb(II) initial concentration, GO@ZIF-7 nanocomposite dosage, and conductivity. All the investigated factors are statistically significant since their p-values are <0.05 [101] To understand the effects of these factors on Pb(II) removal better, response surface plots are regenerated and displayed in Figure 16. Our findings reveal that the highest level of Pb(II) removal reached 98.4% when applying a GO@ZIF-7 adsorbent dosage of 600 mg/L and a conductivity of 12 mS/cm, with a current density of 50 mA/cm², and Pb(II) initial concentration of 50 mg/L. These conditions also facilitated the in-situ production of aluminum hydroxide coagulant on site which helped in absorbing pollutants from the synthetic wastewater. The EC

treatment method employed herein utilizes current density to generate aluminum hydroxide coagulants that effectively separate contaminants from wastewater by forming flocs. Equations (4.2), (4.3), and (4.4) presented in section 4.4.3 show the complete reaction occurring.

A crucial factor in the efficiency of the EC reactor is the choice of anode material, which determines the release of cations into the solution. These cations then form flocs [173]. The formation of electrocoagulants governed by the Faradays law is influenced by the strength of the current resulting from the anode dissolution. Thus, it affects the EC process. The rate of reaction in the cell mainly depends on parameters applicable to all electrochemical techniques. Increasing current intensity enhances Pb(II) removal [174]. It is also important to provide current to the EC cell as it directly impacts how quickly hydrogen and oxygen are released during the EC process [175]. The quick release of oxygen and hydrogen in the EC process is crucial for enhancing its efficiency and effectiveness. Faster gas release improves coagulation and flotation, leading to better pollutant removal, reduced energy consumption, and more efficient floc formation [176]. Additionally, it helps prevent electrode passivation [177]. These aspects highlight the importance of gas release kinetics in optimizing the EC process for wastewater treatment. Current density, which refers to the amount of current flowing over an area of an electrode, plays a role in EC [34]. It controls factors such as dosage, the rate of bubble generation, floc size and increase in the bubble size, the reaction kinetics, and the energy consumption, ultimately regulating the reaction rate in the EC process [178]. Current density directly influences the rate at which the anode material dissolves to release coagulants, governed by Faraday's law of electrolysis [179]. Properly adjusted current density ensures an optimal amount of coagulant is generated,

balancing the efficiency and effectiveness of the EC process [180]. Too high or too low current density can lead to issues like insufficient treatment or excessive energy use and sludge production [181]. Additionally, current density affects other EC parameters like pH and floc characteristics, which indirectly impact coagulant dosage and overall process performance [182].

Figure 16 displays the RSM graphs that demonstrate the relationships between the factors that influence the efficiency of Pb(II) removal. Each figure from the four shows the impact of two factors while keeping the other two consistent. Figure 16A examines the relationship between current density and the Pb(II) initial concentration in the condition of a fixed adsorbent dosage of 400 mg/L and a conductivity of 8 mS/cm. The response surface reveals a double convex form, suggesting that the removal efficiency rises as both the current density and Pb(II) initial concentration rise until reaching a specific point, beyond which the efficiency decreases. This implies that although both factors have a favorable impact, there is a point at which no additional improvement in removal efficiency is observed. The second figure, 16B illustrates the correlation between the Pb(II) initial concentration and the adsorbent dosage used while maintaining a constant current density of 1 mA/cm² and a conductivity of 8 mS/cm after 30 min of contact time. The RSM graph suggests a linear relationship where removal efficiency increases with higher adsorbent dosage across all concentrations of Pb(II), highlighting the significance of adsorbent dosage in the removal process. On the other hand, figure 16C demonstrates the impact of adsorbent dosage and conductivity on the overall efficiency of the system with fixed current density and Pb(II) initial concentration. The RSM graph shows that Pb(II) removal efficiency appears to be responsive to the variations in adsorbent dosage and conductivity, indicating that higher

dosages and conductivity are associated with improved efficiency within the range of the study. It is clear from the results that higher amounts of conductivity of the NaCl electrolyte help to remove Pb(II) from the synthetic wastewater at higher rates. This correlation is presented in Tables 10 and 11 and confirmed by the RSM modeling graphs presented in Figure 16. Several studies in the literature have noted that conductivity is considered a time-dependent factor with a strong influence on the removal efficiency of all types of ionic species [183, 184], a trend that our results support. The change in conductivity is a crucial factor in the early stages of the electrochemical process, as well as in maintaining a desired electric current density in later stages [183]. The concurrent existence of electrical conductivity and current density contributes to the enhancement of ion release from the anode, hence resulting in the efficient removal of pollutants. Figure 16D analyzes the interaction between current density and conductivity, maintaining Pb(II) initial concentration and adsorbent dosage constant at 100 mg/L and 400 mg/L. The response surface demonstrated after 90 min of contact time indicates a complex interaction between current density and conductivity. Removal efficiency encounters a significant relationship with both current density and conductivity within specific ranges. The graph's red area shows the highest removal efficiency, indicating the best combination of the two factors that maximizes the removal of Pb(II). As the surface gradually descends from these high removal efficiency areas it suggests that there is a decrease, in the removal efficiency of Pb(II) as the current density and conductivity increase or decreases further. This could be due to several reasons. Excessive current can result in a drop and affect the overall performance of the electrochemical cell [185]. Electric current flowing from electrodes helps control the release of metal ions, from them resulting in improved metal removal

effectiveness until optimal conditions are reached [186]. If much current is consumed it can lead to dissipation of electrical energy resulting in water heating. There is a threshold of density beyond which there is no improvement in the quality of treated water. Several researchers have investigated how current density affects the efficiency of EC under conditions [187, 188]. As shown by the RSM graph, the relationship between current density and conductivity indicates that although both factors are significant for the process, their effect is not linear. To summarize, the RSM graphs analysis offers a deep understanding of the complex interactions among the operational factors studied. The findings indicate that the removal effectiveness is influenced by the current density and Pb(II) initial concentration, but the adsorbent dosage stands out as a critical factor that improves the overall performance of the system under different conditions. However, conductivity exhibits a relatively smaller influence within the examined range. These findings emphasize the significance of adjusting the electrical and chemical factors of the EC/A hybrid system to achieve the highest possible removal efficiency in the Pb(II) treatment process. Moreover, the amount of time the hybrid EC/A system operates, referred to as contact time has an influence, on the release of aluminum from the electrodes. This released aluminum reacts with ions and forms electrocoagulants that impact the efficiency of Pb(II) removal [189, 190]. Longer contact times have shown an increase in Pb(II) removal effectiveness, as depicted in the results establish relationships between removal efficiencies and response time. The obtained experimental results regularly prove an increase in the Pb(II) removal percentages as we move from 15 min to 90 min of contact time as demonstrated.

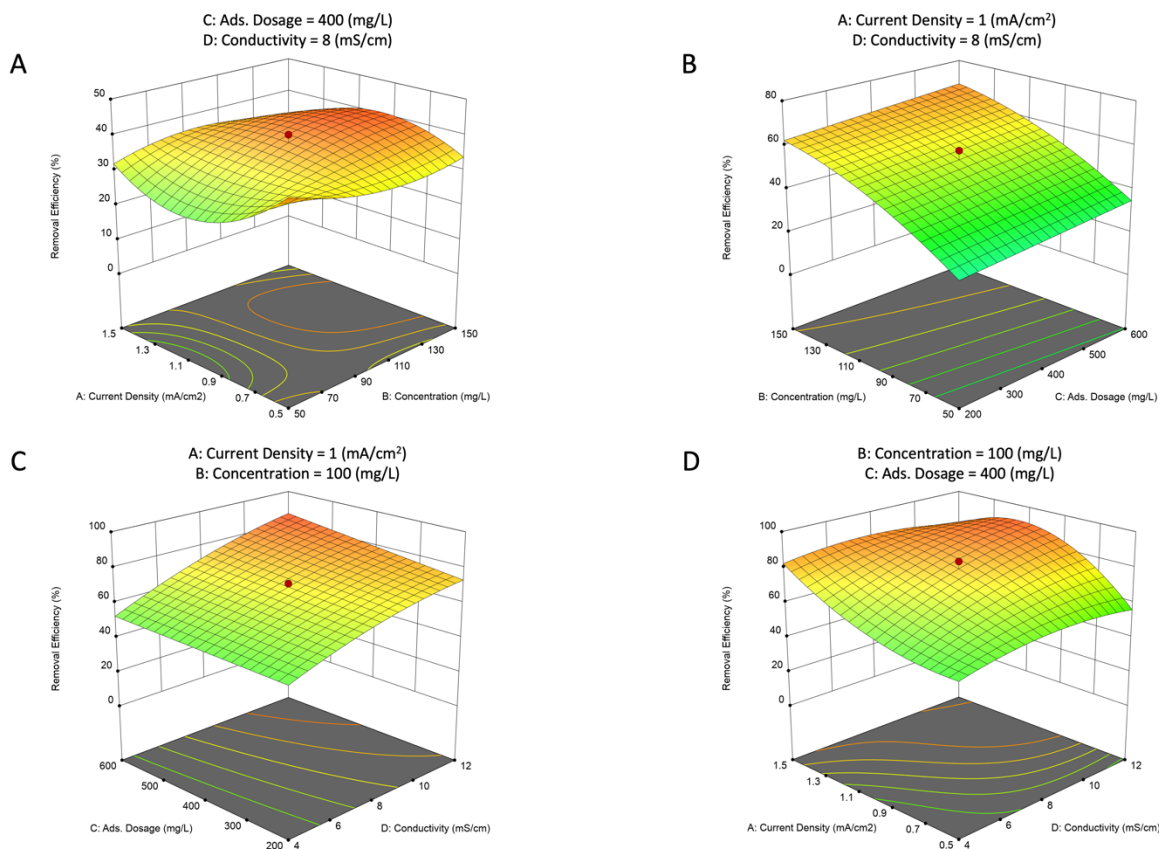


Figure 16: RSM modeling graphs A) current density and Pb(II) initial concentration effects at a fixed adsorbent dosage of 400 (mg/L) and conductivity of 8 (mS/cm) after 15 min of contact time, B) Pb(II) initial concentration and adsorbent dosage effects at a fixed current density of 1 (mA/cm²) and conductivity of 8 (mS/cm) after 30 min of contact time, C) adsorbent dosage and conductivity effects at a fixed current density of 1 (mA/cm²) and Pb(II) initial concentration of 100 (mg/L) after 60 min of contact time, and D) current density and conductivity effects at a fixed Pb(II) initial concentration of 100 (mg/L) and adsorbent dosage of 400 (mg/L) after 90 min of contact time

Figure 17 shows a set of two-factor interaction (2FI) graphs between the studied factors. Figure 17A demonstrates how the interaction between current density (Factor A) and Pb(II) initial concentration (Factor B) affects the Pb(II) removal efficiency. This interaction is analyzed while maintaining constant levels for the other two factors of the model: adsorbent dosage (Factor C) at 400 mg/L and conductivity (Factor D) at 8 mS/cm. In this graph, the black line represents the trend in Pb(II) removal efficiency as the Pb(II) initial concentration increases from 50 mg/L to 150 mg/L, while keeping the current density fixed at its lowest level of 0.5 mA/cm². On the other hand, the red line corresponds to a higher current density of 1.5 mA/cm². The divergence of these lines from parallelism is a sign of a significant interaction between the current density and Pb(II) initial concentration. Specifically, this variation suggests that the efficiency of Pb(II) removal is not only dependent on either the current density or the initial concentration in isolation but rather on the combined effect of these two factors. It should be noted that parallel lines imply the absence of interaction between the studied factors, while unparallel ones indicate the presence of interaction. The greater the degree to which these lines split away from being parallel, the more powerful the interaction between the studied factors is [191]. Accordingly, the unparallel lines shown in Figure 17A reveal the presence of interaction between factors A and B and confirm that Pb(II) removal efficiency is dependent on the interaction between these two factors. Figure 17B demonstrates the interaction between factor B and factor C (i.e., adsorbent dosages) at fixed current density and conductivity levels. Clearly, the parallel nature of the lines representing the change in Pb(II) removal with changing its concentration (factor B) at different adsorbent dosages (factor C), indicates that there are no significant interactions between these two factors. Figure 17C,

on the other hand, depicts the interaction between factor C and factor D (i.e., conductivity). As displayed in this figure, there is an interaction between adsorbent dosage and conductivity, which is more pronounced at the lowest conductivity level of 4 mS/cm. Finally, Figure 17D shows fairly parallel lines representing the interaction between factor A and factor D, suggesting that the interaction between these two factors is statistically insignificant, with a consistent removal efficiency of Pb(II) across different conductivity levels expected. Together, these figures provide insights into how various factors and their interactions affect the efficiency of Pb(II) removal using the hybrid EC/A system. These insights can be crucial in guiding further experiments and/or process refinements.

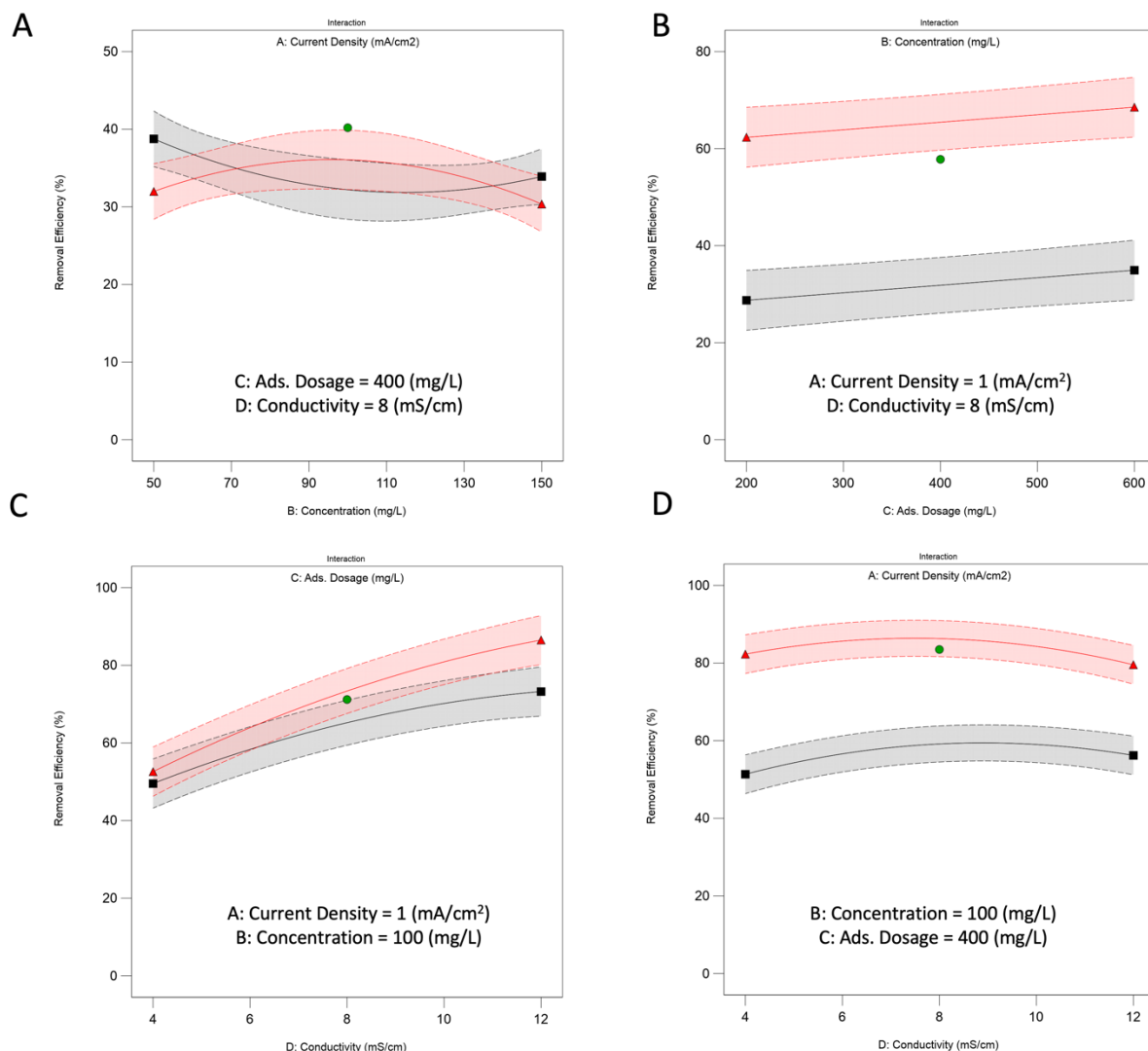


Figure 17: Interactions between the studied factors graphs. A) current density and Pb(II) initial concentration interaction at a fixed adsorbent dosage and conductivity after 15 min of contact time, B) Pb(II) initial concentration and adsorbent dosage interaction at a fixed current density and conductivity after 30 min of contact time, C) adsorbent dosage and conductivity interaction at a fixed current density and Pb(II) initial concentration after 60 min of contact time, and D) current density and conductivity interaction at a fixed Pb(II) initial concentration and adsorbent dosage after 90 min of contact time

4.4.5 Machine learning modeling

When it comes to machine learning modeling, the selection of a model depends on the characteristics of the data and the specific task involved. ANNs are preferred due to their ability to identify patterns in data. ANNs draw inspiration from the structure of the human brain, which comprises interconnected neurons processing a wide range of information [192]. They are created with the intention of replicating how humans learn and comprehend information. In terms, a neural network consists of units named neurons. Generally, a neural network (Figure 18) consists of input layers (representing independent variables), hidden layers, and an output layer (representing dependent variables). The count of input and output neurons depends on the specifics of the research. However, XGBoost employs an ensemble model approach by averaging multiple simple models to estimate and effectively capture complex information present in the data [193]. Individual decision trees are easily interpretable, though their interpretability diminishes when combined into RandomForestRegressor due to the aggregation of numerous trees. Despite this, RandomForestRegressor generally offers improved performance on predictive tasks [194]. For our analysis, we trained three predictive machine learning models using our Pb(II) removal results obtained from the hybrid EC/A system; ANN, Xgboost, and RandomForestRegressor. Each model underwent training to capture nuances and variations present in the data. Our model architecture, designed for a regression task, featured a multi-layer structure. It started with an input layer that had 5 neurons using rectified linear unit (ReLU) activation, which helped kickstart the learning process with a number of neurons (Table 12). To avoid overfitting, we added a dropout layer with a dropout rate set at 50%. The structure also comprised three layers: the first layer contained 128 neurons, the second layer contained 64 neurons, and the third layer equipped with 32 neurons. These layers

used ReLU activation to introduce linearity and facilitate complex pattern learning in the data. The network ended with an output layer consisting of one neuron specifically designed for regression purposes. To optimize this setup, we used the Adam optimizer, known for its efficiency in handling gradients and adaptive learning rates. The model's learning process was guided by the squared error loss function, which is particularly suitable for regression tasks as it focuses on minimizing the squared discrepancies between the predicted and actual values. Following training, we evaluated the models' performance using the dataset to gauge their capabilities and accuracy. During evaluation, it was observed that both XGboost and RandomForestRegressor performed well. The XGboost model achieved an R^2 value of 0.90 while RandomForestRegressor achieved an R^2 value of 0.85. These high R^2 values indicate that both models effectively captured and predicted variances, within the dataset. This finding has offered knowledge, about the efficient models for the specific dataset enabling well-informed decision-making, for future analyses or applications.

Table 12: Summary printout of the ANN training model (Anaconda)

Layer (type)	Output Shape	Param #
dense_4 (Dense)	(None, 128)	768
dropout_1 (Dropout)	(None, 128)	0
dense_5 (Dense)	(None, 64)	8256
dense_6 (Dense)	(None, 32)	2080
dense_7 (Dense)	(None, 1)	33
Total params: 11,137		
Trainable params: 11,137		
Non-trainable params: 0		

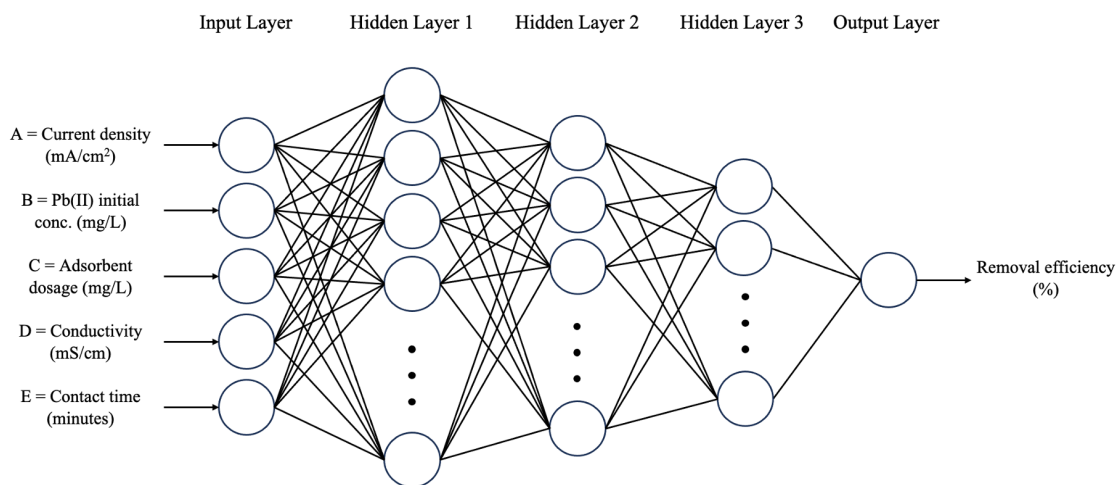


Figure 18: ANN architecture (5, 128, 64, 32, 1) for the hybrid EC/A system for the Pb(II) removal

4.5 Conclusions

This study introduced an innovative hybrid EC/A system using aluminum electrodes integrated with a novel GO@ZIF-7 nanocomposite for the effective removal of Pb(II) from contaminated water samples. The hybrid EC/A system significantly outperformed the standalone EC and adsorption processes at all the examined times. The Pb(II) removal efficiency using the hybrid EC/A system is quite high, reaching more than 98% under optimized process conditions. The findings of this study illustrated the noticeable influence of current density, particularly at 1.5 mA/cm^2 , in achieving high Pb(II) removal levels. The Pb(II) initial concentration and the dosage of the GO@ZIF-7 nanocomposite emerged as critical factors affecting the Pb(II) removal efficiency. The statistical models derived in this work showed great accuracy and reliability. The increase in the prediction accuracy of these models was found to be time-dependent, with the 90 min model demonstrating the highest precision. The findings of this study indicate that the hybrid EC/A system employing aluminum electrodes integrated with a novel GO@ZIF-7 nanocomposite has significant commercial potential, as suggested by its remarkably high Pb(II) removal efficiencies and effective treatment of water contaminated with Pb(II). Moreover, our work emphasizes the efficacy of machine learning models in environmental applications. The ANN, XGBoost, and RandomForestRegressor models shown strong predictive abilities for estimating the removal of Pb(II), with XGBoost and RandomForestRegressor displaying notably high R^2 values, highlighting their potential for future investigations and practical implementations in related fields.

CHAPTER 5

Conclusions and Recommendations

5.1 Summary

The current research aimed to innovate in the field of wastewater treatment by synthesizing a novel GO@ZIF-7 nanocomposite by combining GO with ZIF-7, to enhance contaminant removal from synthetic wastewater. Before delving into the innovative exploration of the GO@ZIF-7 nanocomposite capabilities for wastewater treatment, this study embarked on an extensive review of the existing literature in the field. The literature review meticulously surveyed the current state of water treatment technologies, with a specific focus on the methodologies employed for heavy metal removal, including both adsorption and EC technologies. It highlighted the increasing reliance on nanocomposite adsorbents and their emerging role in environmental remediation, particularly for the adsorption of heavy metals from aqueous solutions. The review also encompassed the principles and applications of EC as a standalone method, evaluating its effectiveness, operational parameters, and potential limitations. Furthermore, the literature review critically analyzed existing research on hybrid systems that combine EC with adsorption processes, pointing out the innovative approaches and their outcomes while highlighting the scarcity of studies that employ both EC and advanced nanocomposite materials like GO@ZIF-7. The gap in the literature became a pivotal point for this research, suggesting a novel system for achieving higher removal efficiencies of contaminants, particularly heavy metals, from wastewater.

The second part of the research intended to benchmark the adsorption performance of the GO@ZIF-7 nanocomposite against standalone GO and ZIF-7, employing RSM to optimize key adsorption parameters. Additionally, the research sought to analyze the isotherms of lead adsorption onto GO@ZIF-7, marking the first study of its kind on the use of ZIF-7 for lead removal from contaminated water, thus highlighting its novelty and significance. A first-of-its-kind study on lead adsorption onto GO@ZIF-7 was conducted, showcasing the material's novelty and potential. Through meticulous synthesis and characterization processes, including XRD and FTIR, the study affirmed the composite's superior adsorption capability, particularly at higher lead concentrations. The obtained results position the GO@ZIF-7 nanocomposite as a promising adsorbent for wastewater treatment applications.

The final part of the research demonstrated a significant advancement in water treatment technologies, offering insights into the synergistic effects of combining EC with nanocomposite adsorbent for effective heavy metal removal. The research elucidated the effectiveness of the hybrid EC/A system, utilizing the novel GO@ZIF-7 nanocomposite, in the removal of lead from synthetic wastewater. Characterization analyses, including XRD and FTIR, validated the successful synthesis of the materials. The hybrid system demonstrated a significant enhancement in lead removal efficiency compared to standalone EC and adsorption processes. Additionally, ML models such as ANN, XGBoost, and RandomForestRegressor were adeptly trained and validated, showing robust predictive capabilities for lead removal. This multifaceted approach underscores the synergy between advanced material science and computational modeling in optimizing wastewater treatment technologies. The integration of both studies' findings suggests a complementary

potential, leveraging the rapid removal capabilities of EC with the specificity and efficiency of adsorption techniques. This combined approach of the hybrid EC/A system could overcome current water treatment limitations by offering a more comprehensive, efficient, and versatile solution for removing a wide range of pollutants, including heavy metals, from contaminated wastewater.

5.2 Conclusions

This research has made significant contributions in the field of wastewater treatment, successfully synthesizing the GO@ZIF-7 nanocomposite and integrating it within an innovative hybrid EC/A system, employing aluminum electrodes for the effective treatment of lead from synthetic wastewater. The novel GO@ZIF-7 nanocomposite not only demonstrated a remarkable lead adsorption capacity, vastly outperforming its constituent materials with capacities reaching up to 5,000 mg/g, relative to about 500 and 600 mg/g obtained using the pristine ZIF-7 and GO, respectively. but also showcased the potential for commercial application in treating lead-contaminated wastewater. The extensive evaluation of different operational factors, including initial pH, initial lead concentration, and adsorbent dosage, revealed their crucial role in optimizing the adsorption process, further supported by RSM optimization. Moreover, the study identified that the lead adsorption adhered to the Freundlich isotherm trend, indicating multilayer adsorption, which aligns with the high uptake capacity observed.

The hybrid EC/A system significantly enhanced lead removal efficiency and significantly outperformed the standalone EC and adsorption processes at all the examined times. The lead removal efficiency using the hybrid EC/A system is quite high achieving over 98%

under optimal conditions and surpassing the results of standalone EC or adsorption methods. The research highlighted the noticeable influence of current density, particularly at 1.5 mA/cm², in achieving high lead removal levels. The lead initial concentration and the dosage of the GO@ZIF-7 nanocomposite emerged as critical factors affecting the lead removal efficiency. The statistical models derived in this work showed great accuracy and reliability. The increase in the prediction accuracy of these models was found to be time-dependent, with the 90 min model demonstrating the highest precision. Additionally, the adoption of machine learning models, including ANN, XGBoost, and RandomForestRegressor, proved instrumental in accurately predicting lead removal, showcasing the models' robust predictive capabilities, and emphasizing their applicability in environmental management and water treatment technologies.

The findings from both sections of this study underscore the synergy between advanced material science and hybrid treatment systems, offering a promising solution to the challenges of heavy metal pollution in water bodies. The combined approach not only opens avenues for the practical application of such novel composites in water treatment infrastructure but also highlights the potential for leveraging computational modeling for process optimization and scalability. This research contributes significantly to the field, suggesting a shift towards more sophisticated, efficient, and sustainable water treatment methodologies, with a strong emphasis on the commercial viability and environmental impact of such innovations.

5.3 Research contributions to the literature

The research resulted in three different research papers published or under review in internationally indexed journals and a successful filing of a patent for the novel GO@ZIF-7 nanocomposite. The following are the details of the contributions:

- “Synthesis and application of novel GO@ZIF-7 nanocomposite for the removal of lead from aqueous solutions” (Published Paper: emergent mater. (2023). <https://doi.org/10.1007/s42247-023-00571-3>).
- “Novel Al-electrodes/GO@ZIF-7 hybrid electrocoagulation/adsorption system for efficient Pb(II) removal: experimental and machine learning modeling studies” (Under review).
- “GO@ZIF-7 nanocomposite for Pb(II) removal from contaminated waters” (Invention disclosure with a green light status Ref. 2023-078-ISM).
- “A State of the Art on Performance of Hybrid Electrocoagulation/Adsorption Systems for the Treatment of Wastewater” (To be submitted).

5.4 Recommendations for future investigations

The journey towards the commercialization of the studied hybrid EC/A system is fraught with a significant number of challenges that still require extensive investigation. A key area of research that demands immediate attention involves the application of the hybrid EC/A system in the treatment of real industrial wastewater, which is characterized by its complexity due to the presence of a wide range of pollutants. Despite the high removal efficiencies of the hybrid EC/A system in treating synthetic wastewater, the body of

research focusing on its effectiveness in removing various heavy metals in conjunction with other organic and inorganic substances remains not studied. This gap in the research highlights the urgent need for comprehensive studies aimed at exploring the efficiency of the hybrid EC/A system in more complex conditions.

Moreover, a critical area that demands further exploration is the optimization of the process to reduce electrode consumption while simultaneously improving the efficacy of pollutant removal. The prospect of achieving these goals lies in the investigation into advanced electrode materials. Utilizing enhanced electrodes could lead to a more efficient process by reducing the rate of electrode consumption, thereby offering a potential reduction in the operational costs associated with the process. This approach not only addresses the economic considerations but also contributes to the environmental sustainability of the technology.

In addition to material improvements, the necessity for thorough energy consumption evaluations cannot be overstated. Conducting in-depth studies that focus on the long-term energy usage of the hybrid EC/A process is crucial. These evaluations should be carried out in settings that closely mimic real-world industrial conditions, specifically at the pilot scale and under continuous flow operations. Such detailed assessments will provide invaluable insights into the energy efficiency of the hybrid system, a factor that plays a critical role in its viability for commercial application.

Another significant stride that needs to be taken towards the commercialization of the hybrid EC/A system is the development of detailed numerical models. These models are helpful in predicting the performance of the hybrid system under various conditions. The

creation and refinement of these models are expected to facilitate a better understanding of the process dynamics, thereby expediting the transition of the EC/A technology from the laboratory to the industrial applications.

In summary, while the potential of the hybrid EC/A system in treating complex industrial wastewaters is immense, realizing its commercial viability necessitates a concerted research effort. This includes advancing our understanding of the process in the presence of a diverse pollutants, optimizing the technology to reduce costs and increase efficiency, rigorously evaluating energy consumption, and developing predictive models to guide its commercial implementation.

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Vitae

Name : Waleed Khalid Alnowaiser

Nationality : Saudi

Email : nowaiserw@gmail.com

Address : P.O. Box 11165, 3034 Dhahran 31261, Saudi Arabia

Academic Background : MSc in Civil Engineering, KFUPM

Publications :

- “Treatment of synthetic hypersaline produced water employing electrocoagulation-membrane bioreactor (EC-MBR) process and halophilic bacteria,” J Environ Chem Eng, vol. 6, no. 2, pp. 2442–2453, Apr. 2018, doi: 10.1016/J.JECE.2018.03.049.
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