



T.C.

TOKAT GAZİOSMANPAŞA UNIVERSITY

GRADUATE EDUCATION INSTITUTE

DEPARTMENT OF CHEMISTRY

MASTER PROGRAM WITH THESIS

**MAGNETIC SOLID PHASE MICROEXTRACTION OF CADMIUM IN WATER
AND FOOD SAMPLES ON *ESCHERICHIA COLI* (*E.coli*) IMMOBILIZED TO
MAGNETIC CONDUCTIVE CARBON BLACK (VULCAN XC-72) PRIOR TO ITS
DETERMINATION BY FLAME ATOMIC ABSORPTION SPECTROMETRY**

MASTER THESIS

MOHAMMED MAJID MOHAMMED ALI

SUPERVISOR

Prof.Dr. MUSTAFA TÜZEN

TOKAT – 2024

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TOKAT
JULY-2024

ETHICS CONTRACT

The thesis was prepared according to the thesis writing guide of Tokat Gaziosmanpaşa University Graduate Education Institute. The master thesis titled “ Magnetic Solid Phase Microextraction of Cadmium in Water and Food Samples on *Escherichia Coli* (*E.coli*) Immobilized to Magnetic Conductive Carbon Black (Vulcan XC-72) prior to its determination by Flame Atomic Absorption Spectrometry ” Which I prepared under the supervision of Prof.Dr.MUSTAFA TÜZEN is an original study in accordance with scientific and ethical values and rules, and if the contrary is determined, all kinds of legal sanctions will be imposed. I declare that I will accept.



01/07/2024

MOHAMMED MAJID MOHAMMED ALI

JURY ACCEPTANCE AND APPROVAL

The defense examination of the thesis study titled “ ‘ Magnetic Solid Phase Microextraction of Cadmium in Water and Food Samples on *Escherichia Coli* (*E.coli*) Immobilized to Magnetic Carbon Black (Vulcan XC-72) prior to its determination by Flame Atomic Absorption Spectrometry” prepared by Mohammed Majid Mohammed Ali, was held on the June-2024 and the following jury voted unanimously with the Tokat Gaziosmanpasa University Graduate Education Institute. It has been accepted as a Master's thesis in the Department of Chemistry.

Member of Jury

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APPROVAL

01/07/2024

Prof.Dr.

Director of Graduate Education Institute

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Mohammed Majid Mohammed

01/07/2024

ABSTRACT

MAGNETIC SOLID PHASE MICROEXTRACTION OF CADMIUM IN WATER AND FOOD SAMPLES ON *ESCHERICHIA COLI* (*E.coli*) IMMOBILIZED TO MAGNETIC CONDUCTIVE CARBON BLACK (VULCAN XC-72) PRIOR TO ITS DETERMINATION BY FLAME ATOMIC ABSORPTION SPECTROMETRY

Mohammed Majid Mohammed Ali

Master Thesis

Tokat Gaziosmanpasa University, Graduate Education Institute, Chemistry Department

Supervisor: Prof.Dr. Mustafa Tüzen

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A new solid-phase microextraction method using magnetic conductive carbon black (Vulcan XC-72) loaded with *E. coli* bacteria was developed as a new magnetic biosorbent composite. Vortex-assisted extraction was used to extract analyte ions, and magnetic biosorbent composite separation from the solution was performed by using a neodymium magnet. A selected parameter, such as pH, adsorbent dosage, vortex time, and sample volume, were optimized for optimal performance. Elution of adsorbed cadmium ions was achieved using 0.3 mL of 1.0 mol L⁻¹ HNO₃. The adsorption capacity was found to be 90.3 mg g⁻¹. The preconcentration factor and enhancement factor were found to be 100 and 88. The limit of detection (LOD), limit of quantification (LOQ), and linear range were found to be 0.6 µg L⁻¹, 2.0 µg L⁻¹, and 2-40 µg L⁻¹. Intraday and interday RSD values were found to be 1.88 % and 1.98 %. A factorial design was used for the optimization of all parameters. The accuracy of the method was performed by analyzing standard reference materials. The optimized method was successfully applied to water and food samples.

Keywords: FAAS, magnetic adsorbent, cadmium, solid phase microextraction, water and food samples.

ÖZ

MANYETİK KARBON SİYAHINA (VULCAN XC-72) İMMOBİLİZE EDİLMİŞ *ESCHERICHIA COLI* ÜZERİNDE SU VE GIDA NUMUNELERİNDE KADMIYUMUN ALEVLİ ATOMİK ABSORPSİYON SPEKTROMETRESİ İLE TAYİNİNDEN ÖNCE MANYETİK KATI FAZ MİKRO EKSTRAKSİYONU

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Tez Danışmanı: Prof. Dr. Mustafa Tüzen

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Elimizde manyetik iletken karbon siyahı (Vulcan XC-72) ile yüklenmiş *E. coli* bakterilerini kullanan yeni bir katı faz mikroekstraksiyon yöntemi geliştirildi. Bu yeni manyetik biyosorbent kompozit, analit iyonlarını ekstrakte etmek için vortex destekli ekstraksiyon kullanıldı ve çözelti içerisinde manyetik biyosorbent kompozit ayrımı bir neodimyum mıknatıs kullanılarak gerçekleştirildi. pH, adsorbent dozu, vortex süresi ve örnek hacmi gibi seçilen parametreler optimal performans için optimize edildi. Adsorbe edilmiş kadmiyum iyonlarının elüsyonu, 1.0 mol L⁻¹ HNO₃'ün 0.3 mL'si kullanılarak sağlandı. Adsorpsiyon kapasitesinin 90.3 mg g⁻¹ olduğu bulundu. Ön konsantrasyon faktörü ve arttırma faktörü sırasıyla 100 ve 88 olarak bulundu. Tespit limiti (LOD), miktar belirleme limiti (LOQ) ve doğrusal aralık sırasıyla 0.6 µg L⁻¹, 2.0 µg L⁻¹ ve 2-40 µg L⁻¹ olarak bulundu. Gün içi ve günler arası RSD değerleri sırasıyla 1.88 % ve 1.98 % olarak bulundu. Tüm parametrelerin optimizasyonu için faktöriyel tasarım kullanıldı. Yöntemin doğruluğu, standart referans materyalleri analiz edilerek gerçekleştirildi. Optimizasyonu yapılan yöntem başarıyla su ve gıda örneklerine uygulandı.

Anahtar Kelimeler: FAAS, magnetik adsorbent, kadmiyum, katı fazlı mikroekstraksiyon, su ve gıda örnekleri

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ICONS AND ABBREVIATIONS

<u>ICONS</u>	<u>Description</u>
g.cm^{-3}	gram per cubic centimeter
$^{\circ}\text{C}$	Celsius degree
$^{\circ}\text{F}$	Fahrenheit degree
K	Kelvin degree
mmHg	millimeter per mercury
$\text{\AA}$	Angstrom unit
ppm	part per million
mM	milli molar
mg.kg^{-1}	milligram per kilogram
μL	micro liter
nm	nano meter
Kcal/mol	Kilo calories per mol
mol/g	mol per gram
$\text{M}\Omega.\text{cm}^{-1}$	Mega ohm per centimeter
ml	milli liter
ng.L^{-1}	nanogram per liter
g/ml	gram per milli liter
rpm	revolutions per minute

Abbreviations

Descripton

CCB(VXC-72)

Conductive carbon black (Vulcan XC-72)

FAAS

Flame atomic absorption spectrometry

ICP-MS

Inductively coupled plasma mass spectrometry

SPME

Solid phase microextraction

UV radiation

Ultraviolet radiation

SOM

Soil organic matter

WHO

World Health Organization

EU

European union

IARC

International agency for research on cancer

USEPA

United States Environmental Protection Agency

ROS

Reactive oxygen species

MTs

Metallothioneins

CSCs

Cancer stem cells

PTH

Parathyroid hormone

HCL

Hallow cathode lamp

LPME

Liquid phase microextraction

PDMS

Polydimethylsiloxane

PEG

Polyethylene glycol

PA

Polyacrylate

EDTA

Ethylene diamine tetra acetic acid

NIST-SRM

National Institute of Standard and Technology-standard reference material

PAH

Polycyclic aromatic hydrocarbon

DVB

divinyl benzene

NPs

Nanoparticles

1. INTRODUCTION

Despite the long history of heavy metals as recognized human poisons, the issue of heavy metal toxicity remains broad due to the wide variety of ways in which these substances may damage human health (Mehrandish et al., 2019). As the rate of population and human activity rises significantly in many regions across the worldwide, the toxicity of heavy metals poses an increasing danger. The wide range of applications for these pollutants in agriculture, industry, technology, and medicine has dramatically increased their environmental disposal. According to reports, heavy metals are the primary environmental pollutants (Pandey, 2016). Heavy metals can be described as a group of metals that have been linked to contamination and toxicity (Duruibe et al., 2007a). Chemically, these transition elements with a specific gravity of more than 5.0 g cm^{-3} include Fe, Cu, Co, Cr, Hg, Mn, Mo, Ni, Pb, Ag, Au, V, Zn, Ti, Ar, Bi, Cd, No, Pt, Sb, U and Zr (Huamain et al., 1999). In an environment, some heavy metals in trace amounts can serve as micronutrients that plants need, while living in a polluted environment that contains elevated amounts of heavy metals can cause plants to collect heavy metals in high quantities (Sauerbeck & Helal, 1990; Voutsas et al., 1996).

During the past century, industrialization has been growing rapidly. As a result, there is now a greater demand for the reckless exploitation of earth's natural resources, making environmental degradation a global issue (Pathania, n.d.). Human activities are the primary cause of pollution, and one consequence is the development of heavy metal contamination. The primary causes of this problem are metal-dependent operations (such as foundries, mining, and smelting) and the leaching of metals from numerous sources (such as trash cans, waste products, waste dumps, runoffs, vehicles, and construction). A secondary cause of heavy metal contamination has been the use of heavy metals in agriculture, which includes herbicides, insecticides, fertilizers, and other chemicals (Duruibe et al., 2007b). Additionally, natural factors such as volcanic eruptions, rusting of metals, metal evaporation from soil and water, sediment re-suspension, soil erosion, as well as geological weathering can contribute to the rise of heavy metal pollution (Briffa et al., 2020; Li et al., 2022). Extreme levels of these metals in food have been linked to various illness etiologies, particularly those that affect the neurological system, the kidneys, the heart, and the bones. The distribution of heavy metals into the environment may occur through various activities and channels, including combustion, extraction, and processing of the metals, surface water runoff, and releases from storage and transportation, and soil, and

therefore into groundwater and crops (Järup, 2003). Due to their toxicity and cumulative behavior, heavy metals are a major environmental hazard. One of the most extensively utilized heavy metals in industrial processes is cadmium since these metals have been used in different industrial processes (Godt et al., 2006).

1.1 Objective of the thesis

The objective of this dissertation was to develop efficient and sensitive analytical techniques based on green chemistry principles for detecting and quantifying cadmium metal in foods and drinking samples purchased from the market in (Tokat City, Turkey) using flame atomic absorption spectrometry (FAAS) and to evaluate the highest level of concentration found in environmental samples in order to identify pollution and the presence of these dangerous substances in order to lower the emission of these hazardous metals into the environment. Due to structural flaws and matrix effects caused by the complex structure of actual samples, FAAS systems do not have the sensitivity to directly determine target analytes at trace levels. Improving FAAS sensitivity was the goal instead of purchasing more sensitive and costly equipment like ICP-OES. In order to achieve this objective, various extraction techniques have been invented to remove the target analytes from the complex matrix medium and preconcentrate them in the appropriate concentrations.

The development of solid phase microextraction (SPME) methodologies for extracting and concentrating trace amounts of cadmium in environmental samples involved the preparation of a highly effective sorbent with a strong affinity for absorbing cadmium under specific conditions. This was achieved via parameter optimization, including pH, adsorbent amount, extraction time, and sample volume. Additionally, the solid phase microextraction (SPME) technique is used prior to its application to an actual sample, followed by determination using FAAS. The suggested approaches could be used as alternatives for FAAS in determining cadmium elements, hence avoiding the need for expensive equipment with significant acquisition and operating expenses.

1.2 Hypothesis

The primary hypothesis of the thesis is expected to be that a new technique called solid-phase microextraction with a new magnetic biosorbent composite could potentially be used to achieve the separation and extraction of trace cadmium ions in environmental matrices samples prior to their spectrometric detection. This can be achieved before the metals are actually determined by FAAS. The use of the procedures that have been developed will make it possible to conduct precise measurements of the cadmium ion concentrations in environmental samples. Furthermore, the removal of the ions matrix was a significant contributor to the reduction of matrix effects, which finally resulted in an improvement in sensitivity and accuracy. The proposed techniques were used to minimize the influence of both organic and inorganic matrix constituents on the signal of the analytes, as well as to concentrate them to levels that can be detected and measured by the instrument. The procedures used corresponded with eco-friendly methods, which aim to avoid the use of harmful organic solvents and instead apply environmentally friendly extraction solvents.

2. LITERATURE REVIEW

2.1 Cadmium

Cadmium has atomic number 48 with an electron configuration $[\text{Kr}] 4d^{10}5s^2$. Burning cadmium in the air produces brownish amorphous cadmium oxide (CdO); cadmium oxide dissolves in acid and ammonium salts while it's insoluble in alkali water. When cadmium reacts with nitric acid, hydrochloric acid, and sulfuric acid produces cadmium nitrate $\text{Cd}(\text{NO}_3)_2$, CdCl_2 , and CdSO_4 . Cadmium nitrate $[\text{Cd}(\text{NO}_3)_2]$ is a white solid that can be dissolved in water, ethanol, and acetone, and it is also soluble in diethyl ether.

Commercial cadmium chloride is a combination of hydrates that is soluble in water and acetone, slightly soluble in methanol and ethanol, and insoluble in diethyl ether. It appears as tiny rhombohedral or hexagonal crystals that range in color from colorless to white. Cadmium sulfate crystallizes as colorless to white orthorhombic crystals and is soluble in water but insoluble in ethanol, acetone, and ammonia. (Atsdr, 2012; Saini & Dhaniala, 2020). This element that occurs between zinc and mercury has a deformed, hexagonal, close-packed crystal structure and has an oxidation state in most compounds is +2, while some have been observed to have a +1 oxidation state. Cadmium has eight naturally occurring isotopes, with masses ranging from 106 to 116. In addition, cadmium will easily combine with the halogens selenium, sulfur, phosphorus, and tellurium to generate stable compounds. Cadmium is most frequently found in complex copper-lead-zinc ores, zinc ores, and lead ores that contain zinc, where it typically takes the form of an isomorphic impurity in the zinc mineral sphalerite (ZnS). Because of this, cadmium is virtually always recovered as a byproduct from the processing of zinc, lead, and copper ores. Since it is water-insoluble and inflammable, Cd is employed as a protective plate that resists corrosion (Carballo et al., 2013; Genchi, Sinicropi, et al., 2020a).

Cadmium concentration in the earth's crust is 0.15 ppm, moreover, greenockite (CdS) is the most common form of the cadmium mineral. (Sharma & Rawal, 2015). Other elements of cadmium are released into the environment from natural activities, such as volcanic eruptions, forest fires, wind-blown dust, and sea spray are among the natural sources of cadmium and may also participate in the distribution and enter soil, water, and air in which contaminate and enter to the human body through eating or drinking contaminated food and water. Cadmium exists in various kinds of rock, igneous and metamorphic, and sediment rock; phosphorite rock

contains a high amount of cadmium since a substitution occurs between Cd^{2+} and Ca^{2+} , which have similar ionic radii (Zachara et al., 1991). Conversely, Zinc, lead, and copper ores, which are mostly made up of sulfides and oxides, typically have high Cd concentrations (Bi et al., 2006).

Cadmium emissions from volcano eruptions and forest fires are two other important natural sources. Every year, volcanic activity emits around 820 metric tonnes of cadmium into the atmosphere, while forest fires emit up to 70 metric tonnes (Hayat et al., 2018).

Cadmium production and consumption have significantly increased in the majority of industrialized countries over the second part of this century. A major industrial application for cadmium is found in the non-ferrous metal sector. Due to its unique chemical and physical properties, such as its high corrosion resistance, low melting point, excellent electrical conductivity, excellent resistance of cadmium compounds to chemicals and high temperatures, and production of intense colorings (Cd pigments) in the shades of yellow to red, cadmium is widely used in special alloys, dyes, coating stabilizers, as well as for the majority (almost 70% of its use), rechargeable nickel-cadmium batteries (Genchi, Carocci, et al., 2020; Rahimzadeh et al., 2017). Due to these uses, cadmium is released into the environment, including 70% of atmospheric emissions, liquid effluents and wastewater, sludge, and solid waste.

The application of an electroplating technique incorporates the electrodeposition of a thin metal over another metal; during this process, metal is dissolved and deposited at the anode and cathode while electricity flows through an electrolytic bath. One of the primary sources of metal ions contaminating the environment is wastewater produced during electroplating (Rajoria et al., 2022a). Since the first mention of its cyanide plating solution in 1849, cadmium coating has been used as a sacrificial protective layer on steel surfaces (Wang & Chang, 2018). In cadmium electroplating, cyanides are the most significant complexing ions; a cadmium-cyanide bath has the ability to give a dense, fine-grained deposit that may be made highly shiny and bright (Koby et al., 2010) despite its toxicity and high cost, cadmium plating is favored because it can provide many basic metals, particularly iron and steel, a corrosion-resistant covering with a beautiful appearance. Cadmium is primarily used as thin coatings because of its comparatively high cost. Common outside usage includes those for aircraft, ships, and the military. Because it is simple to solder and has low contact resistance, Cd-plate is used on steel and other metals in the electrical sector.

To reduce galvanic corrosion, cadmium plating is frequently applied to sections of assemblies made of metals other than brass and steel (Islamoglu et al., 2006). It has been documented that these emissions have negative effects on land, water, and the atmosphere. Chemical fertilizers of the superphosphate group can pollute the soil, depending on their level of purification, and they contain a range between 0.05 and 170 ppm of cadmium. Over the past thirty to forty years, the resulting industrial cadmium emissions have steadily decreased. Because of strict rules and guidelines, especially in the metal industry, and due to the enormous progress in pollution management technologies, cadmium emissions are now strictly regulated. Additionally, the recycling of Cd-bearing products is always improving. Therefore, its transfer to the environment is predicted to continue to decline in the near future. Cadmium is also present as an impurity in other classes of products: nonferrous metals (zinc, lead, and copper), iron and steel, fossil fuels (coal, oil, gas, peat, and wood), cement, and phosphate fertilizers. Cadmium emissions from products with contaminants of cadmium have not been lowered in the same manner as those from industrial Cadmium products during the past few decades, and they continue to be a source of contamination for which additional efforts may be achieved in the future (Cook and Morrow, 1995).

2.2 Environmental pollution of cadmium

For many years, it has been known that the concentrations of specific elements can have either a good or harmful impact on plants and animals. Cadmium is known to be extremely poisonous and can compete with other divalent metals, particularly zinc, which shares chemical similarities with cadmium. Cadmium is not known to serve any useful function for organisms. Cadmium is known to enter the aquatic environment via waste discharge from factories, surface drainage, and the deposition of cadmium, which is also highly absorbed into sediments and soils. This is a well-known fact. The use of phosphate fertilizers, the burning of coal, iron alloys, stainless steel, and cement, and household trash disposal are all examples of human activities that contribute to the release of cadmium into aquatic environments. Furthermore, non-ferrous metal mining is a substantial source of cadmium release into aquatic ecosystems. There are many ways in which cadmium may be taken into the body, including via food consumption, consuming water, smoking cigarettes, or even breathing in contaminated air.

Both anthropogenic sources include smelters, mining, the power station business, and the use of metal-containing fertilizers, pesticides, and sewage sludge. and natural sources led to the distribution of cadmium in soil and absorbed by plants and microorganisms. According to estimates, the amount of cadmium from anthropogenic sources in the soil exceeds the amount from natural sources. Agricultural soils could be permanently harmed by soils contaminated with cadmium (Dokmeci et al., 2009; M. Wang et al., 2021). The cadmium adsorption behavior in the soil differs depending on the soil type and is influenced by soil characteristics like pH, soil organic matter (SOM), ion exchange capacity, and clay concentration. High cadmium levels are mostly linked to the soil's granulometric properties and proximity to major traffic routes. Acidic soil pH is thought to be the most significant factor affecting how much cadmium is absorbed by crops.

Another factor that can prevent cadmium from being absorbed from the soil solution is the existence of organic materials in the soil. The presence of organic and inorganic materials can impact the mobility and bioavailability of metals. To decrease the mobility and bioavailability of metals, it is usually advised to add organic-rich materials like compost, sawdust, tree bark, or granulated or powdered lignite (Zwolak et al., 2019). Due to cadmium's chemical stability, only a small fraction of the metal that enters the soil is absorbed by the soil medium. The rest is transported and transforms the soil environment, leading to the contamination of the soil with cadmium. Plants absorb significant amounts of cadmium from contaminated soil, and when animals of various species consume the edible parts of these plants, the metal enters the food chain (Wang et al., 2022). The bioaccumulation of cadmium in crops and its potential dangers to human health through the food chain have made a global concern to control the accumulation of Cadmium in whole grains; the continuous application of pig manures for 10 years was also seen to increase the amount of cadmium in the subsurface layers dramatically. Furthermore, because aggregates are the fundamental building block of soil and a crucial site for chemical and biological reaction activities, the size distribution of soil aggregates may significantly impact the availability of Cadmium (Rao et al., 2018). The adsorption and desorption processes of cadmium that take place in the soil are extremely important processes responsible for regulating the quantity of cadmium present in soil environments. The movement, transformation, bioavailability, and ecotoxicity of the element in soil-plant systems are all directly impacted as a result of this, which in turn has an effect on the quality of agricultural products and the environment. Therefore, research on the adsorption and desorption properties

of cadmium is very significant in the practical aspect. This is because an understanding of the ability to regulate and predict the behavior of cadmium in the soil-plant system will be required. (F. Wang et al., 2022) . It is crucial to comprehend the migration and distribution of cadmium in different types of soils to effectively avoid cadmium contamination on farms with low to medium yields, minimize the buildup of cadmium in the food chain during migration, and promote sustainable agricultural growth (Y. Li et al., 2020).

The value of water to the ecosystem is now widely acknowledged on a global scale. The significant environmental load is increasing as a result of water contamination and shortages, and natural water sources are disappearing as a result of this trend (Rajoria et al., 2022b). Water contamination, often known as water pollution, occurs when foreign substances contaminate water, lowering its quality. Water pollution includes all types of liquid pollution, such as that found in rivers and the ocean; also, liquid pollution occurs in lakes, streams, groundwater, and bays. According to the water cycle, water will naturally be absorbed by the soil around us, flow through rivers from upstream to downstream, and then be released into the sea (Verma & Dwivedi, 2013). Numerous industrial processes, including electrolysis, electroplating, metal smelting, and chemical pollutants in the environment, are responsible for the accumulation of cadmium in water (Saleh et al., 2022). On the other hand, forest fires, rock mineral weathering caused by geological processes, and lava flows from volcanic activity that occurs over land and deep water produce around 60% of the total natural discharge that is released into the environment; as a result, mixing with water bodies increases with surface runoff (Chrastný et al., 2015). Various anthropogenic and natural variables could impact the chemical composition of surface water and sediment, upsetting the equilibrium of pollutants in the water and sediment system. Particularly, sediment contamination causes great worry since it is a storage of cadmium and other heavy metals, and could be a secondary source of contamination. Cadmium associated with sediment could be harmful to aquatic life and could leak into the water column in the event of disturbance or acidity (X. M. Zhao et al., 2018). Depending on the fact that the solubility of cadmium in water is highly dependent on pH, an environment that is more acidic dissolves more than a medium that is more alkaline. (Honma et al., 2016). The already contaminated sea bed sediments have also undergone severe disruption due to increased dredging, reclamation, and site development activities. As a result of these actions, these activities may expose anoxic sediments to oxic conditions. Metals in sediments may remobilize due to changing environmental factors like redox potential (Choi et al., 2006). The presence of

cadmium, even in trace amounts, is extremely poisonous and non-essential. Additionally, it may remain for a very long time and accumulate in living organisms (Siswoyo et al., 2019). Chronologically, cadmium toxicity in aquatic creatures inhibits the development of the immunological, endocrine, and reproductive systems, as well as growth and reproduction. The general public has been warned that cadmium exposure may be higher in areas where shellfish and fish meat are frequently consumed by people (Ali et al., 2013). Due to the health dangers involved with using groundwater as drinking water, groundwater contamination has become a serious problem (Ab Razak et al., 2015). The corrosion of galvanized water supply pipes, the use of utensils with paint coatings, or water storage tanks that are mostly plated with Cadmium and Zn all contributed to a rise in the level of cadmium pollution in drinking water. Also, leachate from landfills, which is formed from municipal garbage, industrial waste used to manufacture cadmium, or other waste products from the processing of metals, is another factor contaminating drinking water (Abd El-Salam & Abu-Zuid, 2015; Salehi et al., 2017). The corrosion of galvanized steel roofs was found to cause higher levels of cadmium contamination in rainwater than cemented or Al-Zn-coated steel roofs. Similarly, constructing catchment and storage tanks also contributes to Cd pollution of rainwater (Asiima et al., 2015; St-Hilaire et al., 2016). The World Health Organization (WHO) set a permitted limit for Cadmium ions in drinking water of 0.003mg.L^{-1} due to the harm that cadmium species can cause (Vikrant et al., 2019).

2.3 Toxicity of cadmium and its impacts on organisms

The enormous industrialization of recent years has resulted in increased soil, water, and air pollution. Cadmium pollution has created an increase in sudden environmental pollution occurrences, causing high concentrations of cadmium to enter the environment quickly and cause significant harm. The most significant aspect of cadmium toxicity is that it is not biodegradable and has long-term consequences on food safety, necessitating urgent remediation measures.

Cadmium toxicity is related to the release of cadmium into the environment from both artificial and natural sources into the atmosphere, soil, and water. Cadmium then enters the food chain and becomes consumed by people and other species, causing various disorders in living things and harming the environment. Since cadmium has no function for organisms, a trace amount of cadmium could be toxic and harmful. Cadmium has been classified as a Category 1B, Group

1, and Class B hazardous metal by the European Union (EU), the International Agency for Research on Cancer (IARC), and the United States Environmental Protection Agency (USEPA), respectively. Subsequently, bringing Cadmium toxicity to the attention of researchers; since cadmium tends to accumulate in the body, even small quantities of continuous contact can have a negative impact on human health (Maddela et al., 2020; D. Zhao et al., 2023). when cadmium gets absorbed by humans, it accumulates during their lifetimes. It accumulates in the body, primarily in the liver and kidney, interacts with tissue proteins that contain sulfhydryl groups (-SH), and biochemically replaces zinc, causing hypertension and liver and kidney damage. Hepatotoxic and nephrotoxic agents like cadmium are widely known. Small amounts of cadmium can damage the proximal renal tubules of the human kidney, resulting in renal disease (Bhattacharya, 2018). Cadmium primarily accumulates in the liver, where its metallothioneins can interact with the metal to form CdMT complexes. The functions of MTs, which are present in the blood, urine, plasma, liver, and kidney, include transporting metals, detoxifying the body, and scavenging free radicals (Genchi, Sinicropi, et al., 2020b; Nordberg & Nordberg, 2022). Cadmium may damage cells by creating reactive oxygen species (ROS), which induce oxidative stress and toxicity. Too much ROS may produce oxidative stress, which damages single-strand DNA and disrupts protein and nucleic acid synthesis (Ebrahimi et al., 2020), generating cancer cells in different organs in the human body.

In plants, a trace amount of cadmium enters the body through water absorption and stomata, leading to plant hyperaccumulation due to soil bioavailability of cadmium. This can interfere with the intake of essential minerals, causing signs like leaf chlorosis and decreased photosynthetic rate. High cadmium concentrations can cause growth retardation, leaf chlorosis, water balance disturbance, and damage to photosynthesis machinery (Shaari et al., 2024). Cytoplasmic enzymes are sensitive to high cadmium concentrations, and cadmium poisoning can replace zinc-sensing molecules. Cadmium stress also lowers chlorophyll concentration, preventing photosynthesis and reducing nitrate absorption (Adil et al., 2020; Huybrechts et al., 2019; Manzoor et al., 2021; Perez-Millan et al., 2021). Animals and humans primarily get cadmium from green plants consumed by herbivores and then transferred to carnivore animals. Animals can be exposed to cadmium pollution through air, food, and contaminated water, and it accumulates in their body and with long-term consumption increases the risk of cancer and other body disorders (Khafaga et al., 2019; Njoga et al., 2021).

2.4 Separation and preconcentration methods

Due to the fact that several industrial, environmental, and medicinal contexts require their research, the capability to identify trace-level elements is an essential component of the process of extraction and enrichment. A growing number of people are starting to recognize the significance of trace element analysis as the harmful effects of these elements on ecosystems and human health become more apparent. Food, drink, and other products for consumption must undergo trace element monitoring since certain elements could potentially harm the health of individuals. If we want to know where pollution comes from and how to stop it, we must analyze trace elements. Finally, in this field, analytical chemistry is attracting the attention of researchers who are trying to understand and control pollution levels caused by many things, including natural disasters, industrial processes, and others (Makoś et al., 2020; Tewari, 2002). The development of standards and maintaining a level of quality control are two additional important functions of these types of studies. The use of instrumental analytical techniques is favored since the direct identification of trace elements is often difficult to perform. It is not only associated with lower sensitivity but also with the matrix in which the analyte exists. Thus, it is necessary to begin by separating the trace element from the matrix environment and then enriching it (Mendil et al., 2010; Tuzen & Soylak, 2006).

Trace element analyses involve the examination of trace elements within an environment called the matrix, this environment contains the sample's main components. There are a variety of elements that might make up the matrix environment, including metals, minerals, chemicals, water, aqueous solutions, and organic and biological components (Antoniadis et al., 2019). Analytical measuring instruments with high selectivity and sensitivity have been created in order to meet the requirements of this situation. These devices include (FAAS, ICP-OES, ICP-MS, GFAAS, and others. In this case, it is important to design procedures that are sensitive, accurate, and rapid in the quantitative and qualitative analysis of matrices (Sun et al., 2018). Analytical devices, even though very sensitive analytical measuring instruments have been produced, are often insufficient and poor when it comes to determination in matrix issues. Accurate, sensitive, and repeatable results in trace analyses depend on both the suitability of the measurement method and the sample preparation method. The sample preparation method should avoid contamination and analyte loss while fully converting the analyte into a measurable form. In such a case, a highly accurate and reliable measurement may be obtained by enhancing selectivity and ensuring the separation of the analyte from the surrounding matrix

(Oviedo et al., 2021). Additionally, increasing the detection limit can be achieved by concentrating the analyte previously. Pretreatment is frequently necessary to concentrate (enrich) and extract (separate) analytes from matrix environments (Lemos et al., 2019).

In research involving trace elements analysis, the separation approach is often used in three different methods. The first one includes the process of separating trace elements from a solid or dissolved sample while the major component remains in the solution; this is known as micro-macro separation. When the main component is removed from the sample, and the trace elements stay in the solution, this process is referred to as macro-micro separation. On the other hand, the technique of separating trace elements from each other is known as micro-micro separation. The first application is particularly commonly employed in trace element analysis. The process of group separation of trace elements is frequently employed in atomic emission and absorption spectrometry analyses. If there is interference between trace components, such as spectral interference, it may be necessary to separate the trace elements from each other (Sarafraz-Yazdi & Amiri, 2010; Yamini et al., 2019). The pre-treatment process involves moving the trace elements to a different platform and extracting them in smaller quantities using techniques referred to as the enrichment process. The application of enrichment and extraction techniques in trace element analysis offers the following advantages in the determination processes:

- The method's detection limits get improved by rising trace element concentrations.
- The method's sensitivity is enhanced since the effect of the environment is avoided by placing trace components in a suitable environment.
- Ground interference reduces due to substituting the matrix, which is known to cause disruptions, with an appropriate matrix.
- The enrichment technique increases the selectivity of the method (Sajid & Płotka-Wasyłka, 2018a).

The inclusion of trace elements in the known matrix during separation procedures makes it simpler to compare the sample matrix with standard solutions. The process of enriching trace elements involves a variety of methods, including adsorption on solid surfaces, electrolytic deposition, co-precipitation and volatilization enrichment, ion exchange, solid-liquid

extraction, and liquid-liquid extraction. Several research has investigated the process of enriching certain heavy metals at low concentrations utilizing the extraction technique (Hagarová & Nemček, 2021; Oviedo et al., 2021). Out of all the techniques available, the extraction technique is considered one of the oldest procedures used in chemistry for separating substances. Extraction is a chemical procedure in which a component is transferred from one liquid phase to another liquid phase that is immiscible with the first phase.

The extraction procedure used in trace element analysis typically involves two phases: water and an organic solvent that is insoluble in water. Alternatively, one solvent may exhibit polar characteristics while the other solvent has less polarity (Rahman et al., 2013). This approach is highly regarded among the enrichment methods used in trace analysis for its simplicity, speed, and versatility. It is often used in atomic absorption spectrometry measurements for solution analysis. Still, the commonly used solid phase extraction approach and other methods are characterized by their time-consuming nature, complicated extraction stages, and the need for substantial quantities of waste (Sajid & Płotka-Wasyłka, 2018a).

These procedures need the use of materials and solvents, which might be harmful to the health of people working in laboratories. The current situation, which is not favorable, has led to a growing interest in microextraction methods in the 21st century. These methods aim to reduce the use of organic solvents, enable automation, simplify extraction steps, enhance enrichment, protect the environment, and eliminate additional waste costs (Pacheco-Fernández & Pino, 2019; Płotka-Wasyłka et al., 2017). Using microextraction techniques, studies have been conducted in the following fields: geology, environmental science, electronics, pharmacology, air pollution, and human and animal health. In many diverse domains, such as soil contamination, water pollution, plant health, criminology, and archeology, it is not taken into consideration (Farajzadeh et al., 2020).

2.5 Microextraction method

Despite the fact that they are widely used and universally applicable, the two sample preparation procedures that were stated before (LLE and SPE) each have their own set of limitations. These include difficulties related to automation, significant waste production, high volume of sample requirements, and the consumption of toxic organic solvents. These drawbacks make these methods time-consuming, nonfriend with the environment, and

expensive as well (Płotka-Wasyłka et al., 2016; Sajid & Płotka-Wasyłka, 2018b). Microextraction techniques were employed to deal with these drawbacks. The microextraction techniques are essentially derived from the simplification of the two basic extraction methods. Recent years have seen a number of efforts aimed at developing novel and environmentally friendly procedures that provide greater benefits than traditional extraction methods. These advantages include lower chemical consumption, higher extraction efficiency, cheap cost, as well as rapid analysis (Yan et al., 2014). Microextraction methods may be primarily classified into two main groups: solid-phase microextraction (SPME) and liquid-phase microextraction (LPME) (Jalili et al., 2020b).

2.5.1 Liquid phase microextraction (LPME)

To overcome the drawbacks of traditional LLE that have already been mentioned, many LPME methods have been developed and put into effect in recent times. LPME is a technique for pre-treating samples that is capable of extracting an extensive range of analytes from various samples using a minimal quantity of extraction eluent (acceptor phase), typically in the (μ L) range (Hashemi et al., 2017; Rutkowska et al., 2019). One of the most flexible sample pre-treatment techniques is known as liquid phase microextraction (LPME), which may be used with various mixing procedures and instruments. The flexibility of the method allows for modifications that can enhance the environmental friendliness and extraction efficacy of the methods. By providing a sufficient analyte enhancement when paired with devices that are substantially less sensitive, it enables the identification of analytes at trace levels (Chormey et al., 2020).

In the past several years, researchers have focused their efforts on the development of novel solvents that can be utilized in LPME procedures in accordance with the principles of green chemistry. Although the most optimal approach is to produce extraction techniques that are completely free of solvents, it still to be very optimistic (Armenta et al., 2015; Carabajal et al., 2020). The most commonly favored LPME methods include single-drop microextraction (SDME) (Kailasa et al., 2021), dispersive liquid-liquid microextraction (DLLME) (Carabajal et al., 2021; Jamali et al., 2023), solidified floating organic drop microextraction (SFODME) (Hussein et al., 2023), switchable solvent liquid phase microextraction (SS-LPME) (Musarurwa & Tavengwa, 2021; Santos et al., 2024), hollow fiber-based liquid phase

microextraction (HF-LPME) (Moret et al., 2023; Pinto et al., 2023), and cloud-point microextraction (CPME) (Abd Wannas et al., 2023; ANZUM et al., 2022) .

2.5.2 Solid phase microextraction (SPME)

Arthur and Pawliszyn initially described the solid phase microextraction method SPME in 1990. Today, the technique is widely used, and there are increasingly more new articles describing it. The initial investigations were conducted using optical fibers constructed of fused silica or coated with a polyimide stationary phase (Prosen & Zupančič-Kralj, 1999). SPME can be employed for aqueous or gaseous samples. Analytes are distributed across the sample matrix and the stationary phase in both situations. A separation factor, or partition coefficient (K), is calculated by dividing the concentration of the analyte in the stationary phase by the concentration of the analyte in the sample:

$$K = C_f / C_s$$

C_f represents the analyte concentration in the stationary phase, while C_s represents the analyte concentration in the sample.

Solid phase microextraction (SPME) is a novel, non-exhaustive sample preparation method that combines sampling, preconcentration, and extraction into a single step. The analytes that have been retained can afterward be quickly introduced to analytical instruments like chromatographic systems. (Jalili et al., 2020a). Traditional SPE uses higher quantities of extraction phases, whereas SPME is a solvent-free sample preparation method that is usually believed to deliver high sensitivities by minimizing extracting most of the extracted analytes directly into the analytical instrument (Peng et al., 2022). A wide range of concentrations and analytes can be measured using SPME, which is comparatively easy to use, quick, solvent-free, sensitive, and produces linear findings. For the SPME technique to be successfully used in a variety of situations, a strong sorbent must be chosen appropriately (Delińska et al., 2021). SPME operational modes selection, depending on the nature of the investigation, include direct immersion solid phase microextraction (DI-SPME) (Yang et al., 2021a), headspace solid phase microextraction (HS-SPME) (Lancioni et al., 2022), and hollow fiber membrane-protected solid phase microextraction (HFM-SPME) (Asadi & Maddah, 2022). Another classification is based on the shape of the adsorbent, such as thin film microextraction (TF-

ME) (Mahmoudian et al., 2023), fiber-in-tube solid phase microextraction (Fiber-in-tube SPME) (Souza et al., 2021). Among the commonly used commercial sorbents are polydimethylsiloxane (PDMS), polyethylene glycol (PEG), polyacrylate (PA), divinylbenzene (DVB), carboxy (CAR), and their composites. Instability, peeling, and low operating temperatures are issues with them. Aside from carbon-based materials, metal oxides, molecularly imprinted polymers, ionic liquids, monoliths, and metal-organic frameworks have also been investigated as SPME sorbents (Hussain et al., 2020).

Many effective extraction coatings have been studied, including those made of nanomaterials, mesoporous materials, carbon nanotubes (CNTs), graphene, ionic liquids, aerogels, covalent organic frameworks (COFs), metal-organic frameworks (MOFs), and others. To some extent, the appearance of these coatings compensates for the short life and poor selectivity of commercial coatings, and the development of extractive coatings with strong selectivity and high enrichment efficiency has always been a research emphasis in the SPME sector. (Feng et al., 2021). Many different adsorbents have been reported for extracting heavy metals using solid-based extraction methods since traditional adsorbents are used. However, they don't produce sufficient results. Including silica fiber coated with poly (dimethylsiloxane), polypropylene microporous membrane, polyhydroxybutyrate-b-polyethyleneglycol block copolymer, and aminothiazole-containing sulfonamide resin (W. A. Khan et al., 2020). Additionally, Nanoparticles (NPs) can be utilized as sorbents for a successful SPME of numerous analytes in various environmental sample types. NPs have emerged as a possible substitute for conventional materials for SPME of analytes from environmental samples, which frequently need time-consuming and expensive methods due to their special characteristics of small size, broad surface area, and high catalytic activity. Due to their exceptional catalytic activity, strong magnetism, and high specific surface area, Fe_3O_4 magnetic nanoparticles (Fe_3O_4 MNPs) have sparked widespread attention (Murtada, 2020).

Nanofibers with diameters less than 100 nm provide a broad range of environmental applications because of their high porosity and great surface-to-volume ratio. They're frequently utilized in solid-phase microextraction (SPME) procedures to extract target substances from ambient water samples. Many nanofibers have been created for SPME analysis, including polyaniline functionalized basalt fiber, poly(dimethylsiloxane)-coated carbon nanofibers, and polyurethane nanofibers. These nanofibers have been shown to extract UV filters, polycyclic aromatic hydrocarbons (PAHs), chlorobenzenes, pesticides, phenolic

chemicals, and other analytes. The incorporation of nanofibers into SPME procedures improves efficiency and sensitivity, making them valuable environmental analysis tools (Pereao et al., 2019).

In the field of SPME, a novel adsorbent has been used for the microextraction of heavy metals; these include using biological biomass such as dead bacteria or fungus after being modified and applied as a biosorbent. Many biosorbents, such as magnetic biochar (Trakal et al., 2016), *Bacillus cereus* RC-1 immobilized magnetic biochar (Deng et al., 2022), maghemite coated *Bacillus subtilis* (Devatha & S, 2020), mango seed (Q. Wang et al., 2022), nutshells (Dias et al., 2021) These kinds of adsorbents are preferred because of their various advantages, such as their availability, cheapness, environmental friendliness, ease of preparation, ability to modify, and use for preconcentrating a wide number of heavy metals.

2.6 Biosorption

Biosorption is an environmentally friendly method wherein specified pollutants are passively immobilized by inert biomass from a solution or liquid environment (Richards et al., 2019). When referring to their structures, biological materials that are often utilized as adsorbents typically contain functional groups such as carboxyl, phenol, amino, hydroxyl, phosphate, and sulfate. Biomass that has a high concentration of these active groups on its surface is capable of adsorbing positively charged metal ions that are found in the surrounding environment. The word "biosorption" actually refers to a broad category of passive removal activities, including ion exchange, coordination, complexation, physical and chemical adsorption, and chemical precipitation (Beni & Esmaeili, 2020).

These biological materials, which include bacteria, algae, fungi, and agricultural by-products, are examples of biomass that can be employed as adsorbents in biosorption processes. There has been a rise in attention during the duration of recent years in discovering biomass that can be utilized in biosorption processes. The main factor to take into account while choosing these biological materials is their price and availability. Multiple procedures are necessary for biological substances to be utilized as biosorbents in biosorption procedures. Naturally occurring biomass, such as algae, fungi, or bacteria, can be rendered nonviable by subjecting them to acid and/or base solutions, then drying and sieving them to obtain biosorbents. Certain

biosorbents can only be achieved by mechanical methods (such as size reduction, grinding, crushing, and sieving) (Nguyen & Nguyen, 2019; Vijayaraghavan & Balasubramanian, 2015).

When choosing biomass to extract heavy metals using biosorption techniques, the supply must be derived from one of the following options of biosorbent materials, including waste from industrial processes, natural biological materials in abundance, and organisms undergoing fast proliferation and growing in a culture environment for biosorption purposes. The literature reports that the biosorption approach employed for heavy metal removal offers a number of benefits when compared with other methods, including cheapness, effectiveness, and high metal recovery (Beni & Esmaeili, 2020).

Polysaccharides are fundamental building components that make up the structural structure of microorganisms. Extensive studies have been conducted to investigate how natural polysaccharides display ion exchange properties. These qualities facilitate the interaction between divalent metal ions and oppositely charged ions that are present inside these polysaccharides (He et al., 2019; Mi et al., 2015). Friis and Myers found that lead and uranium ions were contained within the cell wall and cytoplasmic fraction of *Streptomyces longwoodensis* during their investigation of the organism's biosorption of these metals. The authors hypothesized that this occurrence is a result of ion exchange between ions with opposite charges in the phosphodiester residues (Friis & Myers-Keith, 1986). This implies that there is an intricate connection between the cell walls of microorganisms and metal ions, which provides a valuable understanding of the possible mechanisms that drive biosorption processes in environmental situations.

2.7 Biosorbents characteristic

The availability of biomass plays a crucial role in choosing which kind of biomass will be used for the purpose of retaining metal ions. Preference should be given to biomass kinds that are easily accessible in nature, especially those present in waste products. While biosorbents have the ability to bind heavy metals randomly, some forms of biosorbents may exhibit selectivity and only bind particular types of metals. The first determinant to consider while choosing biomass for metal biosorption is the source of the biomass. It is recommended to choose microorganisms that may be derived from industrial waste or the environment that has a rapid reproduction rate. Naturally occurring biomass, such as algae, fungus, or bacteria, may be

eliminated by subjecting them to acid and/or base solutions and then drying and sieving them to yield biosorbents (Bilal et al., 2021; Qin et al., 2020).

2.8 Immobilization process of biomass

Immobilizing biomass onto a solid base enables the achievement of the suitable dimensions, mechanical strength, hardness, and porosity essential for using samples in heavy metal removal. Within the area of academic research, a number of different methods for the immobilization of biomass have been extensively described (X. Wen et al., 2018).

Additional inoculum is added to the support material after the original culture has been inoculated and sterilized. This inoculum is then allowed to continue in the continuous culture until a layer of microbial film is formed on the support material (Meringer et al., 2021). One method that is often used to immobilize biomass on an inert support material is adsorption. Using this technique, a film layer of biomass is immediately adsorbed onto the support material. This film layer creates an ideal condition for the presence of biological reactions. It is possible to use this method of adsorption in a wide variety of industrial applications since it is a technology that is both flexible and cost-effective.

Nanoparticles are a novel class of technology for environmental remediation that may effectively eliminate harmful contaminants, particularly heavy metals and metalloids. In addition, nanoparticles serve as flexible and adaptable platforms for microbial cells, offering an impressive ratio of surface area to volume (Giese et al., 2020). Magnetic immobilization refers to the process of trapping microbial cells inside magnetic nanoparticles. These cells, once they have been trapped, become sensitive to magnetic fields and may be influenced by applying magnetic fields from external sources. Magnetic separation of biosorbents from groundwater and wastewater flows is the primary use of microbial nano-particles, which are used as a novel approach. (Abdel Maksoud et al., 2020).

2.9 Analytical Performance Studies

One of the fundamental objectives of validation of methods in analytical chemistry methodology is to provide evidence that an analytical technique is appropriate for the application for which it was designed. Consequently, this guarantees the dependability and

precision of the results that received from the procedure. Thus, the validation of a method requires the creation of a number of documents that detail the numerous performance metrics that are necessary for determining the dependability of the technique. A few examples of these characteristics include accuracy, the limit of detection, precision, the limit of quantification, robustness, selectivity, specificity, and sensitivity. In general, method validation is essential to ensure the dependability of analytical procedures. However, the inclusion of conflicting information in validation papers might complicate the process. It is crucial to address these inconsistencies and provide precise instructions to ensure uniformity and precision in the validation of methods across various labs and organizations (Raposo & Ibelli-Bianco, 2020a).

2.9.1 Accuracy

Accuracy is a term that is specifically defined within the framework of validation processes in the field of analytical chemistry. Accuracy measures how well the measured values fit with the real or expected values. Typically, accuracy is evaluated by making many measurements at various concentrations and comparing the observed values obtained from the analytical technique to known or predicted values (Alladio et al., 2020a; Sushila Dagadu Chavan & Deepa Mahendra Desai, 2022). Accuracy can be calculated as follows:

1. Percent recovery: this method employs the comparison, in which the measured value is compared to the value that is known or expected, and the result is expressed as a percentage (Kumar et al., 2021). The accurate method yields ideally 100 % :

$$\text{Recovery\%} = \text{Measured value} / \text{True value} \times 100$$

2. Bias: The difference between the average value that was measured and the actual value is what is meant to be measured by bias. A calculation of the intra-day accuracy may be performed using the three replicates that are assessed on each validation day. Additionally, the assessment of the inter-day accuracy can be performed using the 12-day period that is included in the overall validation method (Alladio et al., 2020b). When the bias is zero, it shows that the accuracy is ideal; calculating it may be done using the following formula:

$$\text{Bias} = \text{Measured value} - \text{real value}$$

The other way accuracy of the method can be stated in terms of the percentage of bias, which may be quantified in the following manner:

$$\text{Bias \%} = (1 - \text{real value} / \text{experimental value}) \times 100$$

2.9.2 Precision

The precision of an analytical technique may be described as the degree to which a series of measurements obtained from multiple samplings of the same standardized sample under the prescribed conditions are in close agreement with one another. Precision is often evaluated by repeated examination of validation samples, and it is typically stated in the form of "imprecision" such as absolute standard deviation (S or SD), relative standard deviation (RSD%), coefficient of variation (CV), or variance (S^2), among other statistical measures (Kumar et al., 2021; U. V. et al., 2020). Relative standard deviation can be found by the following equation:

$$\text{RSD\%} = \text{SD} / \text{mean} \times 100$$

It is significant to differ between precision and accuracy, where accuracy is a concept that covers both random and systematic errors, defining the total analytical error. This indicates that accuracy includes both precision, which is associated with random error, and trueness, which is associated with systematic error, in the analytical method (Raposo & Ibelli-Bianco, 2020b). In method validation, inter-day precision (reproducibility) refers to the level of accuracy of measurements conducted on separate days. It involves evaluating results from several days to see how regularly and efficiently the analytical approach performs over time. Meanwhile, intra-day precision (repeatability) is related to the degree of precision in measurements performed within a single day. The process involves assessing the precision and reliability of the analytical method's effectiveness during brief time periods, usually within one day (Gab-Allah et al., 2021; Güzel & Canli, 2020; Perelsonia et al., 2021a).

2.9.3 Limit of detection

The lowest concentration of an analyte that can be consistently identified in the test sample is referred to as the limit of detection (LOD) or the detection limit (DL) (Gegenschatz et al., 2022). Both of these terminologies are used frequently. To determine the LOD (Perelsonia et al., 2021a) we used the slope of the calibration curve (m) and the standard deviation of the response (σ) according to the equation :

$$\text{LOD} = 3 \sigma / m$$

2.9.4 Limit of quantification

Limit of quantitation (LOQ) or quantification limit (QL) is the term used to describe the lowest concentration level at which a measurement is considered to have quantitative significance (Kumar et al., 2021; Perelsonia et al., 2021b) Typically, this is calculated by multiplying the signal-to-noise ratio by tens. Hence, the LOQ is equal to ten times the standard deviation (σ) of the response and the slope (m) of the calibration curve, as provided in the equation :

$$\text{LOQ} = 10 \sigma / m$$

2.9.5 Linearity

The linearity of a technique is a measurement that determines the degree that a calibration plot of response vs concentration matches a straight line. The linearity assessment may be carried out by taking single measurements at several different analyte concentrations. Following that, a linear least-squares regression is used in order to analyse the data. The slope of the plot, the intercept, and the correlation coefficient (r^2) that were obtained as a consequence give the information that is required about linearity (Reçber et al., 2022; U. V. et al., 2020). The presence of a linear range for a certain range indicates a clear relationship between the signal and the concentration of the analyte.

2.9.6 Specificity and selectivity

According to the principles of analytical chemistry, specificity refers to the capability of the analytical technique to identify the analyte of interest from other substances that are present in the sample matrix. To get more specific, the technique should be able to create signals that are unaffected by interference, which will guarantee exact and accurate measurement of the analyte (Raposo & Ibelli-Bianco, 2020b). While selectivity is the capability of an analytical technique to determine and quantify the target analyte regardless of the presence of additional chemicals that interfere with the analysis. Selectivity may be obtained by a variety of techniques, such as the use of certain detection techniques, such as mass spectrometry, or separation techniques, such as chromatography, which separate analytes depending on the physical or chemical qualities that they possess.

3. MATERIALS AND METHOD

3.1 Chemical and reagents

All chemicals in this investigation listed in Table 3.1 were of the highest quality for analytical reagents and were used without further purification. Ultra-pure deionized water (Milli-Q Millipore 18.2 MΩ.cm⁻¹ conductivity) was used for all dilutions. Before being used, every plastic and glassware undergoes a cleaning process by immersing them in a solution of diluted nitric acid in water (1+9) as a solvent, followed by rinsing with filtered water. To prepare calibration standard solutions, 100 mg L⁻¹ of cadmium solution was prepared by diluting from 1000 mg L⁻¹ of cadmium stock solution that was provided by (Merck Darmstadt, Germany) prepared from dissolving cadmium nitrate in 0.5 M nitric acid. During the preparation of stock solutions, high-purity compounds of a variety of elements were used; these stock solutions served as matrix components of the natural water samples and/or created interference effects in flame atomic absorption spectroscopy investigations. During the validation method study, NIST SRM 1570a Spinach Leaves were used as standard reference materials.

As concluded in Table 3.2, a 100 mL buffer solution was made by combining sodium dihydrogen phosphate (Merck Darmstadt, Germany) with a sufficient quantity of (d=1.71 g/mL, 85%) phosphoric acid (Merck Darmstadt, Germany) to reach a pH of 2. The preparation of 100 ml sodium acetate buffers was carried out by adding a sufficient amount of acetic acid (Carlo Erba, Italy) with sodium acetate (Merck, Darmstadt, Germany) solutions, which resulted in the formation of solutions with a pH of 5. For the production of a buffer with a pH of 7, sodium dihydrogen phosphate (Merck, Darmstadt, Germany) and sodium monohydrogen phosphate (Merck, Darmstadt, Germany) are combined in the appropriate amounts. The conductive carbon black CCB(VXC-72), also known as Vulcan XC-72, was acquired from (Nanografi, Turkey). The buffer pH is prepared according to the pK_a value for the weak acid and its salt and calculated according to the Henderson-Hasselbach equation:

$$\text{pH} = \text{pK}_a + \log [A^-] / [HA]$$

where $[A^-]$ refers to the concentration of weak acid salt, $[HA]$ is the concentration of weak acid.

Table 3.1 Chemicals used for the determination of cadmium

Chemical Name	Brand
(Pb) stock standard solution (in 5.0% HNO_3)	Chem-Lab NV, Belgium
Cd stock standard solution (in 0.5 M HNO_3)	Merck, Germany
(Mn, Cu, Cr, Ni,Co,Zn) stock standard solution (in 2.0% HNO_3)	Merck, Germany
Nitric Acid, 65% (HNO_3)	Merck, Germany
Hydrochloric acid, 37% (HCl)	Merck, Germany
Conductive carbon black (Vulcan XC-72)	Nanografi, Turkey
Acetic Acid, 99.9% (CH_3COOH)	CARLO ERBA, Italy
Sodium hydroxide (NaOH)	Sigma-Aldrich, Germany
Sodium Acetate (CH_3COONa)	Merck, Germany
Hydrogen Peroxide, 30% (H_2O_2)	Merck, Germany
NIST SRM 1570a Spinach Leaves	ACROS, Belgium
Disodium hydrogen phosphate (Na_2HPO_4)	Merck, Germany
Sodium dihydrogen phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$)	Merck, Germany
Phosphoric Acid, 85% (H_3PO_4)	Merck, Germany
(Na^+ , Ca^{2+} , K^+ , Mg^{2+} , NH_4^+ , Cl^- , CO_3^{2-} , F^- , I^- , NO_3^- , PO_4^{3-} , SO_4^{2-}) Stock standard solution	Merck, Germany
Iron (III) chloride anhydrous sublimed (FeCl_3)	Riedel-de Haën, France
Iron (II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	Riedel-de Haën, France

Table 3.2 Preparation of buffer solutions

Buffer Solution	Preparation
pH 2.0	245 μ l (14.84M H_3PO_4) + 3.118 g ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) in 100 ml
pH 5.0	8 ml (14.3M CH_3COOH) + 1.296 g (CH_3COONa) in 100 ml
pH 7.0	1.067g ($\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$) + 1.244g ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) in 100 ml

3.2 Apparatus and instrumentation

A flame atomic absorption spectrometer, Perkin Elmer Analyst 700 model (Norwalk, CT, USA), was used to measure the amount of Cd. A deuterium lamp was used to conduct background correction. Table 3.3 displays the hollow cathode lamps (HCL) used in the experiments, along with their respective operating parameters. The other devices used during our experiments research are documented in Table 3.4.

Table 3.3 Conditions for flame atomic absorption spectrometry

Element	Wavelength (nm)	Slit (nm)	Lamp current (mA)	Flow rate of oxidant and fuel	
				Air (L min ⁻¹)	Acetylene (L min ⁻¹)
Cd	228.8	0.7	4	2.0	17.0

Table 3.4 Equipment used in the laboratory for experiments

Laboratory devices	Brand/Model
Analytical balance	Precisa XB 220A SCS
Centrifuge	BIOBASE BKC-TL5II
pH meter	Starter 2100 model (ST2100-F, OHAUS)
Automatic pipette	Eppendorf
Oven	Heraeus D-6450
FT-IR spectrometer	JASCO (FT/IR-4700)
Magnetic mixer hot plate	IKA C-MAG HS7
Orbit shaker	(Multi Bio RS-24 model, Latvia, Biosan) multi-rotator
Vortex	WiseMix (VM-10) Wisd
SEM	JEOL model (jsm-6610)
EDS	OXFORD instrument, UK

3.3 Preparation of the magnetic biosorbent composite

The stages involved in the production of the magnetic biosorbent composite include the magnetizing of conductive carbon black (Vulcan XC-72) CCB(VXC-72). After that, the growth and isolation of *E.coli* bacteria. Finally, a proper procedure was applied to immobilize dead *E.coli* bacteria on magnetic CCB(VXC-72). The immobilized bacteria should be combined with the support material to create a magnetic biosorbent composite. Then, describe the properties and characteristics of the magnetic biosorbent composite and optimize the parameters that influence the microextraction of cadmium. Using batch adsorption studies, assess how well it removes cadmium. Finally, the composite adsorbent can be applied to real

samples such as foods, water, and beverages, and an optimized procedure for the regeneration of the novel adsorbent can be designed in order to reuse the composite and make it recyclable.

3.3.1 Synthesis of magnetic CCB(VXC-72)

The magnetization of our novel adsorbent is accomplished by using a chemical co-precipitation technique that is not only straightforward but also cost-effective. A widely used strategy involves carrying out the steps that include preparing a 400 mL aqueous solution with a molar ratio of 1:2 for ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and ferric chloride (FeCl_3). This solution will act as the first process in generating magnetite (Fe_3O_4) nanoparticles; after that, 3.0 g of CCB(VXC-72) were added. Then, continuously agitate the mixture on a magnetic stirrer hot plate at 85°C to achieve a homogeneous CCB(VXC-72) particle distribution. Applying heat speeds up the chemical reactions in the co-precipitation process, while stirring ensures uniformity and prevents particle aggregation. Then 100 mL of 5 mol. L^{-1} NaOH is added gradually to the mixture that has been heated until the solution turns dark brown. NaOH acts as a precipitating agent, allowing iron ions to chemically co-precipitate to produce magnetite nanoparticles. The dark brown color indicates the formation of magnetite nanoparticles since the CCB(VXC-72) particles become coated with the Fe_3O_4 nanoparticles. After that, we stand the mixture to cool it down to the temperature of the surroundings. A neodymium magnet field is applied to collect the magnetic CCB(VXC-72) particles from the solution. The collected particles have now been coated with magnetite nanoparticles. The accumulated magnetic CCB(VXC-72) particles are washed with distilled water to eliminate contaminants or unreacted substances. Then, to eliminate any remaining moisture, the particles are dried in an oven at around 100°C for one hour. This process was repeated three times. The composite adsorbent that has been dried is then placed in a container that has been sterilized and is prepared for usage at a later time (Duman et al., 2020; Fu et al., 2016; Jagirani et al., 2021a; Silva et al., 2020).

3.3.2 Preparation of *Escherichia coli* (ATCC35218)

The preparation of a nutrient-agar (NA) medium included the combination of 3 g of beef extract, 12 g of agar, 5 g of peptone, and 8 g of NaCl. 28 g of nutrient agar (NA) was added to 1 L of distilled water and boiled until it reached its boiling point. The medium was then

sterilized in an autoclave at a temperature of 121°C and a pressure of 1 atm for a duration of 20 minutes. Following the sterilization process, the medium was cooled to a temperature range of 40-50°C and carefully placed onto Petri plates that had been previously sterilized. *Escherichia coli* (*E. coli*) was introduced into the solid medium and placed in an incubator at a temperature of 36°C for a duration of one day. Subsequently, the bacterial sample was transferred to a flask containing 2000 mL of sterilized liquid media, namely Nutrient Broth. The Nutrient Broth (NB) medium was subjected to incubation in a shaking incubator at a temperature of 36°C for a duration of 48 hours in order to achieve the stationary phase. The *E. coli* bacteria were separated from the solution by centrifugation at 6000 rpm for 10 minutes. The bacterial biomass was dehydrated at a temperature of 50°C in a drying oven, subjected to three washes with 0.1 M hydrochloric acid, rinsed with distilled water, and left to dry for the duration of the night (G. Cheng & Li, 2009; Gupta & Balomajumder, 2015; Khosravi et al., 2020).

3.3.3 Immobilization of *E.coli* bacteria

During the process of immobilizing bacteria, 100 mg of dried *E. coli* biomass was mixed with 300 mg of magnetic CCB(VXC-72) nanoparticles, and the mixture was well mixed. A homogeneous paste was then formed by adding about 2 milliliters of deionized water to the system to make it wet. After that, the paste was dried to a temperature of around 100 °C for two hours in the oven. This process was used to accelerate the drying process. It has been determined that the drying and wetting procedures have been repeated to improve the interaction between *E. coli* and magnetic CCB(VXC-72) and improve immobilization efficiency. After that, the adsorbent was collected and kept at room temperature so that it may be used in our present study (Arghavani et al., 2024a; Rind et al., 2023).

3.4 Characterization and morphology investigation

The surface functional groups of the composite biosorbent were analyzed using FT-IR spectroscopy JASCO (FT/IR-4700) in the range of 500 to 4000 cm⁻¹. The external morphology of the composite after being coated with gold was investigated using a (JSM-6610) SEM manufactured by JEOL, Japan. EDS (OXFORD instrument, UK) was used to collect signal and elemental mapping of the composite.

3.4.1 FT-IR study

The presence of functional groups, which play a crucial role in the biosorption process, was unequivocally confirmed by analyzing the FT-IR spectra of CCB(VXC-72) (A), *E. coli* bacteria (B), magnetic CCB(VXC-72) (C), and magnetic biosorbent composite (D) in the 500–4000 cm^{-1} range Figure 3.1. The FTIR spectra of conductive carbon black Figure 3.1A predominantly exhibit peaks related to carbon-based substances, including characteristics associated with C=C structures, C-H bending and stretching vibrations, and C-C bonds. A bending around 690 cm^{-1} due to C-H out of plane aromatic band. Moreover, in the spectrum of 1750–2500 cm^{-1} , a triple peak indicates the existence of functional groups linked to carbonyl C=O stretching vibrations (Y. Cheng et al., 2020), thereby validating our research findings.

The biomass that is not immobilized in Figure 3.1B has several absorption peaks, which indicate its complex composition. Volesky and Paven study (Quintelas et al., 2009) determined that the primary functional groups involved in the biosorption process include hydroxyl, carbonyl, carboxyl, sulfonate, amide, imidazole, phosphonate, and phosphodiester groups. Some of these groups are found in the biomass of *E. coli*. In all three spectra, wide transmittance bands were found at 3000–3700 cm^{-1} for N-H bond stretching vibrations in the amino group and at 2800–3000 cm^{-1} for O-H and C-H stretching vibrations. Variations in the spectra were seen throughout the range of 700–2000 cm^{-1} .

The significant peaks seen at 1653 and 1540 cm^{-1} in all three spectra were identified as the amide I and amide II bands, respectively. The band seen at 1460 cm^{-1} was assigned to the deformation of O-H bonds in the carboxyl groups, while the bands around 1410 cm^{-1} were assigned to the carboxyl anion. Furthermore, bands located at 1240 and 1075 cm^{-1} were recognized as phosphoric ester and free phosphate groups related to phospholipids, and thus, they were categorized as phosphate groups (Hosomomi et al., 2016).

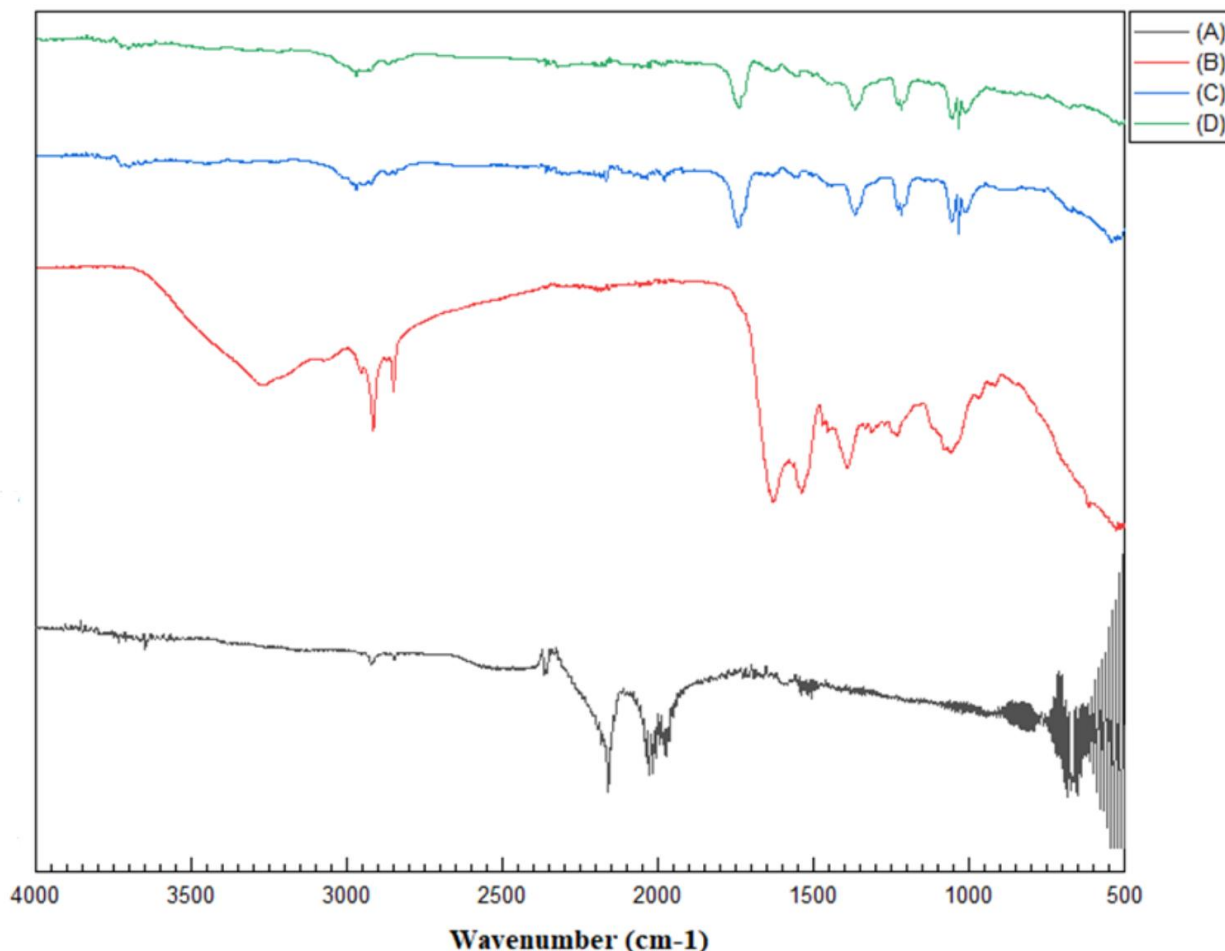


Figure 3.1 FT-IR Spectra of (A) CCB (VXC-72), (B) *E.coli* bacteria, (C) Magnetic CCB(VXC-72), (D) Magnetic biosorbent composite

In Figure 3.1C, the magnetic CCB(VXC-72) spectra showed peaks at 1383 and 587 cm^{-1} , corresponding to the Fe-O bond's vibration and stretching mode. This confirms that the material's magnetization is effective and that Fe_3O_4 has successfully bonded to the surface of the CCB(VXC-72) (Dong et al., 2021a; Jagirani et al., 2021b).

The FT-IR analysis of bacteria-immobilized magnetic CCB(VXC-72) provides spectra that closely resemble those of the bacteria, indicating their complete distribution on the surface of magnetic conductive carbon black nanoparticles Figure 3.1D. Additionally, a small peak at around 590 cm^{-1} suggests the presence of vibration in the Fe-O bond, indicating the composite's magnetic property and its ability to be easily collected by applying a magnetic field (L. Wang et al., 2021).

3.4.2 Morphology study by scanning electron microscopy (SEM)

Porosity, surface structure, and composition are, in general, important factors that need to be studied in order to define the sorption capacity of the composite biosorbent. The produced composite's morphological structures were analyzed using a scanning electron microscope (SEM). The analysis includes the CCB(VXC-72), magnetic CCB(VXC-72), and magnetic biosorbent composite, which showed a unique surface morphology.

As illustrated in Figure 3.2 A-B, The CCB(VXC-72) is characterized by the presence of amorphous aggregation spherical particles, with an average particle size ranging from 35 - 60 nm (Gu et al., 2019; X. Wang et al., 2016). The CCB(VXC-72) aggregation structure may suggest a wide surface area and high extraction capacity. This allows the dead *E.coli* bacteria to be distributed and immobilized easily and for the iron particles attached sufficiently to gain magnetic properties.

Figure 3.2 C-D shows many iron crystal particles with various shapes and brightness features were randomly distributed and tightly attached to the CCB(VXC-72) surface, and this indicates the presence of magnetic characteristics (de Moura Souza et al., 2019; Dong et al., 2021b; Tokaloğlu et al., 2024).

Surface morphology and observed changes in the surface microstructure of magnetic CCB(VXC-72) reported by SEM images at various magnifications Figure 3.2 E-F have been slightly affected by immobilization of *E. coli* on magnetic CCB(VXC-72) In the magnetic conductive carbon matrix, bacteria are distributed equally over a complete membrane, which results in the pore that is bigger than those of CCB(VXC-72). Thus, immobilizing *E.coli* bacteria to the magnetic CCB(VXC-72), dope speeds up the phase reversal, which causes bigger holes to form in the magnetic CCB(VXC-72)/biosorbents. The scanning electron microscopy SEM study revealed the presence of both white and black zones. The white particles indicate a high contain of inorganic elements, including phosphorus and calcium, whereas the black particles mostly consist of proteins containing oxygen, sulfur, and carbon (Dawwam et al., 2023).

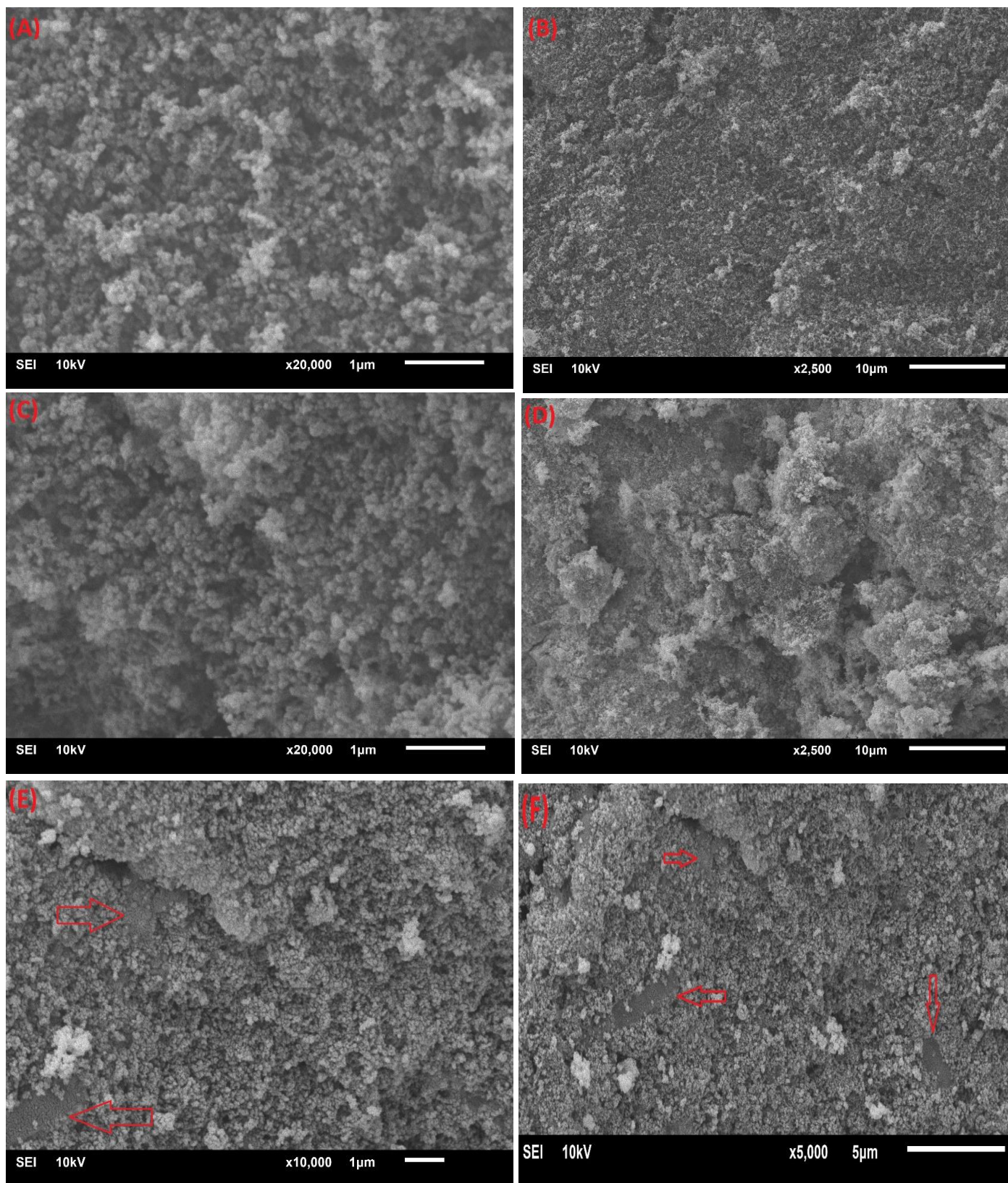


Figure 3.2 SEM image of (A-B) CCB(VXC-72), (C-D) Magnetic CCB(VXC-72), (E-F) Magnetic biosorbent composite

3.4.3 EDS spectra of the composite

The EDS spectrum obtained for the surface of the magnetic biosorbent composite, which also includes the outer cell surface of the immobilized bacteria, and the spectrum result confirms the presence of several metals. The EDS analysis indicates the presence of oxygen, carbon, nitrogen, sulfur, and iron in the magnetic biosorbent composite Figure 3.3. Furthermore, according to the results of an EDS evaluation, the atomic percentages of carbon, nitrogen, sulfur, and oxygen in the magnetic biosorbent composite were found to be 74.8 %, 3.6 %, 0.3 %, and 15.5 %, respectively. The EDS analysis result shows a significant proportion of carbon, oxygen, sulfur, and nitrogen derived from the functional group of the external cell wall of the *E.coli* bacteria that immobilized in the magnetic carbon black improves that the composite contains a binding site for cadmium absorption in the composite and the prepared composite is suitable for microextraction of cadmium in samples. In the EDS mapping micrograph of the surface of the magnetic biosorbent composite, the orange-colored iron atoms compose 5.8 % of the total atomic mass. The iron was used to gain a magnetic property of the bio-adsorbent. The uniformly distributed amount of iron, as shown in Figure 3.3, suggests a uniform interaction between the iron and the bio-adsorbent. The EDX mapping image provided clear verification of the effective synthesis of the magnetic bio-adsorbent (Sürme et al., 2024).

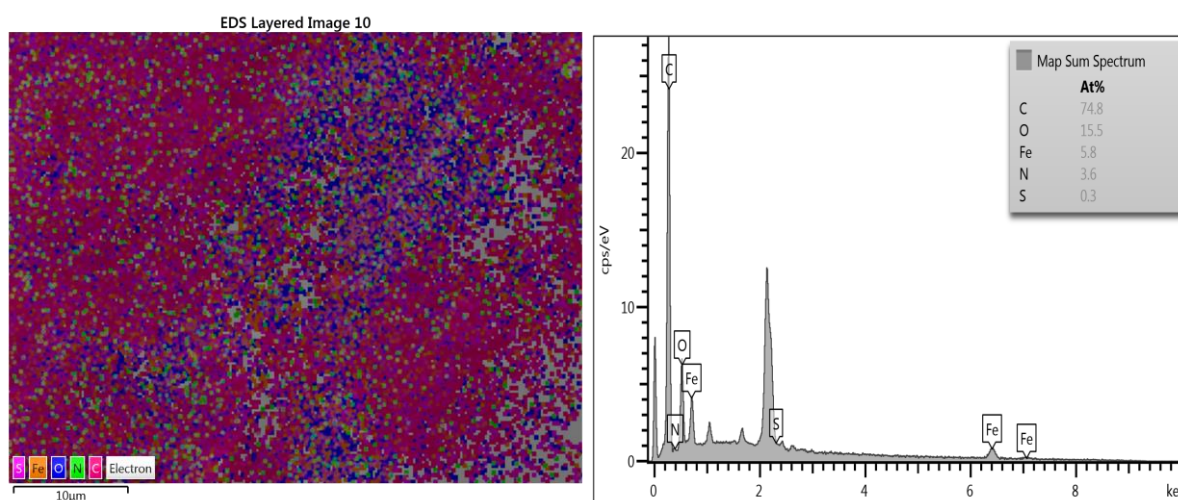


Figure 3.3 EDS spectra of magnetic biosorbent composite

3.4.4 BET surface area study

A Brunauer–Emmett–Teller (BET) automated gas sorption analyzer was used to determine the surface area and the pores diameter of the magnetic biosorbent composite. Prior to the examination, about 0.259 g of a dry magnetic biosorbent composite underwent degassing at a temperature of 150°C while nitrogen was flowing through it for a duration of 12 hours. At a temperature of 77 °K, the experimental results for nitrogen adsorption and desorption were calculated using liquid nitrogen. A calculation was made using the BET equation to determine the specific surface area as well as the pore volume. Both the surface area and the pore diameter of the magnetic biosorbent composite were found to be 46.251 m²/g and 0.3011 cm³/g, respectively, according to the Multi-Point BET technique. The isotherm of adsorption and desorption is shown in Figure 3.4.

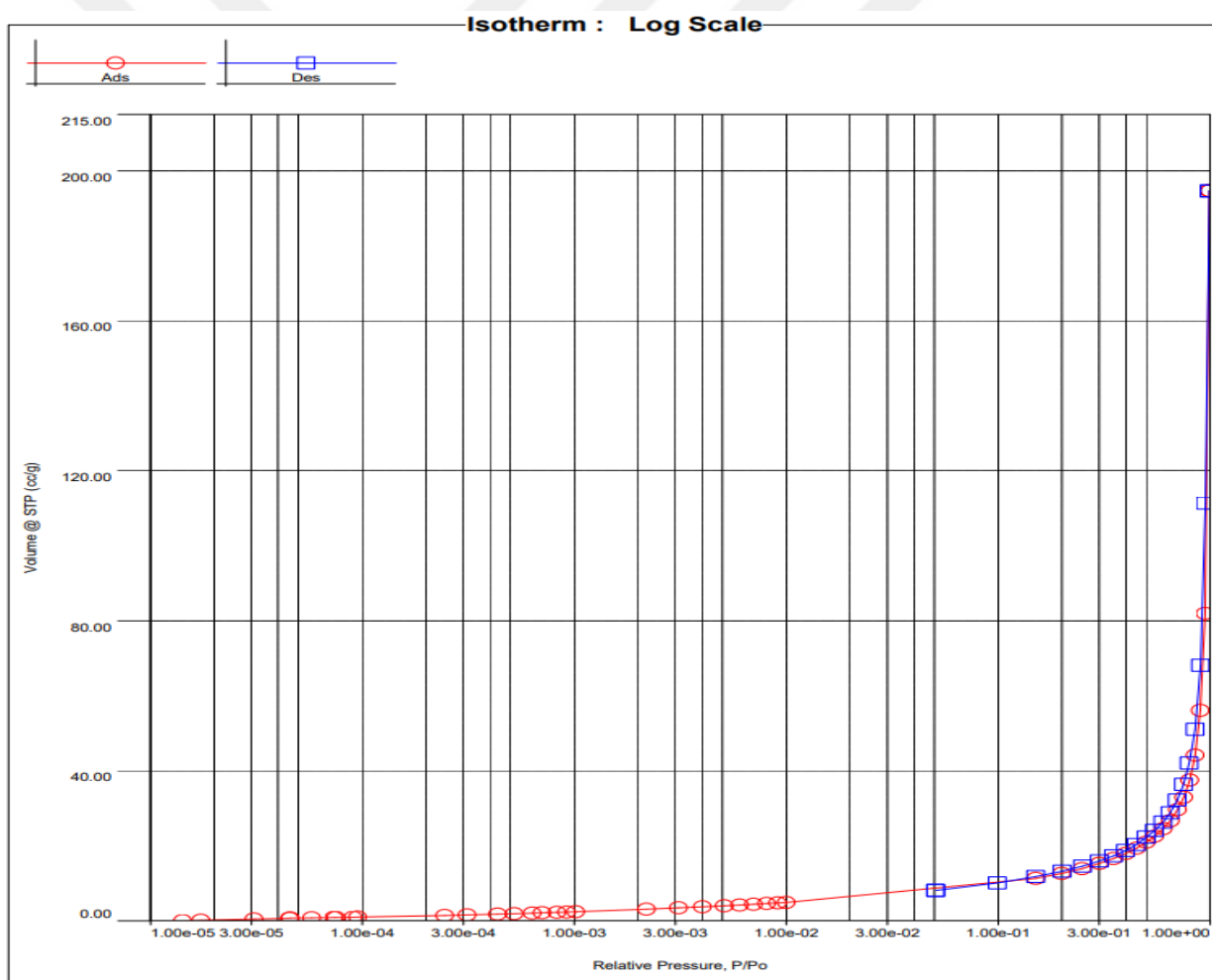


Figure 3.4 Adsorption- Desorption plot of magnetic biosorbent composite

Our research unveils a novel approach in the field of magnetic biosorbent composites. The experimental results indicate a significant number of nanopores on the surface of these composites, contributing to their high specific surface area. This unique property, combined with the immobilization of *E. coli* bacteria, suggests that magnetically CCB(VXC-72) could be a highly efficient adsorbent.

3.5 Model studies

Model solution (30 mL) of cadmium with a concentration of $10 \mu\text{g L}^{-1}$ was buffered to pH 5 by using an acetate buffer solution, and 100 mg of the magnetic composite was added to this solution. Vortex-assisted extraction (10 min) was used to extract analyte ions. The adsorbent was separated from the sample solution using a neodymium magnet. The analyte ions were eluted from the adsorbent by using 0.3 mL of 1.0 M HNO_3 . A blank solution was also carried out the same way but without analyte ions. Cadmium ions were determined by using FAAS. To confirm the results' accuracy, consistency, and reliability, each experiment was repeated three times, and the mean value obtained from these three data sets was used.

3.6 Desorption and reusing studies of magnetic CCB(VXC-72)

Reusing and recycling of used adsorbents has also been a topic of some research. Therefore, they could be reused to enhance the cost-effectiveness of the sorption process. The desorption examinations have mostly been done using diluted acids such as hydrochloric acid (HCl) (Laus et al., 2010; Q. Li et al., 2012) or nitric acid (Karthik & Meenakshi, 2015; X. Li et al., 2015). Our Studies involving batch desorption were conducted to investigate the process of recycling composite materials for use in various cycles. Both nitric acid and hydrochloric acid with a concentration of (0.5-1.0 mol. L^{-1}) and a volume of (0.3 – 1.0 mL) were used for desorption. Cd (II) from the composite adsorbent was extracted using HNO_3 (1.0 mol. L^{-1}) as the solvent. The use of 0.3 mL of nitric acid (HNO_3) resulted in the successful removal of Cd (II) from the adsorbent during the elution process. However, the adsorbent structure may undergo some damage in the presence of mineral acid, or loss of adsorbent mass may also occur; for this reason, ten times through the adsorption-elution were processed, Cd (II) recovery did not decrease significantly by around 25 %. However, the adsorbent's high stability allows up to five repetitions of the adsorption-elution process.

3.7 Sample collection and pretreatment

3.7.1 Water samples

Before microextraction, all water samples had to undergo identical preparation procedures, including mineral water, bottled water obtained from local markets in Tokat, Turkey, and tap water collected from our laboratory. To begin, every single water sample underwent filtration using a 0.45 μm filter paper in order to eliminate any particles that could have been present. After that, the samples were kept in clean containers at a temperature of 4°C in order to maintain their original state. The water samples were not subjected to any further preparation before the microextraction technique was carried out.

3.7.2 Food and drinking samples

In the town of Tokat, Turkey, a number of different beverages and food samples were bought from local markets. The following items were included in this group: strawberry juice, lemon juice, eggplant, apple, mushroom, cucumber, parsley, tomato, ginger, garlic, paper mint, cinnamon, bell pepper, and canned tuna fish. To prepare the vegetable samples, the edible sections were removed, cleaned with ultrapure water, and left to dry in an oven for a whole day. Following that, a mortar and pestle were used to smash the dry sample into small particles, which were then placed in a sterilized container.

3.8 Wet digestion method

A wet digestion approach was applied when preparing solid food samples, Juice, and certified reference material (Akinyele & Shokunbi, 2015; Dehghani et al., 2020). Before the wet digestion process through cleaning and ensuring completely sterilized equipment, the glassware was left overnight to soak in (1+9) HNO_3 . The process of digestion begins by measuring 1 g of the prepared food samples previously, whereas, for drinks, a volume of 1 mL was added to a beaker, followed by the addition of 6 mL of 65% HNO_3 and 2 mL of 30% H_2O_2 in order to prepare a digestive mixture with a ratio of 3:1. While for beverage samples 1 mL of 65% HNO_3 and 0.5 mL of 30% H_2O_2 . The beaker was then covered with a watch glass and heated on a hot plate at a temperature of around 110°C for a duration of 3 to 4 hours. After that, the acid mixture will be added once again, and the liquid will be heated until it becomes transparent. Following that, the sample was cooled, and 5 mL of distilled water was added.

The mixture was then filtered using a blue band filter paper, and the resultant sample was poured into a 100 mL volumetric flask and filled with ultrapure water. In the same manner, the blank digestion was carried out in the same way. Then, the pH of the sample solution will be precisely adjusted using nitric acid and 0.1 M sodium hydroxide before being transferred to polyethylene containers in preparation for the optimum preconcentration stage. The gathered results will be presented using the analytical parameters.



4. RESULT AND DISCUSSION

4.1 Multivariate design strategy

The term "design of experiment" (DOE) refers to a method that is well-organized and offers the ability to evaluate the influence of several factors and their interactions concurrently, as well as to identify the optimal setting for each parameter and to reduce the amount of time and spending money (Bozorgzadeh et al., 2021; Nomngongo & Ngila, 2014). There were two steps in which the experimental design technique was carried out: (i) screening the main parameters affecting the extraction recovery using a Plackett–Burman design and (ii) optimizing the significant factors using a central composite design (CCD). MINITAB 22 was used to analyze the results.

4.1.1 Plackett-Burman design

Plackett–Burman design (PBD) is the experimental design that was employed for the purpose of screening the primary variables that had an effect on the extraction recovery. This strategy is advantageous because it allows for the detection of the most significant variables that have a major impact on the process with just a small number of tests. The Plackett–Burman design is a unique type of screening design that operates on the assumption that the interactions may be fully ignored. As a result, the primary effects can be calculated with less number of experiments.

Choosing an appropriate experimental design that clearly defines response variables is challenging. When it comes to interpretations of this kind, the central composite design (PBD) could be the most suitable option. The primary benefit of this optimization model is its high degree of accuracy and ability to determine the optimal values for variables.

Our study used the PBD design methodology to construct the factorial design. A 3^4 was used to optimize four factors and identify the optimal response. The PBD is designed by analyzing the interaction between all of the factors that are being utilized in this study (Mu'azu et al., 2018).

The Plackett-Burman design (PBD) was used to conduct screens of four parameters for Cd at three levels. including pH and dosage of adsorbent (D) mg, Vortex time (T) min, and sample

volume (V) ml, were used to evaluate the experimental design. These variables were assigned three coded levels: low (-), center point (0), and high (+), as shown in Table 4.1.

Twenty-one experimental runs were conducted to analyze four variables using Minitab software version 22, shown in Table 4.3 below. the recovery of each experiment with a triplicate run and standard deviation were included. The standardized impact of these findings may be examined using the Pareto chart ($P=0.05$) and residual plots.

Table 4.1 Plackett-Burman design and central composite design variables and levels

Variable	Low(-)	Central point (0)	High(+)
pH	2	5	7
Adsorbent dosage (D) (mg)	50	100	200
Vortex time (T) (min)	5	10	20
Sample volume (V) (mL)	10	30	50

A total of 21 experiments were carried out in triplicate, and the mean of the responses was recorded. The analysis of variance (ANOVA) was used in order to identify the most important effects. Table 4.2 provides an illustration of the regression coefficients and the importance of those coefficients for the response of the Placket–Burman design.

Table 4.2 The significance of the regression coefficients for the response of PBD

Term	Effect	Coefficient	Standard error coef	T-Value	P-Value
Constant		55.300	0.835	66.20	0.000
pH	26.933	13.467	0.835	16.12	0.000
Adsorbent dosage	4.267	2.133	0.835	2.55	0.013
Vortex time	2.333	1.167	0.835	1.40	0.167
Sample volume	1.600	0.800	0.835	0.96	0.342
Ct Pt		42.90	1.87	22.97	0.000

Table. 4.3 Result of experiments run (N =3, SD; Standard deviation)

Experiment	pH	D	T	V	Cd Recovery (%)
1	+	+	+	+	54 ± 1 ^{SD}
2	+	+	+	-	75 ± 2
3	+	+	-	+	60 ± 1
4	+	+	-	-	70 ± 2
5	+	-	+	+	77 ± 1
6	+	-	+	-	63 ± 2
7	+	-	-	+	76 ± 2
8	+	-	-	-	61 ± 1
9	-	+	+	+	45 ± 2
10	-	+	+	-	49 ± 1
11	-	+	-	+	50 ± 2
12	-	+	-	-	40 ± 4
13	-	-	+	+	37 ± 1
14	-	-	+	-	35 ± 2
15	-	-	-	+	34 ± 3
16	-	-	-	-	37 ± 1
17	0	0	0	0	95 ± 3
18	0	0	0	0	95 ± 4
19	0	0	0	0	97 ± 2
20	0	0	0	0	96 ± 1
21	0	0	0	0	95 ± 1

4.1.1.1 Pareto chart

A Pareto chart, as shown in Figure 4.1, was used in order to provide a description of the effect that the variables had on the experimental design for the screening process. The significance of the factors is proportional to the horizontal bar length. The vertical red reference line (1.99) indicated that it has effects statistically significant at the 95% confidence level of the variable when the bar line was longer than it was otherwise (Lemes & Tarley, 2021; Santos et al., 2020; Yao et al., 2017).

Both variables, A and B, were able to cross the red line, indicating that they had a considerable impact on the model, as seen by the result below. Other variables that did not fit and were found to be below the red line are regarded as not having a significant effect on cadmium recovery. Based on the Pareto chart, it was determined that the variables pH and adsorbent dosage had a significant influence on the model (Lemes & Tarley, 2021).

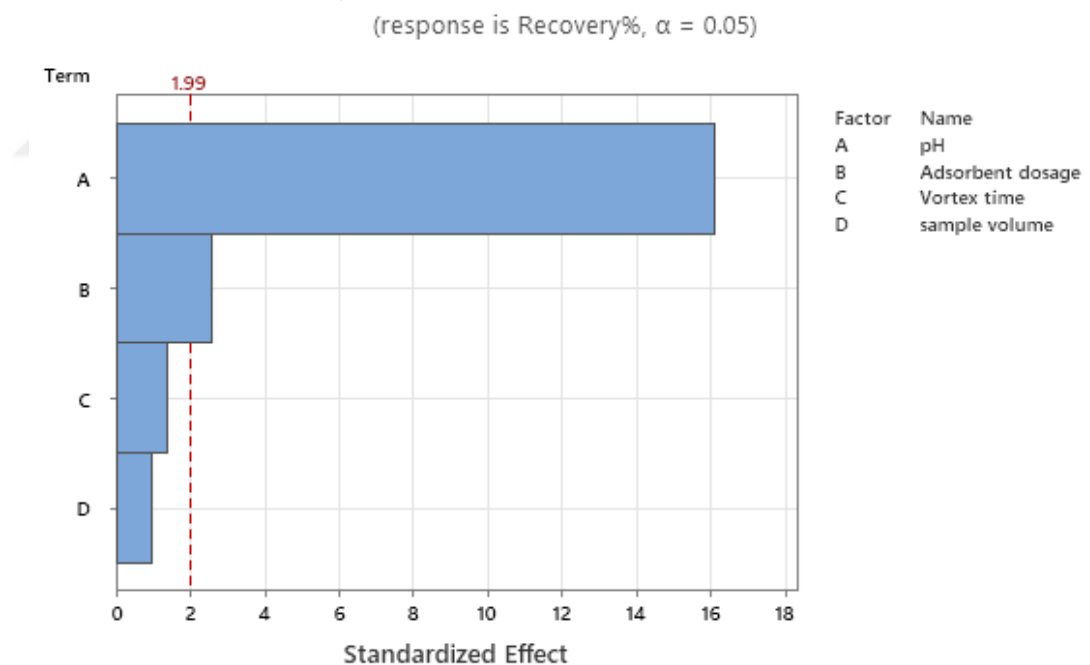


Figure 4.1 The Pareto Chart of the variables influences

4.1.1.2 Residual plots

The residual plots are helpful in determining the quality of the model, and if the model is significant and fits the data, the residuals will typically be dispersed (Matin et al., 2022).

Figure 4.2a illustrates the normal probability against the internally normalized residuals, and it is clear that there is no substantial deviation from the straight line.

The histogram presented in Figure 4.2b illustrates the vertical bar-line distribution of positive and negative values. This particular plot provides evidence that the model exhibits a normal distribution with respect to both significant and insignificant values.

Additionally, the residuals plot versus the fitted values, which can be observed in Figures 4.2c and 4.2d, illustrates that the residuals were distributed with a random pattern on both sides of the critical line. This suggests that there is a good agreement among the results that the model achieved, which serves as evidence that the model is statistically significant (Khan Rind et al., 2023).

From all parameters, it is found that the pH of the cadmium solution is one of the key factors influencing the adsorption of cadmium by the magnetic biosorbent composite since we achieved a high level of quantitative recovery (>95%) at a pH value equal to 5. The reason behind this is that at low pH levels, H^+ ions compete with metal ions. At low pH levels, the cell surface undergoes an increase in positive charge, and this competition reduces the attraction between metal ions and the functional groups on the cell wall. The attraction increases as the pH rises because the cell surface gets more negatively charged. The greatest attraction can be achieved at pH 5. This outcome is in line with previous cases found in the literature (Aydemir et al., 2011; Tuzen et al., 2008).

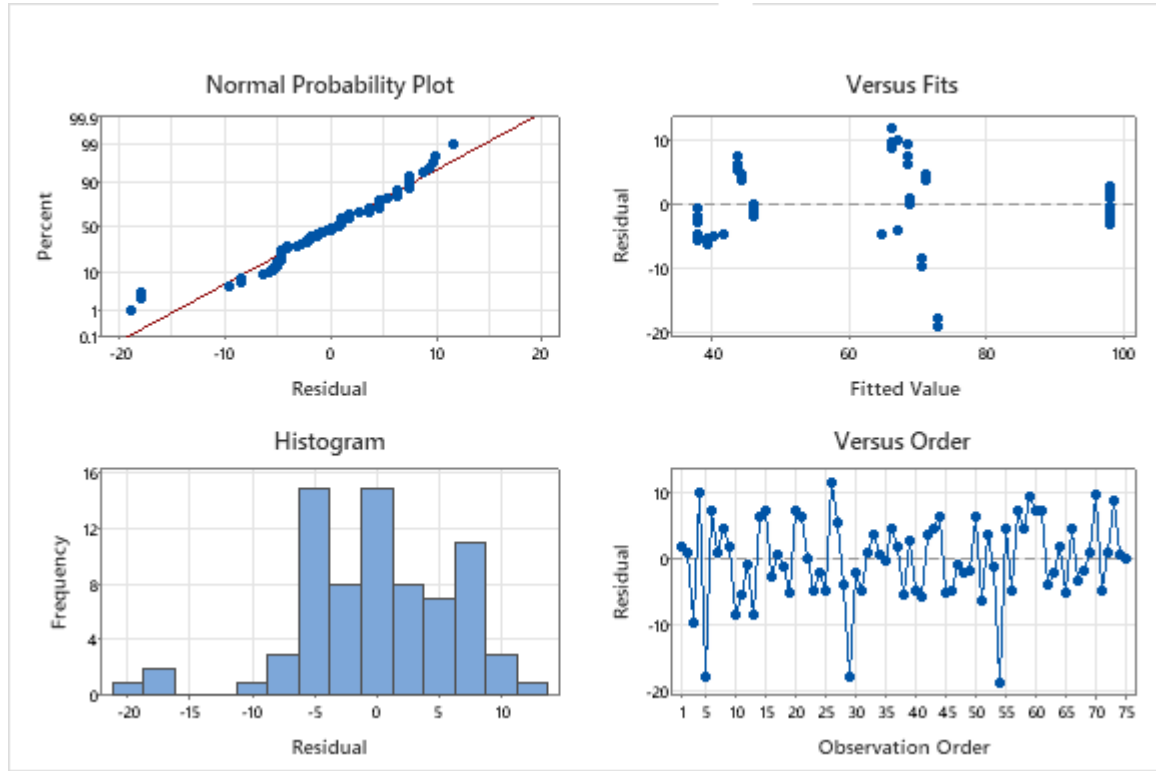


Figure 4.2 Residual plots of (a) Normal probability plot, (b) Histogram, (c) Versus fits, (d) Versus order

4.2 Analysis of variance

The Analysis of Variance (ANOVA) is a dependable statistical tool used to assess the efficiency and significance of an analytical approach's efficacy (Altunay, Hazer, Farooque Lanjwani, et al., 2023). It determines the significance of each variable, which in turn guides the acceptance or rejection of the model, depending on the significance of the variables. This decision is made after reviewing the P-values from the analysis. The MINITAB statistical program, version 22, was used to perform the statistical analysis, after which the response of PBD was produced. ANOVA analyses the variances, significant factors, and their interactions. An analysis of variance was performed to design the statistical data. If the P-value is less than 0.05, the factor is considered to be significant. On the other hand, if the P-value is more than 0.05, it will be considered as non-significant or not fit (Altunay, Hazer, Lanjwani, et al., 2023; Çıtak & Sabancı, 2021a). After all the data is collected and computed by calculating the independent variables' mean value plus the standard deviation ($M \pm SD$) over the specified number of days. The ANOVA result for the factorial design is shown in Table 4.4; according to the findings of the analysis of variance (ANOVA), the model that was used in this study is

extremely significant. The F-value for the model was 159.36, and the p-value was 0.000. This indicates that the independent variables together have a considerable impact on the variable that was being studied. With very low p-values (0.000) and high F-values (259.90 and 527.51, respectively), pH and curvature emerged as the most impactful variables among those that were analyzed. Both of these parameters had highly important effects. This highlights the enormous influence that these factors had on the result of the competition. Also, the adsorbent dosage exhibited statistical significance with a p-value of 0.013, even with a less pronounced effect than pH and curvature. On the other hand, the p-values for vortex time and sample volume were determined to be non-significant, with values of 0.167 and 0.342, respectively. This indicates that these parameters do not significantly impact the response variable. The results of the lack-of-fit test showed a p-value of 0.0554, which is slightly higher than the standard significance level of 0.05 (Marrubini et al., 2020). This indicates that while the model offers an acceptable fit to the data, there may be some small limitations in its capacity to capture all of the variability that is present in the data. The error term represents a relatively small proportion of the variation that cannot be attributed to the model. In general, the model can clarify a significant portion of the variance found in the response variable. The fitted model demonstrated a strong agreement, as shown by the coefficient of determination values of ($R^2=92.03\%$) and ($R^2_{adj} = 91.45\%$) (Jaafari & Yaghmaeian, 2019a).

Table 4.4 The result from the variance analysis (ANOVA) (DF: degrees of freedoms; Adj SS: adjusted sums of squares; Adj MS: adjusted mean squares)

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	33359.1	6671.8	159.36	0.000
Linear	4	11274.2	2818.6	67.32	0.000
pH	1	10881.1	10881.1	259.90	0.000
Adsorbent dosage	1	273.1	273.1	6.52	0.013
Vortex time	1	81.7	81.7	1.95	0.167
sample volume	1	38.4	38.4	0.92	0.342
Curvature	1	22084.9	22084.9	527.51	0.000
Error	69	2888.8	41.9		
Lack-of-Fit	10	107.3	10.73	2.90	0.0554
Pure Error	5.9	218.6	3.7		
Total	74	36247.9			

In terms of actual components as a function of pH, sample volume(V), vortex time period (T), and adsorbent dose (D), the quadratic regression models for Cd removal percentage might be expressed as the following equations:

$$\text{Recovery\%} = 24.36 + 5.387 \text{ pH} + 0.0284 \text{ D} + 0.156 \text{ T} + 0.0400 \text{ V} + 42.90 \text{ Ct Pt}$$

4.3 Response surface methodology (RSM)

The response surface methodology (RSM) is a statistical and mathematical technique used to determine the optimal values of variables. The purpose of the 3D response surface graphs was to determine the overall impact of parameters (Jaafari et al 2019b; Memon et al., 2015; Podstawczyk et al., 2015). Surface response diagrams showing the recovery % of Cd(II) in a three-dimensional design, with the variables of vortex duration, pH, sample volume, and adsorbent dose.

4.3.1 Central composite design (CCD)

With a limited number of specified experiments, we used a central composite design (CCD) to optimize the four parameters (pH, adsorbent dose, vortex duration, and sample volume) (Tamandani & Hashemi, 2022). The response surface plot in Figure 4.3a showed the combined effect of pH and adsorbent dose. The surface plot indicated that at the central pH value and adsorbent dosage were used, an optimal response was achieved

The response plot, which can be found in Figure 4.3b, describes the dual response of pH and vortex time. The plot demonstrates that the surface response decreased as the pH decreased, and a better response was discovered at a higher pH around pH 5. The recovery decreased gradually at higher than pH 5. Additionally, a good response of the 3D plot was discovered at a central value of vortex time, and the adsorption equilibrium was achieved at around 10 min.

The response graphs in Figure 4.3c-d indicate that responses dropped with a decrease in pH and improved at central pH levels. Additionally, the response jumped with a central value of sample volume and vortex time. For the relation between adsorbent amount and vortex time, a high recovery yield with a central value of both variables means the relation is directly proportional. The relationship between the adsorbent dose and sample volume produces a significant recovery at 100 mg and 30 ml, respectively. In terms of the relationship between vortex duration and sample volume, the highest response was reached at 10 minutes and 30 ml, respectively, as shown in Figure 4.3e-f. The 3D plot of four variables (pH, adsorbent

dosage, vortex duration, and sample volume) was analyzed using CCD. The results indicated that a favorable response was obtained in the 3D plot when these variables possess a central value.



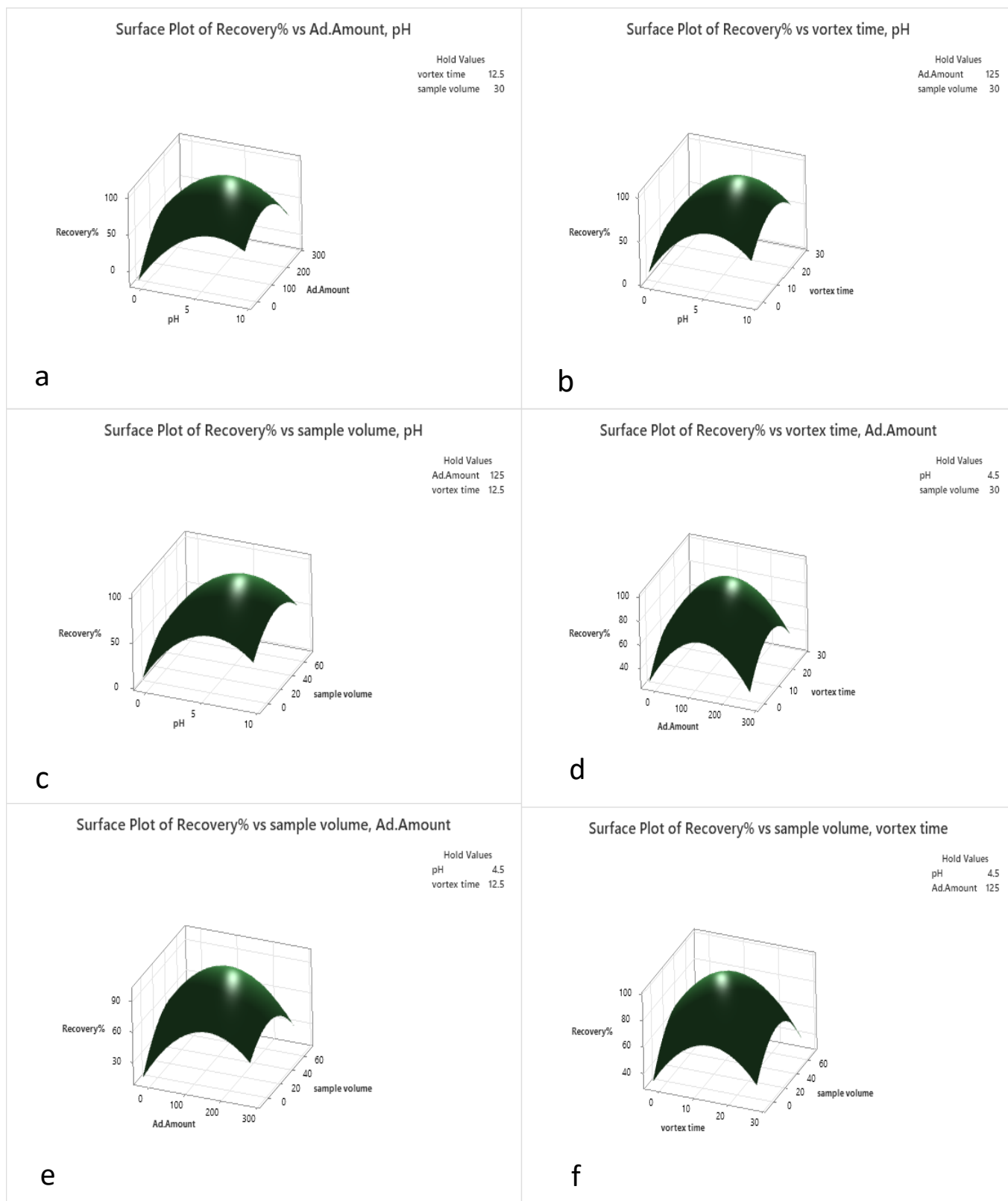


Figure 4.3 Response of surface plot

4.3.2 Contour plot study

The analysis used the two-dimensional contour plots approach in Figure 4.4 a-f to study the coupled effect of the pH value, adsorbent dosage, Vortex time, and sample volume on the response plot, showing the interaction between these independent variables (G. Wang et al., 2016). The adsorption recovery of target metal ions improved with a pH of approximately 5 and an adsorbent dose of around 100 mg, as shown by the green band in Figure 4.4a, which displays recovery >100% at a hold value of vortex duration 12.5 min and sample volume 30 ml. Additionally, it is possible to obtain a recovery of over 100% by reducing the vortex duration to 12.5 minutes and maintaining a pH of approximately 5, using an adsorbent dose of 125 mg and a volume of 30 ml Figure 4.4 b.

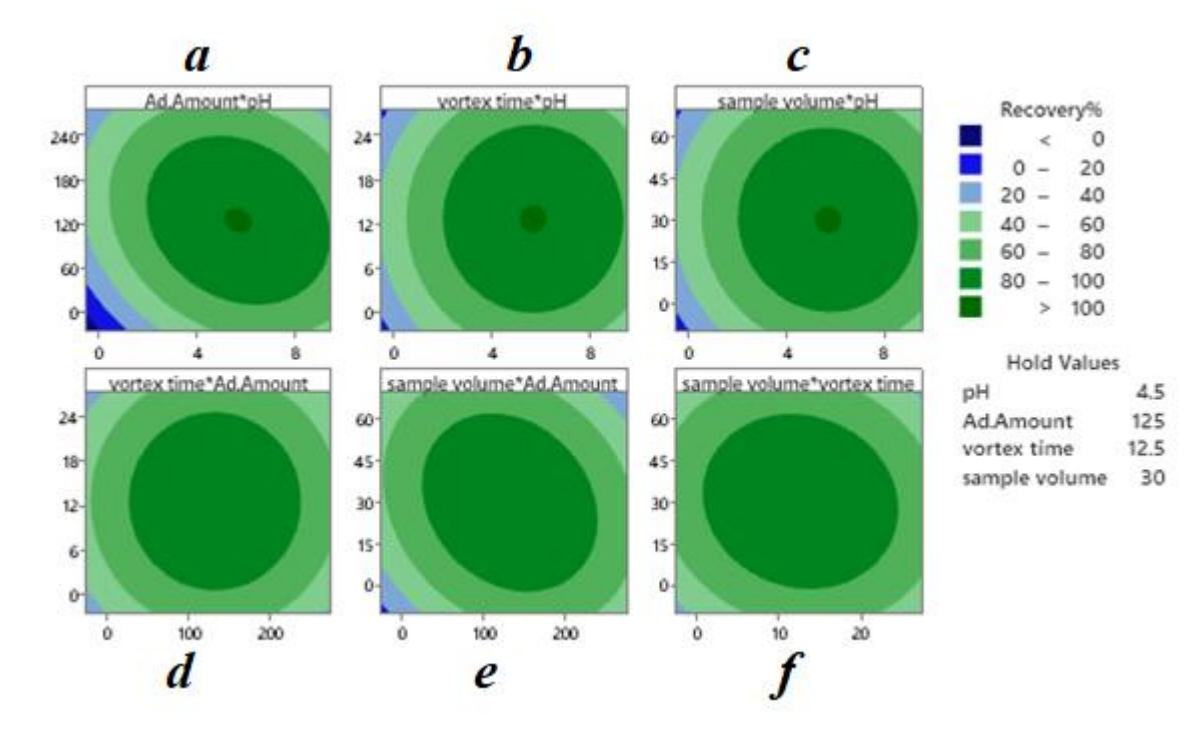


Figure 4.4 Response of contour plot

According to the parameters in Figure 4.4 a-c, a high recovery of >100 was attained at central values for each of the adsorbent doses, vortex duration, and sample volume.

At hold values of pH 4.5, the effect of adsorbent dosage vs vortex time and sample volume is represented by the different forms of interactions shown in Figure 4.4 d-e; Cadmium will be recovered at (>80%) with a central value of sample volume and adsorbent dose and vortex

duration. The interaction between vortex time and sample volume is seen in Figure 4.4f. The recovery of cadmium (>80%) when the vortex duration is 12.5 minutes and the sample volume is 30 ml. Based on the main effect plot, maximum Cd (II) recovery was achieved at pH 5, adsorbent dose of 100 mg, vortex duration of 10 min, and sample volume of 30 ml, as shown in Figure 4.5.

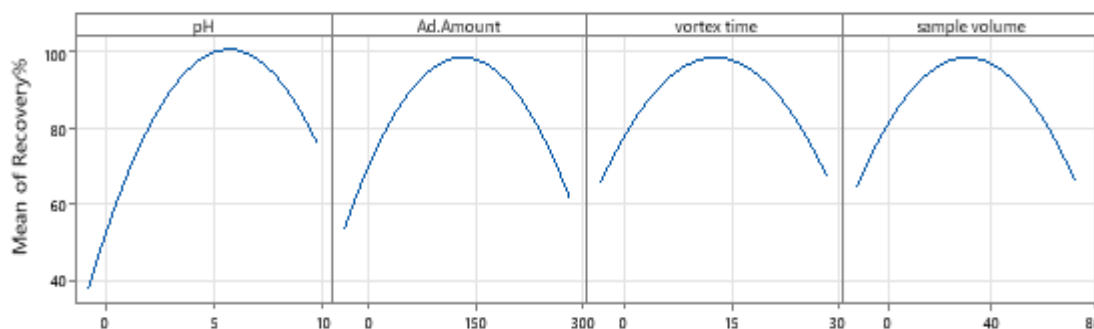


Figure 4.5 Optimum value of all parameters

4.4 Analytical figures of merits

The optimization parameters for the current approach, detailed in Table 4.5, highlight the precision and accuracy of our analytical methodology. Precision, indicating the reproducibility of measurements, and accuracy, reflecting the proximity of the measured value to the real value, have been thoroughly examined under optimal conditions. The linearity range for the recommended technique, maintained at a pH 5 for recovery of Cd(II), was found to be 2.0–40.0 $\mu\text{g/L}$ with $R^2 = 0.9941$, further reinforcing the reliability of our results. In order to determine both the limit of detection (LOD) and the limit of quantification (LOQ), we used particular mathematical equations: $\text{LOD} = 3\text{SD}/m$ and $\text{LOQ} = 10\text{SD}/m$. In this context, SD refers to the standard deviation obtained by analyzing 10 blank samples, whereas m indicates the slope of the linear graph resulting from analyzing 10 blank samples. The LOD and LOQ values obtained for our new approach are very low, measuring at 0.6 $\mu\text{g/L}$ and 2.0 $\mu\text{g/L}$, respectively. The maximum sample volume was determined to be 30 mL, and an eluent of 0.3 mL of 1 M HNO_3 was used. We achieved significant recoveries by using nitric acid as an eluent solution. The preconcentration and enhancement factors were determined to be

100 and 88, respectively. The ratio of the sample's initial volume to its final volume is the formula for calculating the preconcentration factor (PF), which is a measurement of the degree of concentration achieved in the sample during the preconcentration stage. The enhancement factor (EF) shows how much better the sensitivity is when preconcentration is used instead of direct analysis, and it will be calculated by the ratio of slopes of the calibration graph before and after the extraction method.

Table 4.5 Analytical performance of the novel method

Analytical parameters	Result
After Preconcentration	$A=11.8 C + 0.009426$
Linearity, $\mu\text{g L}^{-1}$	2 – 40
Slope(m)	11.8
Intercept	0.0094
Correlation coefficient(r^2)	0.9941
Limit of detection (LOD, $\mu\text{g L}^{-1}$)	0.6
Limit of quantification (LOQ, $\mu\text{g L}^{-1}$)	2
Average relative standard deviation (RSD %) (Intraday)	1.88
Average relative standard deviation (RSD %) (Interday)	1.98
Preconcentration factor (PF)	100
Enhancement factor (EF)	88
Adsorbent capacity (mg g^{-1})	90.3

4.5 Optimal eluent type, volume and concentration

Eluents of nitric acid and hydrochloric acid were selected to desorb target ions; their effects on desorption were studied at concentrations of 0.5 and 1.0 mol.L⁻¹. The best volume of both acids was identified through experiments to recover Cd (II) ions after extraction with the magnetic biosorbent composite. The results showed in Figure 4.6 that the magnetic biosorbent composite could be quantitatively eluted of Cd (II) ions using a 1.0 mol.L⁻¹ nitric acid solution. Therefore, it was selected that the ideal concentration of nitric acid for further studies was 1.0 mol L⁻¹. Moreover, the effect of eluent volume on metal ion desorption from the adsorbent

was evaluated within the range of (0.3, 0.5, 0.7, 1.0) mL. For the purpose of achieving the quantitative recovery of the analyte, it was found that a volume of 0.3 mL of nitric acid, with a concentration of 1.0 mol.L⁻¹, has the highest recovery of cadmium and sufficient values for desorption of Cd(II) from the magnetic biosorbent composite rather than hydrochloric acid.

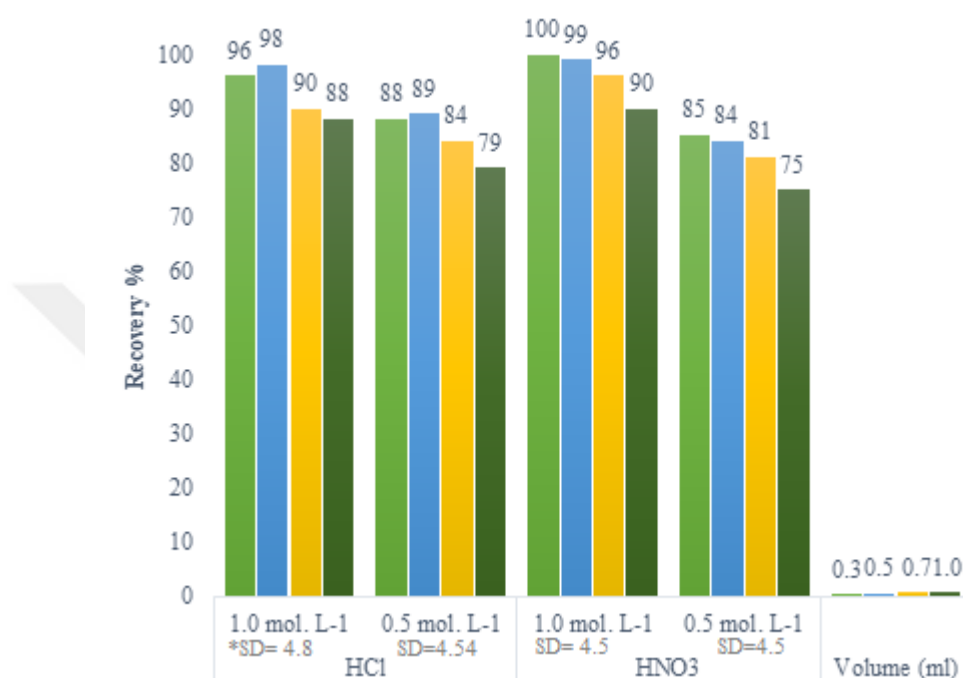


Figure 4.6 Eluent volume and concentration optimization (* standard deviation)

4.6 The adsorption capacity

The adsorption capacity is defined as the maximum quantity of metal that may be absorbed by 1 gram of adsorbent composite, usually expressed in milligrams per gram (mg/g). Thus, identifying the maximum adsorption capacity is an important factor in evaluating the efficiency of adsorbent material in adsorption processes (Arghavani et al., 2024b). For determining the adsorption capacity of our prepared magnetic biosorbent composite, experiments were carried out under optimized conditions, and adsorption capacity (Q , mg. g⁻¹) was determined using the following calculation:

$$Q = (C_0 - C_f) \times V / m$$

The variables C_0 (mg.L^{-1}) and C_f (mg.L^{-1}) represent the first and final concentration of Cd(II), respectively. V (L) refers to the total volume of the solution, and m (g) represents the mass of the magnetic biosorbent composite. The maximum biosorption capacity of immobilized *E.coli* bacteria on magnetic carbon black was determined to be 90.3 mg.g^{-1} Table 4.5. The biosorbent's large surface area and effective interaction with the analyte are two factors that are responsible for the high adsorption capacity of our adsorbent.

4.7 Intraday/interday precision

Both intraday and interday investigations were carried out in order to assess the precision of the optimized approach Table 4.5. For this purpose, a standard solution of Cd(II) was prepared in different concentrations. The intraday precision was determined by analyzing five replicate solutions of Cd (II) at three different concentration levels, including 500, 750, and 1000 ng.L^{-1} . The RSD of 2.44 %, 2.0 %, and 1.2 % was found for 500, 750, and 1000 ng.L^{-1} of Cd (II), respectively. For the determination of the inter-day precision, the identical concentrations were tested in five replicates on five consecutive days. In the experiments, the RSD was determined to be 2.64 %, 1.8 %, and 1.5 % for concentrations of 500, 750, and 1000 ng.L^{-1} of Cd(II), respectively. It was determined that the precision of the approach was suitable since the RSDs that were produced as results of all of the experiments were less than 5 %.

4.8 Selectivity of the method

Interfering ions provides a significant challenge in accurately detecting trace-level elements; however, this issue could be eliminated by using separation techniques. The most frequent interferences in real samples are alkali and alkaline earth elements. These specific groups generally exhibit a reducing enhancing effect on the signals of the analytes. In this case, typical ions that are often found in real samples with various concentrations have been included in model solutions of Cd(II). The purpose was to evaluate the effectiveness of the extraction process when these ions were present. The impact of the foreign ions on flame atomic absorption spectrometric results for the recovery of Cd(II) on *E.coli* immobilized on magnetic CCB(VXC-72) was studied and clearly presented in Table 4.6. The presence of large amounts of matrix ions did not impact the recoveries of the extracted Cd(II) by the magnetic biosorbent

composite; even some transition metals at a concentration of mg L^{-1} did not have any interfering impact on the recoveries of Cd(II) by the magnetic biosorbent composite. So, based on these results, the recommended preconcentration and separation method could be used even with very salinity samples that include metal ions in mg.L^{-1} as well.

Table 4.6 Effect of coexisting ions on enrichment of Cd (II), (N=3, * standard deviation)

Ions	Tolerance limits(mg L^{-1})	Recovery(%) of Cd^{2+}
Na^+	5000	$93 \pm 3^*$
Ca^{2+}	1000	90 ± 2
Co^{2+}	50	96 ± 3
Cr^{3+}	100	92 ± 2
K^+	2000	95 ± 1
Mg^{2+}	2500	93 ± 2
Mn^{2+}	50	94 ± 3
NH_4^+	1000	98 ± 1
Ni^{2+}	100	96 ± 2
Pb^{2+}	50	81 ± 3
Zn^{2+}	50	96 ± 1
Cl^-	5000	91 ± 2
CO_3^{2-}	3000	100 ± 1
F^-	5000	95 ± 1
I^-	5000	93 ± 2
NO_3^-	500	90 ± 2
PO_4^{3-}	6000	96 ± 2
SO_4^{2-}	5000	93 ± 1

4.9 Validation and accuracy of the method

One of the most important steps for validating the optimized method and confirming the microextraction of the analytical approach is to apply it to certified reference materials (CRM). The recommended microextraction process was validated using certified reference materials (CRM). Our analysis used an optimal approach using NIST SRM 1570a Spinach Leaves. One may argue that the recommended procedure's correctness has been confirmed based on the good results obtained. Table 4.7 summarizes the findings.

Table 4.7 Application of the method to CRM (* standard deviation, N=3)

Certified reference material	Cd ²⁺ -certified values (µg g ⁻¹)	Cd ²⁺ measured values(µg.g ⁻¹)	Cd ²⁺ Recovery %	Cd ²⁺ RSD%	RE %
NIST SRM 1570a Spinach Leaves	2.876± 0.058*	2.840 ± 0.039	97 ± 2	2.1	1.25

4.10 Application on real samples

The recommended methods were carried out on foodstuffs and various drinking samples under optimal conditions. The relative recovery (RR%) values at various spiking levels were determined using the following equation in order to assess the efficacy of the suggested sample pre-treatments:

$$RR\% = (C_{\text{final}} - C_{\text{real}}) / (C_{\text{added}}) \times 100\%$$

in this equation, C_{final} , C_{real} , and C_{added} represent the final concentration after the preconcentration procedure, real concentration found in the sample, and concentration spiked to the sample, respectively.

4.10.1 Water and drink samples

As shown in Table 4.8, various types of water and soft drink samples, such as tap water, mineral water, drinking water, strawberry juice, and lemon juice samples obtained from (Tokat City, Turkey), were subjected to the standard additional procedure after being filtered and prepared for applying the optimum preconcentration procedure, while for other soft drink wet digestion technique were carried out to being analyzed.

Table 4.8 Results of water and drink samples (*: standard deviation. **: Not detected, N=3)

Real samples	Cd ²⁺ -added (µg L ⁻¹)	Cd ²⁺ -found (µg L ⁻¹)	Cd ²⁺ RSD (%)	Cd ²⁺ Recovery (%)
Tap Water	–	4.42 ± 0.1*	2.26	–
	5	9.21 ± 0.21	2.28	96 ± 2
	10	13.91 ± 0.19	1.37	95 ± 1
Mineral Water	–	3.74 ± 0.10	2.67	–
	5	8.54 ± 0.11	1.3	96 ± 1
	10	13.1 ± 0.15	1.14	94 ± 1
Drinking water	–	N. D**		–
	5	5.11 ± 0.10	1.96	102 ± 2
	10	10.5 ± 0.12	1.14	105 ± 1
Strawberry Juice	–	N. D		–
	5	5.13 ± 0.11	2.14	103 ± 2
	10	10.0 ± 0.2	2.0	100 ± 2
	–	N. D		–
Lemon juice	5	4.91 ± 0.12	2.4	98 ± 2
	10	10.22 ± 0.11	1.08	102 ± 1

4.10.2 Food samples

We verified our modified method, specifically designed for quantifying the quantity of Cd(II), a harmful heavy metal. Additionally, we successfully employed our method to analyze Cd(II) levels in real food samples. The samples, which consist of a wide variety of items such as apples, ginger, eggplants, tomatoes, mushrooms, canned tuna, parsley, cucumbers, paper mint, cinnamon, and bell peppers, were carefully prepared using wet acid digestion to guarantee precise analysis. However, the basic complexity of natural samples presented a difficulty since several interfering species were found in the sample matrix, resulting in non-specific background absorption. In order to overcome this problem, we used our novel magnetic biosorbent composite, which showed a specific attraction to Cd(II) ions at a pH of 5. The efficacy of this method was shown by the almost complete retrieval of Cd(II) from all examined food samples, as outlined in Table 4.9. The success of this application highlights the strength and flexibility of our technique in practical situations, offering a dependable way to evaluate the presence of Cd(II) contamination in food matrices.

Table 4.9 Application of the method to digested food samples (N= 3, * Standard deviation)

Food sample	Cd ²⁺ added (µg g ⁻¹)	Cd ²⁺ found (µg.g ⁻¹)	Cd ²⁺ RSD(%)	Cd ²⁺ Recovery (%)
Apple	0	0.96 ± 0.01*	1.04	-
	5	5.87 ± 0.07	1.19	98 ± 1
	10	10.55 ± 0.1	0.95	96 ± 1
Mushroom	0	0.70 ± 0.02	2.85	-
	5	5.54 ± 0.1	1.8	97 ± 2
	10	10.5 ± 0.14	1.3	98 ± 1
Canned Tuna	0	1.31 ± 0.02	1.53	-
	5	6.1 ± 0.12	1.92	96 ± 2
	10	10.82 ± 0.14	1.29	95 ± 1
Parsley	0	2.76 ± 0.091	3.3	-
	5	7.62 ± 0.16	2.1	97 ± 2
	10	12.45 ± 0.1	0.8	97 ± 1
Cucumber	0	1.30 ± 0.01	0.77	-
	5	6.01 ± 0.11	1.83	94 ± 2
	10	10.8 ± 0.13	1.2	95 ± 1
Eggplant	0	1.49 ± 0.01	0.67	-
	5	6.22 ± 0.09	1.45	95 ± 1
	10	11.3 ± 0.1	0.88	98 ± 1
Tomatoes	0	2.92 ± 0.019	0.65	-
	5	7.76 ± 0.19	2.45	97 ± 2
	10	12.39 ± 0.15	1.21	95 ± 1
Garlic	0	0.85 ± 0.01	1.18	-
	5	5.65 ± 0.1	1.77	96 ± 2
	10	10.81 ± 0.2	1.85	99 ± 2
Ginger	0	0.95 ± 0.02	2.11	-
	5	5.83 ± 0.08	1.37	98 ± 1
	10	10.54 ± 0.09	0.85	96 ± 1
Paper Mint	0	1.65 ± 0.06	3.64	-
	5	6.7 ± 0.07	1.04	101 ± 1
	10	11.64 ± 0.09	0.77	100 ± 1
Cinnamon	0	0.47 ± 0.01	2.13	-
	5	5.44 ± 0.09	1.65	99 ± 2
	10	10.27 ± 0.1	0.97	98 ± 1
Bell paper	0	1.94 ± 0.04	1.55	-
	5	6.62 ± 0.12	1.8	94 ± 2
	10	11.53 ± 0.09	0.78	96 ± 1

4.11 Comparison of the method with other studies

As can be shown in Table 4.10, different approaches have been compared with the characteristic data of the present biosorption methods for determining the concentration of cadmium in food and drink samples. Comparisons are made between the studies that are shown in this table with regard to the method, instrument, detection limit, enhancement factor, Preconcentration factor, Relative standard deviation, and adsorption capacity that were being used.

It has been noted that the magnetic adsorption technique that we developed has a lower detection limit than some previous research while being higher than other methods published in the literature. Compared to previous approaches, the current biosorption method utilizing *E.coli* bacteria attached to magnetic conductive carbon black (Vulcan XC-72) nanoparticles offers a very high preconcentration factor compared to other methods. It is suitable for processing large sample volumes of up to 30 ml, requires a smaller volume of acid for efficient analyte elution, and produces more sensitive results. Moreover, the enhancement factor exceeds that of other approaches. With the exception of three study techniques, the investigation of the precision of the magnetic biosorption method we created has a lower relative standard deviation than other previous research described in the published literature. In addition, the high adsorbent capacity, among other methods, has a notable ability for adsorption, which suggests its large surface area for removing cadmium from the sample matrix. This approach offers benefits in terms of content and speed while reducing the influence of interferences from other elements.

Table 4.10 Comparing the magnetic biosorbent composite with other methods

Method	Detector	LOD($\mu\text{g.L}^{-1}$) ^a	EF ^b	PF ^c	(RSD%) ^d	AC(mg.g^{-1}) ^e	Refra.
Biosorption	FAAS	0.15	-	31	3.97	-	(Cajamarca et al., 2016)
Biosorption	FAAS	0.25	-	10	1.21	-	(TEĞİN et al., 2023)
Um-SPμE	FAAS	0.065	80.4	71.4	4.52	-	(Lashari et al., 2023)
S-SADF-LPME-SQT	FAAS	0.65	-	96.9	-	-	(Topal et al., 2021)
DI-SPME	GF-AAS	0.005	25	-	2.1	1.5	(Yang et al., 2021b)
HDES-LPME	FAAS	1.6	43	-	3.3	-	(Çıtak & Sabancı, 2021b)
UA-DES-LPME	FAAS	0.73	57	50	2.1	-	(Yahya et al., 2021)
Magnetic SPME	FAAS	0.07	84	100	1.8	82.1	(Altunay et al., 2021)
MSPE	FAAS	0.69	40	40	-	1.43	(M. Khan et al., 2021)
M-d-μSPE	HR-CS-FAAS	1.3	4.9	5	2.1	-	(Soylak et al., 2023)
RS-CPE	ICP-OES	0.01	30	-	<2.81	-	(W. Wen, 2022)
SPE	FAAS	0.093	39.8	40	3.8	-	(M. Khan et al., 2022)
VA-DMSPE	GF-AAS	0.09	33.14	33.14	<0.543	-	(dos Santos Morales et al., 2022)
Magnetic Biosorption	FAAS	0.6	88	100	1.88	90.3	This study

a: Limit of detection ($\mu\text{g.L}^{-1}$), **b:** Enhancement Factor, **c:** Preconcentration Factor, **d:** Relative Standard Deviation(%), **e:** Adsorption Capacity (mg.g^{-1})

FAAS: Flame atomic absorption spectrometry; **GF-AAS:** Graphite furnace atomic absorption spectrometry; **HR-CS-FAAS:** High-Resolution Continuum Source Flame Atomic Spectrometry; **ICP-OES:** inductively coupled plasma optical emission spectrometry **Um-SP μ E:** Ultrasound-assisted modified solid-phase microextraction; **S-SADF-LPME-SQT:** Simultaneous - spray assisted droplet formation-liquid phase microextraction-slotted quartz tube; **DI-SPME:** Direct immersion solid-phase microextraction; **HDES-LPME:** Hydrophobic deep eutectic solvent-liquid phase microextraction; **UA-DES-LPME:** Ultrasound-assisted deep eutectic solvent-based liquid-phase microextraction; **MSPE:** Magnetic Solid phase extraction; **M-d- μ SPE:** magnetic dispersion micro-solid phase extraction; **RS-CPE:** Rapid synergistic cloud point extraction; **SPE:** Solid phase extraction; **VA-DMSPE:** Vortex-assisted dispersive magnetic solid-phase extraction

CONCLUSIONS

The study of trace elements may be achieved via the use of a wide variety of spectroscopic methods. Nevertheless, the direct determination of trace elements in a sample presents difficulties due to the fact that such low concentrations fall below the detection limit of many instruments, in addition to the impact of matrix effects. Therefore, as a basis of this thesis research, a new enrichment process was developed to assist in the identification of trace amounts of cadmium. This technique has shown its effectiveness in achieving these requirements. With this method, analyses could be carried out at low concentrations with a single sample preparation, guaranteeing high accuracy and precision. When it comes to assessing trace elements, the approach is advantageous because of its wide linear range, low detection limit, and minimum chemical interference.

This thesis provides a new method that combines magnetic biosorption with FAAS to detect small amounts of cadmium ions in food and drink samples. Cadmium is extracted using *E. Coli* bacteria that are attached to magnetically CCB(VXC-72), working as a new composite adsorbent for the enrichment process. The recovery of cadmium ions was optimized by investigating several factors such as pH, sample volume, vortex duration, and adsorbent quantity. The preconcentration factor was calculated in order to determine the detection limit of the method. In order to evaluate the precision and accuracy of this enrichment technique. The novel magnetic biosorbent applied for analysis NIST SRM 1570a Spinach Leaves.

The research started with the optimization of the parameters since it was recognized that they have a significant influence on the recovery of Cd(II). Factorial design were applied for this purpose. Trace amounts of analyte ions were recovered using the developed method in an environmental model solution. However, real samples from the environment where the element of interest is found frequently include other species that are not present in the used model solution and may cause a matrix effect. Thus, the impacts on the recovery of analyte ions preconcentrated by the recommended microextraction process were studied as several alkali and alkaline earth cations, anions, and trace metals, also known as interfering ions, probably present in environmental samples, and could interfere with FAAS results. These

potentially interfering species were deliberately introduced into model solutions, which were then buffered to pH 5 before the microextraction process was carried out. Remarkably, the methodology demonstrated a high degree of tolerance, as quantifiable recovery values were obtained for every ion tested. This robustness of the technique assures the audience of its reliability and accuracy, even in the presence of potentially interfering substances.

A novel magnetic biosorbent was developed to achieve high analytical evaluation performance for microextraction purposes. This technique was then applied to increase the concentration of Cd(II) in different drinks and food products, and the concentration was measured utilizing FAAS. Using flame atomic absorption spectrometry (FAAS), the approach makes it possible to accurately determine the amount of cadmium present in samples that have been prepared in a variety of liquid and aqueous solutions. In light of the fact that human activity has increased the amount of cadmium in the environment, which may enter the food chain and induce toxicity in a variety of food samples, a number of significant food samples that hold important dietary were examined since this study focused on evaluating the toxicity level of cadmium in various kinds of food items, such as canned fish, mushrooms, garlic, ginger, bell peppers, cinnamon, peppermint, tomatoes, eggplant, cucumber, parsley, and apples were selected for study. Furthermore, the efficacy of the approach was evaluated in extracting cadmium from a diverse range of samples, including mixed fruit juice, tap water, potable water, river water, and mineral water, all of which often contain foreign ions. The results were encouraging, indicating that the presence of foreign ions had a negligible impact on the quantitative recovery of cadmium. This versatility of the approach in handling complex sample matrices instills optimism about its potential for practical applications in the analysis of environmental samples.

Finally, this method shows exceptional efficacy as a result of a greater preconcentration factor, enhancement factor, and adsorption capacity compared to other methods described in this research, with a lower detection limit, greater preconcentration and enhancement factors, and higher adsorption capacity. In addition, unlike several techniques, there is no need for a filtering process to remove the adsorbent from the aqueous solution after adsorption. Instead, a strong neodymium magnet is used for this purpose, providing an important time-saving benefit to the thesis research. Furthermore, it provides an application with simple and efficient

procedures, a more friendly environment, and more economical cadmium analysis than other microextraction methods since this approach does not involve the use of organic solvents and is free from high-hazard waste production. This approach is also useful because it can be applied to measure cadmium concentrations in different kinds of samples with even higher sample volumes due to its high preconcentration factor, availability, and decreased use of reagents. Furthermore, the approach may be used even when very few samples are available. Using a flame atomic absorption spectrometer for analysis provides a notable benefit compared to other expensive analytical procedures.

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