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**Possibility of Dye Removal from Water by Alternating Two
Processes: Electro-Fenton and Electrocoagulation**

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Thanks



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أما بعد، أتوجه بخالص الشكر والامتنان إلى أستاذي المشرف **الدكتور هرباجي عبد المجيد** على دعمه وتوجيهاته القيمة طيلة فترة هذا العمل. كما أشكر **الدكتور أيت بارة عادل**، مساعد المشرف، على ملاحظاته البناءة ومساندته المتواصلة. لقد كنتم سندا حقيقيا في إنجاز هذا البحث، فلكما مني كل التقدير. وإنّ إشرافكما الكريم، وما منحتما من وقت وجهد، كان له الدور الأبرز في إخراج هذه الرسالة العلمية بالصورة التي هي عليها اليوم.

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لجميع هؤلاء المساهمين، أتقدم بجزيل الشكر والاحترام والامتنان

Kherabi Abba





Dedication

فرحين بما اتاهم الله من فضله

اهدي ثمرة جهدي المتواضع

الى من وهبوني الحياة والامل والنشأة على شغف الاطلاع والمعرفة ومن علموني ان ارتقي سلم الحياة بحكمة
وصبر، برا واحسانا و وفاء لهما

الى من كلفه الله بالهيبة والوقار، الى من علمني العطاء بدون انتظار، الى من احمل اسمه بكل افتخار، الى
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الى كل من ساعدني وكان له دور من قريب او من بعيد في اتمام هذه الدراسة، سائلة المولى ان يجزي الجميع
خير جزاء في الدنيا والاخرة

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الى نفسي التي لم تخذلني يوما.... والتي علمتني ان القوة ليست في الوصول، بل في الاصرار على الاستمرار
لقد كنت قوية و مازلت

ثم الى كل طالب علم سعى بعلمه ليفيد الاسلام و المسلمين بكل ما اعطاه الله من علم و معرفة

بكل فخر و امتنان

Kherabi Abba



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List of abbreviation:

AOPs – Advanced Oxidation Processes

BOD – Biological Oxygen Demand

CD – Current Density

COD – Chemical Oxygen Demand

DS – Dissolved Solids

DO – Dissolved Oxygen

EAOPs – Electrochemical Advanced Oxidation Processes

EC – Electrocoagulation

EF – Electro-Fenton

Fe²⁺ / Fe³⁺ – Ferrous / Ferric ions

H₂O₂ – Hydrogen Peroxide

NTU – Nephelometric Turbidity Unit

O.M. – Organic Matter

ORR – Oxygen Reduction Reaction

pH – Potential of Hydrogen (acidity/alkalinity indicator)

Rpm – Rotation per minute

TDS – Total Dissolved Solids

TOC – Total Organic Carbon

UV-Vis – Ultraviolet–Visible Spectroscopy (implied in analysis)

λ_{max} – Wavelength of Maximum Absorbance

General Introduction

Hydrogen and oxygen—two of the most abundant elements in the universe—combine to form water, a substance that is widely distributed throughout the solar system. On Earth, water exists naturally in all three physical states—liquid, solid, and gas—and covers approximately 71% of the planet's surface. Of this amount, about 96.5% is contained in the oceans [1]. Although the planet holds sufficient freshwater to meet the needs of its global population—currently estimated at around eight billion people—this resource is unevenly distributed across both space and time. Moreover, a significant portion is wasted, polluted, or exploited unsustainably. Consequently, access to safe drinking water remains a persistent challenge in many parts of the world. While water scarcity can arise from natural factors, it is frequently intensified by anthropogenic activities [2].

In Algeria, water resources have been severely strained by prolonged droughts in recent years. This situation is further exacerbated by pollution, primarily from industrial and agricultural activities, which is most concentrated in the northern regions of the country [3].

Among the various forms of water pollution, contamination by synthetic dyes represents a major environmental concern. These dyes are extensively used in industries such as textiles, cosmetics, food, and pharmaceuticals. However, they are often discharged into wastewater without adequate treatment. Their complex aromatic structures, high chemical stability, and low biodegradability render them resistant to conventional biological treatment methods, resulting in significant ecotoxicological risks [4]. Additionally, synthetic dyes reduce light penetration in aquatic environments, thereby disrupting photosynthesis and disturbing aquatic ecosystems [5].

In response to the limitations of conventional wastewater treatment techniques, electrochemical processes—particularly electrocoagulation (EC) and the electro-Fenton (EF) process—have emerged as promising alternatives for the removal of persistent organic pollutants. Electrocoagulation involves the electrolytic dissolution of metal electrodes, typically iron or aluminum, which generates coagulant ions that promote the flocculation and sedimentation of pollutants [6]. This method is appreciated for its simplicity, efficiency, and cost-effectiveness.

In contrast, the electro-Fenton process relies on the in situ generation of hydrogen peroxide and hydroxyl radicals ($\bullet\text{OH}$), highly reactive species capable of breaking down complex organic compounds [7]. These two methods are complementary: while one enables

the physical removal of pollutants, the other ensures their chemical degradation. Recent studies have highlighted the advantages of combining or alternating these processes to enhance treatment efficiency and reduce operating costs. For instance, Bouafia et al. demonstrated the effectiveness of a sequential system combining EC and EF for treating synthetic dye effluents. Using three-dimensional electrodes composed of aluminum and graphite, they achieved a 99.91% color removal rate and significant reductions in chemical oxygen demand (COD) and total organic carbon (TOC). Furthermore, the treated effluents exhibited improved biodegradability, allowing for subsequent biological treatment[8].

This work aims to evaluate the feasibility and effectiveness of alternating between electro-Fenton and electrocoagulation processes for the removal of synthetic dyes from wastewater. The study seeks to assess the synergistic potential of these two techniques when applied in combination or sequence, to optimize operational parameters such as pH, current density, electrolysis time, and electrode material, and to propose a sustainable treatment approach applicable to industrial effluents. The ultimate goal is to contribute to the development of more environmentally responsible and efficient methods for treating dye-contaminated wastewater.

The thesis is divided into three chapters:

- Chapter 1 discusses the environmental impact of synthetic dyes and their role in water pollution.
- Chapter 2 provides a bibliographic review of electrochemical processes used in dye treatment, including electro-Fenton and electrocoagulation.
- Chapter 3 concentrates on the experimental setup, including the presentation, interpretation, and discussion of the experimental results, as well as the materials, apparatus, and analytical techniques that were utilized in the study.
 - Impact of pH on Process Performance
 - Impact of Applied Current Intensity
 - Influence of Initial Dye Concentration
 - Evaluation of the Combination of Both Processes
 - Performance Analysis Based on Experimental Parameters
 - Comparison with Literature Data

In conclusion, we provide a concise overview of the primary discoveries from this investigation and suggest potential avenues for future research to further develop the outcomes.

I. Chapter I: Water Pollution and the Impact of Dyes

Water is the essence of life, supporting all human activities—from sustaining ecosystems to enabling industry and daily consumption. However, water pollution remains a pressing global issue, with industrial dyes among the most harmful contaminants to aquatic ecosystems due to their widespread use in everyday human life (e.g., in the textile, food, cosmetic, and pharmaceutical industries).

As a result, discharging such colored water into natural environments is considered inappropriate, as it can degrade water quality and negatively affect aquatic organisms, posing risks to human health. These dyes often contain chemical compounds capable of altering the visual appearance of materials and liquids.

Hence, it is essential to understand the interactions between water and dyes, as well as the treatment methods that can mitigate their environmental impact[9].

I.1 Water Pollution: An Environmental Issue

According to the 2021 UNESCO World Water Development Report, global freshwater use has increased six fold over the past century. This dramatic rise is driven by rapid population growth, economic development, the expansion of irrigated agriculture, and changing consumption patterns, all of which have contributed to the emergence of two major global challenges: water scarcity and water pollution.

Today, these challenges pose serious threats to human health, environmental integrity, and sustainable development. Alarmingly, water pollution is estimated to cause the deaths of nearly 14,000 people every day. Modern industrialization, intensive agricultural production, and rapid urbanization have led to significant environmental degradation and pollution. These developments have directly impacted vital water bodies such as rivers and oceans—resources essential for life—thereby affecting public health and impeding sustainable social development.

Globally, it is estimated that approximately 80% of industrial and municipal wastewater is discharged into the environment without any prior treatment, resulting in serious harm to both human health and ecosystems. This percentage is even higher in less developed countries, where wastewater treatment facilities and sanitation infrastructure are either inadequate or completely lacking[9].

I.1.1 Definition of Water Pollution

Pollution is defined as the introduction of foreign substances into a natural environment, resulting in its alteration. Such disturbances can have harmful effects at multiple levels—including health, ecological, and economic. For instance, particulate pollutants contribute to increased water turbidity and siltation, among other impacts. A common and immediate way to classify these compounds is based on their size (see Table I 1).

Table I1. Classification of effluent compounds according to their size

Classification	Diameter	Characteristic	Example of compound
Soluble	<0.08 μm		Simple carbohydrates, amino acids, volatile fatty acids, proteins, polysaccharides (starch, cellulose)
Colloidal	0.08-1 μm	Boundary between solid and soluble phase	Fats free bacteria cellular debris....
Supra-colloidal	1-100 μm	Fine suspended matter, visible, to the naked eye, contributes to water turbidity	Cellulosic fibers, lipid aggregates, bacterial flocs, macro-proteins....
Particle	>100 μm		

[10]Water pollution refers to the contamination of water bodies—such as lakes, rivers, oceans, aquifers, and groundwater—by substances that are harmful to living organisms and the environment. This contamination is often the result of human activities, including industrial processes, agricultural runoff, improper waste disposal, and sewage discharge. Common pollutants include chemicals, microorganisms, plastics, heavy metals, and excess nutrients, all of which degrade water quality and disrupt aquatic ecosystems [11].

I.1.2 Indicators and Parameters of Water Quality

Water quality is assessed using a range of physical, chemical, and biological indicators. These parameters help determine the condition and suitability of water for various uses, including drinking, agriculture, industry, and recreation. Regular monitoring of these indicators is essential to safeguard aquatic ecosystems and protect public health[11].

I.1.2.1 Chemical parameters

Chemical parameters are a crucial aspect of assessing water quality and understanding the properties of various substances.

A. Hardness (total): Hardness is a term used to describe the characteristics of water with high mineral content. The dissolved minerals in water cause problems such as scale buildup in hot water pipes and difficulty in forming soap lather. Calcium (Ca^{2+}) and

magnesium (Mg^{2+}) ions are responsible for most of the hardness in natural water. It reflects the nature of the geological formations the water has been in contact with[12] see **Figure I 1** and **Table I 2**.

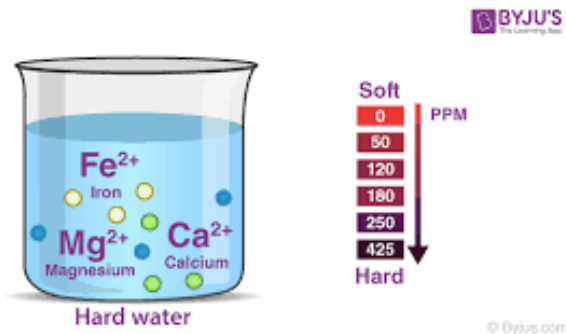


Figure I 1.water hardness [13]

Table I 2.Classification of water hardness[13]

Hardness range mg/l as $CaCO_3$	Degree of hardness
0-75	Soft
75-150	Moderately soft
150-300	Hard
Above 300	Very hard

B. Dissolved oxygen (DO): One of the most important water quality parameters is the amount of dissolved oxygen present. It is the amount of oxygen in the dissolved state in the water/wastewater see **Figure I 1**. DO determination helps to find the efficiency of biological treatment and good quality of fresh water[14]. These are the factors that affect DO levels:

- Temperature;
- Photosynthetic activity;
- Decomposition activity;
- Mixing and turbulence.

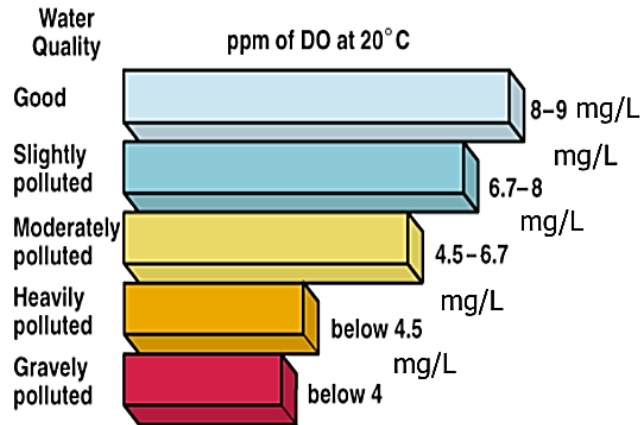
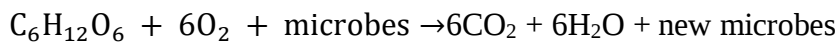


Figure I 2. ppm of DO at 20°C

C. Biological Oxygen Demand (BOD): BOD is defined as the amount of oxygen required by bacteria in decomposing organic material in a sample under aerobic condition at 20°C over a period of 5 days see Figure I 3.



This converts the major elements present in plant matter (C, H, N, S) into CO_2 , H_2O , NO_3^- and SO_4^{2-} , respectively. If no oxygen is present in the water, organic material will still be broken down. Instead of the material being oxidized, it is reduced. The process is once again microbiological and is known as anaerobic decay, The final products are CH_4 , NH_3 , and H_2S , Iron in the form of Fe^{2+} can deplete oxygen by oxidation to Fe^{3+} , Because of low solubility of O_2 in water, strong wastes are always diluted [14].

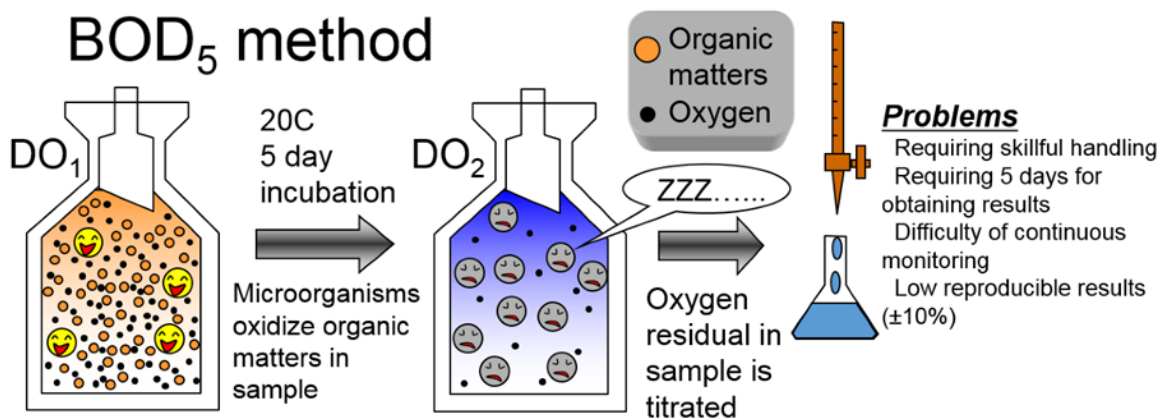


Figure I 3. Schematic diagram of the BOD classical analysis

D. Chemical Oxygen Demand (COD): COD can be defined as amount of oxygen required to chemically oxidize organic matter using a strong oxidizing agent like potassium dichromate ($K_2Cr_2O_7$) under acidic condition (silver nitrate used as a catalyst) see Figure I 4.

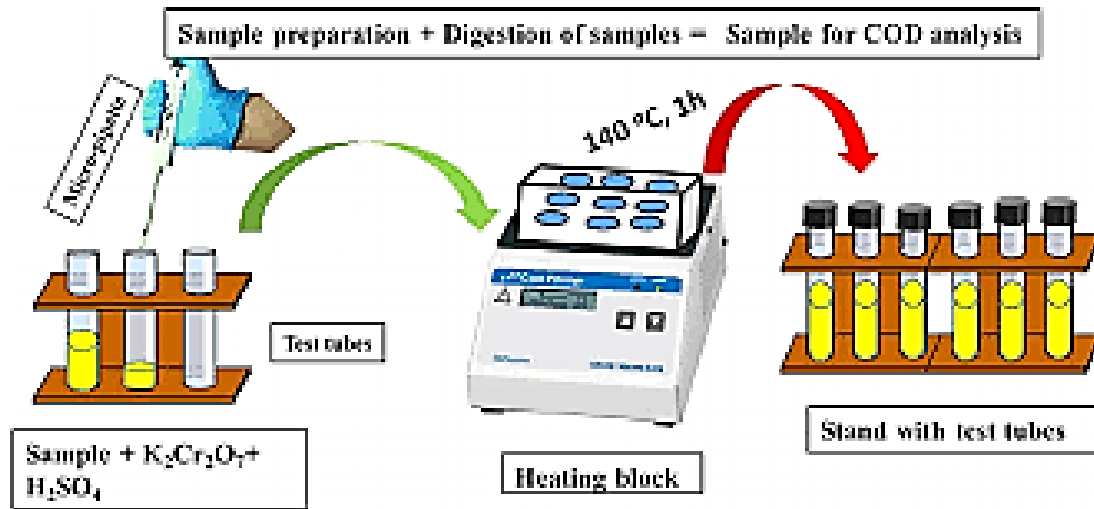
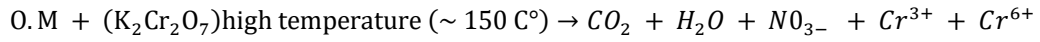


Figure I 4. Schematic diagram of the COD analysis [15]

E-pH potential hydrogen: pH is the negative logarithm of hydrogen ion concentration; more precisely hydrogen ion-activity $pH = -\log[H^+]$ Indicates how acidic or basic water is. Affects chemical reactions and toxicity see **Figure I 5**.

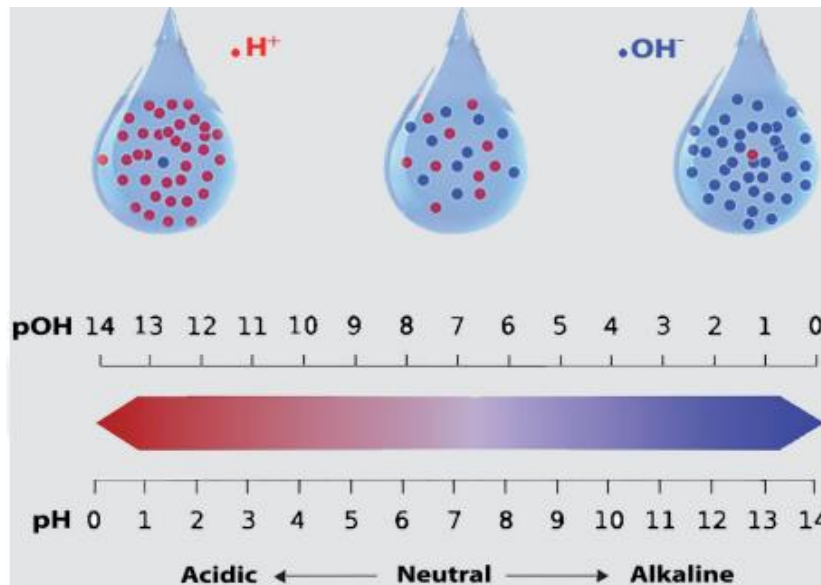


Figure I 5. pH of water[16].

I.1.2.2 Physical parameters:

A. Turbidity: It is a measurement of the clarity of water see **Figure I 6**, used to indicate the quality of water discharge and natural waters with respect to colloidal and residual suspended matter. It is an important measurement for drinking water because

microorganisms usually attach themselves to suspended particles. Turbidity in natural waters reduces light transmittance and affects the species that may live in the water.



Figure I 6. Turbidity of water [17]

Nephelometric used to measure the turbidity of water and wastewater. It measures the amount of scattered light electronically. Expressed in terms of Nephelometric Turbidity Unit (NTU)[18]. Material that causes water to be turbid include:

- Clay
- Silt
- Finely divided organic and inorganic matter
- Soluble colored organic compounds
- Plankton
- Microscopic organisms

B. Electrical conductivity: Reflects the total ionic content in water and is often used as an indicator of salinity[19].

C. Dissolved Solids (DS): DS are substances that are truly in solution and pass through a filter. They are homogeneous and consist of a single phase of the total dissolved solids. About 90% of dissolved solids are in true solution, while the remaining 10% are colloidal. Overall, dissolved solids are approximately 40% organic and 60% inorganic[20].

I.1.2.3 Main Sources of Water Pollution

Water pollution primarily stems from industrialization, agricultural activities, natural causes, and inadequate water supply and sewage treatment infrastructure.

A. Agricultural sources: Agricultural activities contribute significantly to water pollution through various sources:

- **Fertilizers:** Excessive application of nitrogen and phosphorus fertilizers can lead to nutrient runoff into water bodies, causing eutrophication and harmful algal blooms[21].
- **Pesticides and Herbicides:** Chemicals used to control pests and weeds can be washed into rivers, lakes, and groundwater, harming aquatic life and contaminating drinking water sources[22].

15 APHA (2022). Standard Methods for the Examination of Water and Wastewater

- **Animal Waste:** Runoff from livestock farms carries manure, which contains pathogens, nutrients, and organic matter that can pollute water sources[23].
- **Sediment Runoff:** Tilling and plowing soil can increase erosion, causing soil particles to wash into water bodies, which can degrade water quality and harm aquatic ecosystems[24].
- **Irrigation Runoff:** Inefficient irrigation systems can lead to waterlogged soils and runoff carrying salts, fertilizers, and other pollutants into nearby waterways[24].

B. Industrial sources: Industrial activities are a major source of water pollution, with key contributors including the distillery, tannery, pulp and paper, textile, food processing, iron and steel, and nuclear industries. These sectors often release a variety of harmful substances during production, such as toxic chemicals, both organic and inorganic compounds, solvents, and volatile organic compounds.

When industrial waste is discharged into aquatic ecosystems without sufficient treatment, it poses serious threats to water quality. Notably, heavy metals like arsenic, cadmium, and chromium are among the most hazardous pollutants commonly found in industrial wastewater. As urbanization continues to accelerate, the volume of wastewater generated by industrial processes is steadily increasing, intensifying the risk of water contamination[25].

C. Domestic sources: Domestic activities produce large amounts of wastewater from kitchens, bathrooms, laundry, and toilets. This wastewater contains organic matter, food residues, grease, detergents, and pathogens. If it is not properly treated before being discharged, it can lead to the contamination of rivers, lakes, and groundwater, causing health hazards and ecological imbalances[26].

In addition, many household cleaning products, especially laundry and dishwashing detergents, contain phosphates and surfactants. When these chemicals enter the water system, they can stimulate excessive algae growth, leading to eutrophication, which depletes oxygen levels and harms aquatic life[27].

I.1.2.4 Ecological and Health Consequences

Contaminated water poses a significant threat to human health. As highlighted in UNESCO's 2021 World Water Development Report, approximately 829,000 people die each year from diarrheal diseases linked to unsafe drinking water, poor sanitation, and inadequate hand hygiene. Alarming, nearly 300,000 of these deaths are among children under the age of five, representing 5.3% of all deaths in that age group[25].

In addition, water pollution has severe impacts on ecosystems, leading to several key detrimental effects. Nutrient overload from agricultural runoff and wastewater discharges causes eutrophication, which can lead to oxygen-depleting algal blooms. Toxic substances, such as heavy metals and pesticides, reduce aquatic biodiversity and threaten species like the Atlantic salmon[28]. Pollutants also accumulate in aquatic organisms, disrupting food chains and posing health risks to humans. Furthermore, sedimentation and chemical changes in water degrade aquatic habitats, which harms native species and plants[29].

I.2 Dyes and Their Environmental Impact

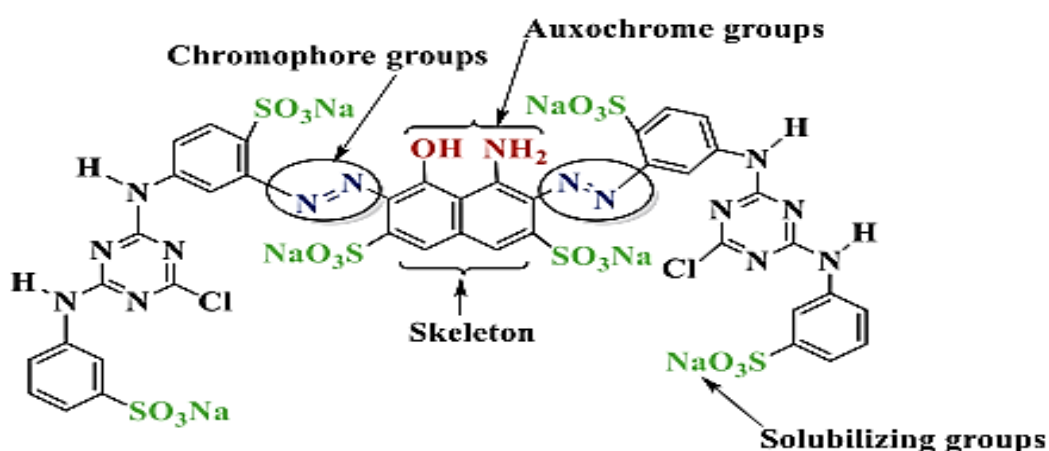
Awareness of dye-related health risks began in the 1890s, focusing on heavy metal content in synthetic dyes. By 1960, toxicological testing became mandatory for all commercial dyes. Research revealed that amine-based dyes could cause skin irritation, eczema, and ulcerations, especially in dye factory workers. Additionally, azo, anthraquinone, and naphthalene-derived dyes were linked to allergic reactions, asthma, and eczematous dermatitis[30].

I.2.1 Definition and Chemical Nature of Dyes

Dyes are colored organic compounds used to impart color to a variety of materials such as textiles, paper, food, hair, and pharmaceuticals[30]. They are defined by their ability to absorb light within the visible spectrum (380 to 750 nm). The conversion of white light into colored light—through reflection, transmission, or diffusion—is the result of selective energy absorption by specific atomic groups known as chromophores. The dye molecule itself is referred to as a chromogen the easier the chromophore can donate an electron, the more intense the resulting color[30]. Each dye possesses a distinct chemical structure that defines its color. In the case of textile dyes, this structure typically comprises three key components **see Figure I 7:**

- A molecular framework (or skeleton),
- Chromophore groups (which are responsible for the dye's color),

- Auxochromes (which enhance the dye's ability to bond with the substrate),
- And solubilizing groups (which determine solubility in water or organic solvents).



Name : C.I.Reactive Blue 171

Molecular Formula : $C_{40}H_{23}Cl_2N_{15}Na_6O_{19}S_6$

CAS Registry Number : 77907-32-5

Molecular Weight : 1418.93(g/mol)

Molecular Structure : Double azo class

Figure I 7. Chemical structure of a textile dye

Auxochromes are functional groups containing lone electron pairs that not only increase color intensity but also play a crucial role in the dye's fixation and interaction with light. While auxochromes alone do not impart color, their presence alongside chromophores in an organic compound intensifies and modifies the color produced.

Thus, a textile dye's effectiveness and appearance rely on the interplay between its chromophore, which imparts color, and its auxochrome, which enhances light absorption and improves substrate affinity [31].

I.2.2 Classification of Dyes

Dyes can be classified according to various criteria [32]:

- **Origin:** They may be natural (derived from plants, animals, or minerals) or synthetic.
- **Chemical composition:** Classification is often based on the type of chromophore they contain, such as azo, anthraquinone, or triarylmethane groups.
- **Application technique:** Dyes are categorized by their method of use, including acid, mordant, direct, reactive, and vat dyes.

- **Solubility:** This criterion distinguishes between dyes, which are soluble in water or organic solvents, and pigments, which are insoluble.

A dye can exist either in solid form—as a pigment—or in solution, in which case it retains the name "dye." A pigment is composed of fine particles that are insoluble in the medium to which they are applied. To adhere to a surface, pigments must be combined with specific additives. In contrast, dyes are used on a wider variety of substrates, including textiles, leather, paper, and hair. The dyeing process typically occurs in the liquid phase, where the dye is partially or fully soluble in a solvent. Unlike pigments, dyes require a specific affinity with the substrate to ensure proper absorption and fixation[33].

Among these approaches, the two most commonly used classifications are based on chemical structure and dyeing properties.

I.2.2.1 Classification based on dyeing properties

- A. Reactive Dyes:** Reactive dyes contain halogen-based reactive groups that form covalent bonds with fibers, becoming an integral part of the fabric structure. These dyes are commonly used for coloring cotton fabrics due to their water solubility and anionic nature. They offer excellent wash fastness, resulting in reduced wastewater generation compared to other dye types. The formation of strong covalent bonds ensures that the dye adheres firmly to the fabric. While primarily used for dyeing cotton, reactive dyes can also be applied to protein-based and polyamide-based materials[34].
- B. Direct dyes:** Due to their strong affinity, these dyes can be applied directly to fabric and are therefore called direct dyes. They are mostly composed of sodium salts of sulfonic or carboxylic acids, with azo being the primary chromophore group. These dyes are water-soluble and anionic in nature. They are commonly used to color cellulose fibers, and also protein fibers [34].
- C. Vat dyes:** Vat dyes are used primarily for application on cellulose fibers, especially cotton, due to their exceptional fastness to a wide range of factors such as washing, bleaching, and light. This high level of fastness is largely attributed to their insolubility in water [35].

I.2.2.2 Classification based on chemical structure

- A. Azo dyes:** Azo dyes represent the largest category of synthetic dyes, accounting for 60% to 70% of the entire dye industry. This is due to their versatility, cost-effectiveness, ease of use, high stability, and intense coloration. Azo dyes are characterized by the azo

functional group (-N=N-) 2, which links two identical or different alkyl or aryl groups (symmetric or asymmetric azo compounds) see **Figure I 8**. These structures, typically based on an azobenzene framework, are aromatic or pseudo-aromatic systems connected to an azo chromophore group [36].

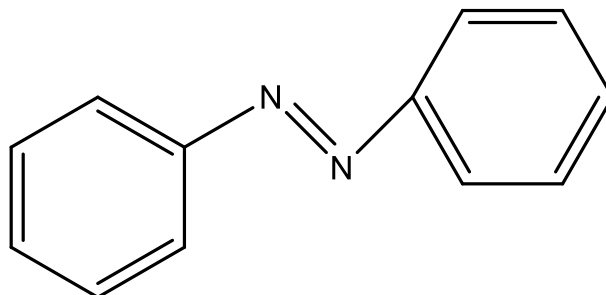


Figure I 8.Chemical structure of an azo dye

B. Triarylmethane dyes: Triphenylmethane dyes are widely used in the textile industry, particularly for dyeing protein fibers such as wool and silk, when they contain two sulfonic acid groups (SO_3H). They can also be used as indicators if they contain only one sulfonic acid group (SO_3H) in their chemical structure see **Figure I 9**. These dyes are known for their water solubility and wide, intense range of colors[37].

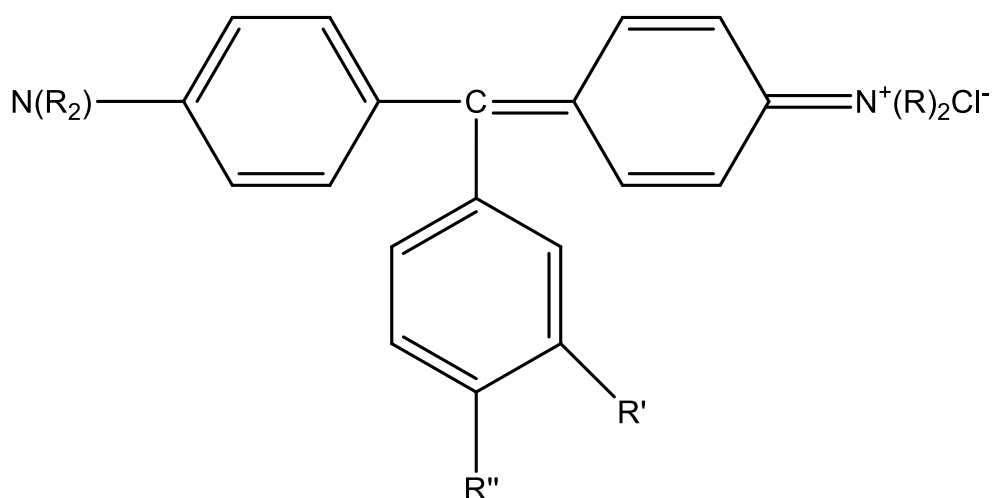


Figure I 9.Chemical structure of triarylmethane dye

C. Triphenylmethane dyes: From a commercial perspective, these dyes are the most important after azo dyes. Their general formula see **Figure I 10** is derived from anthracene, indicating that the chromophore is a quinonoid nucleus containing hydroxyl or amine groups [38].

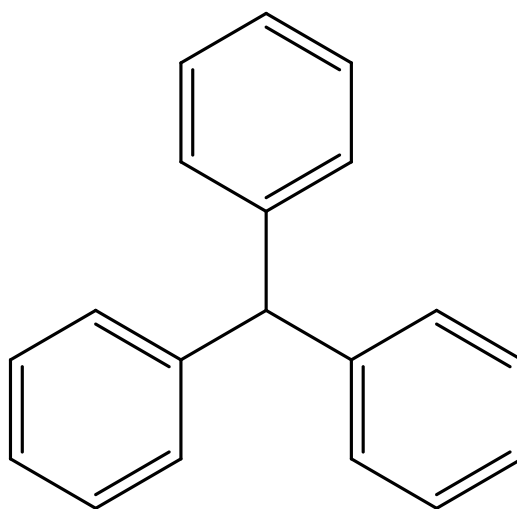


Figure I 10. Chemical structure of triphenylmethane dye

D. Anthraquinone dyes: Anthraquinone compounds have long been widely used in the textile dyeing industry, especially for red dyes. These dyes are known for their water solubility, bright colors, and excellent fastness properties. The anthraquinone structure see **Figure I 11** can also form linkages with azo dyes[37].

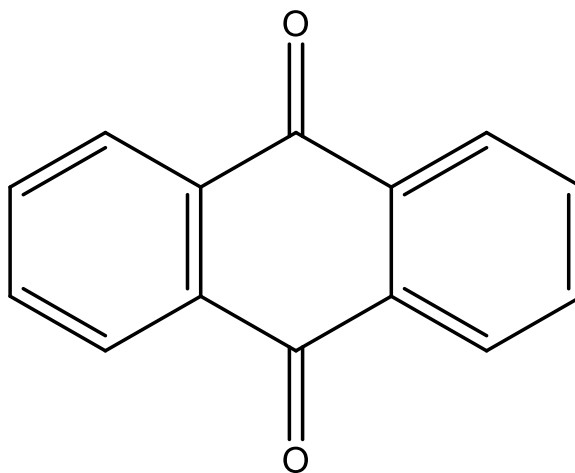


Figure I 11. Chemical structure of anthraquinone dye

I.2.2.3 Industrial Uses of Dyes

For a dye to be suitable for use, it must exhibit four essential properties[39]:

- It must have color.
- It should be soluble in water and/or an organic solvent.
- It must have the ability to be absorbed and retained by a fiber (substantivity) or to form a chemical bond with it (reactivity).
- It should be resistant to washing, dry cleaning, and exposure to light.

There are many different industrial sectors that use dyes, as shown in the **Table I 3**.

Table I 4. Some important aspects of the applications of synthetic dyes in the service sectors and in industry [40]

Sectors	Dyes Used	Application
Cosmetics	• Pigments are the main colorants used in the cosmetic industry. • Dyes are also used, but in smaller amounts. • Over 80% of colorants used are organic compounds. • Azo pigments make up more than 60% of the organic colorants.	• Lipsticks, blushers, eye shadows, eyeliners, nail polishes, and hair dyes are major cosmetic products. • Hair dyes alone represent nearly 80% of cosmetic products in Europe.
Food and Pharmaceutical	• Over 60 synthetic dyes are currently approved for food products. • Some colorants, like Tartrazine, must be used within regulated maximum limits.	• Examples of products containing colorants include carbonated beverages, fruit juices, energy drinks, candies, cereals, desserts, and snacks.
Leather and Tanning	• Most leather is dyed with azo dyes or metal complex dyes. • The dye structures used in leather often differ from those in textile applications.	• About 1% to 10% of pigments used in the leather industry are lost as waste. • The amount of pigment loss varies based on tanning and dyeing technologies used.

I.2.3 Toxicity and Environmental Effects of Dyes

The textile industry produces large amounts of highly contaminated wastewater containing dyes, salts, chemicals, and heavy metals like lead, chromium, and arsenic. Processing 20,000 kg of textiles can generate over 3,000 liters of wastewater daily. About 40% of dyes contain carcinogenic organochlorine compounds. Dyes are persistent in the environment because of their thermal and photo-stability. Azo dyes, commonly used on cotton, are particularly resistant to conventional treatment methods, posing serious environmental and health risks[31].

Textile dyes reduce sunlight penetration in water, hindering photosynthesis in algae and aquatic plants, which disrupts the food chain and re-oxygenation of water bodies. Their persistence in the environment leads to toxic effects, accumulation in sediments and aquatic species, and potential formation of carcinogenic or mutagenic compounds [41].

I.2.4 Regulations and Restrictions on Dye Discharges

In the European Union, the use of azo dyes in consumer products—such as cosmetics, clothing, toys, and food—is strictly regulated. Under the REACH regulation (Registration, Evaluation, Authorization, and Restriction of Chemicals), 24 aromatic amines have been identified as hazardous and toxic to human health. As a result, azo dyes that can release 30 mg/kg or more of these amines are banned in products intended for direct and prolonged contact with the skin. Additionally, REACH restricts the use of other colorants to concentrations below 0.1% of the total product weight [41].

II. Chapter II: Electrochemical Processes for Dye Treatment

II.1 Electrochemical Processes for Dye Treatment

In the previous chapter, we discussed the toxicity and environmental impacts of dyes when discharged with wastewater from various industrial processes, which have become a significant environmental challenge due to their toxicity, persistence, and aesthetic impact on natural water bodies. Many synthetic dyes are resistant to biodegradation and conventional treatment methods, leading to their accumulation in aquatic environments and potentially causing harm to ecosystems and human health.

Electrochemical processes have emerged as an effective and sustainable alternative for dye removal from wastewater. These methods rely on electrochemical reactions to degrade dye molecules or convert them into less harmful substances. They offer several advantages, including high treatment efficiency, versatility, minimal use of chemicals, and the potential for complete mineralization of pollutants.

- In this chapter, we will explore the principles, types, advantages, and limitations of electrochemical treatment processes for dyes, highlighting their role in developing
- environmentally friendly water treatment technologies[42].

II.2 Electro-Fenton Process: An Advanced Oxidation Process

Electrochemical advanced oxidation processes (EAOPs) based on Fenton's reaction chemistry have recently gained significant attention as environmentally friendly methods for water treatment. Among these, the electro-Fenton (EF) process stands out as the most widely studied.

The Electro-Fenton process stands apart from conventional electrochemical methods and advanced oxidation processes (AOPs) by producing the key reagents—hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+})—in situ, without the need for external chemical additives.

These reagents then initiate hydroxyl radical formation via the Fenton reaction. Specifically, molecular oxygen and ferric ions are simultaneously reduced at the cathode, generating H_2O_2 and Fe^{2+} [43].

Furthermore, since the process is powered by electricity—a clean energy source—it minimizes the formation of secondary pollutants. The absence of hazardous chemical reagents also reinforces its status as an environmentally sustainable solution for water and wastewater treatment[44].

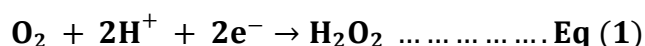
II.2.1 Principle of the Electro-Fenton Process

The electro-Fenton (EF) process is an advanced oxidation process (AOPs) that integrates electrochemistry with Fenton's reaction to generate hydroxyl radicals ($\bullet\text{OH}$) for the degradation of organic pollutants in water and wastewater treatment[45].

II.2.2 Generation of Hydroxyl Radicals and Oxidation Mechanism

The core mechanism of the electro-Fenton process involves the in situ generation of hydrogen peroxide (H_2O_2) and the catalytic production of hydroxyl radicals through the following steps[45]:

- **Electrochemical Generation of H_2O_2 :** The EF process operates through the in situ generation of hydrogen peroxide via the two-electron reduction of oxygen at the cathode surface in an acidic medium, as shown in Eq. (1).



- **Fenton Reaction:** This hydrogen peroxide then reacts with externally added ferrous ions in the electrolytic cell, triggering Fenton reactions that produce highly reactive hydroxyl radicals (Eq. 2).



- **Regeneration of Fe^{2+} :** The ferric ions formed during these reactions are subsequently reduced back to ferrous ions at the cathode (Eq. 3), thus sustaining the Fenton reaction cycle.



This cycle allows for the continuous production of $\bullet\text{OH}$ radicals, which are highly reactive and non-selective oxidants capable of degrading a wide range of organic contaminants.

The typical mechanism of the E-F process is illustrated in **Figure II 1**.

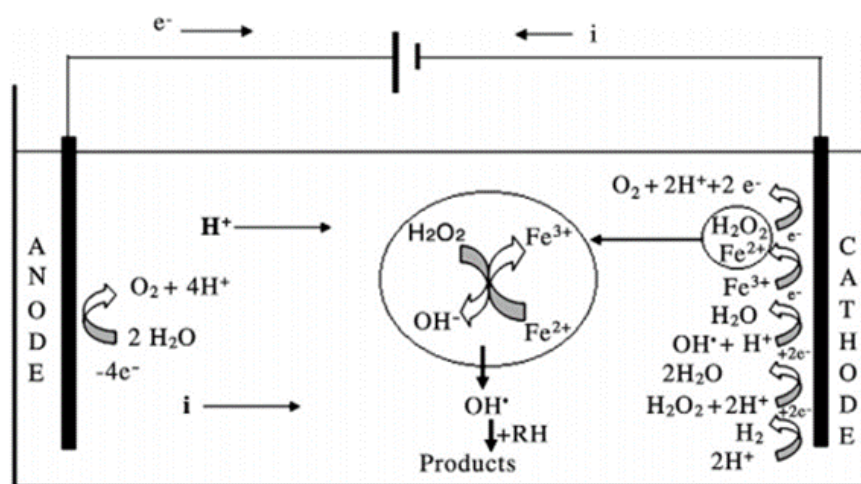


Figure II 2. Reaction mechanism of E-Fenton process [46]

II.2.3 Influence of Experimental Parameters

The efficiency of the Electro-Fenton (EF) process depends on several operational parameters, including pH, electrolyte composition, applied current, concentration of catalyst (Fe^{2+}) and duration of treatment.

- **Solution pH:** pH is particularly critical, with an optimal value around 2.8 and a functional range between 2.5 and 3.5. Higher pH causes iron precipitation, while lower pH leads to the formation of less reactive peroxonium ions, reducing process efficiency[47]. Fenton's process is very effective at pH 3, and most of the case external addition of acid is required for adjusting the required pH[47].
- **Applied current intensity :** Current density is a pivotal parameter in the Electro-Fenton (EF) process, significantly influencing the generation of reactive species[48].
 - ✓ Increasing current density enhances the production of hydrogen peroxide (H_2O_2) at the cathode and the regeneration of ferrous ions (Fe^{2+}) from ferric ions (Fe^{3+}).
 - ✓ This amplification accelerates the Fenton reaction, leading to a higher generation of hydroxyl radicals ($\bullet\text{OH}$), which are crucial for degrading organic pollutants.
- **Concentration of catalyst (Fe^{2+})** Fe^{2+} reacts with electrochemically generated hydrogen peroxide (H_2O_2) to produce $\bullet\text{OH}$ through the Fenton reaction [49].
- **More Fe^{2+} = More $\bullet\text{OH}$,** up to a point, increasing degradation efficiency.
 - ✓ -At **low Fe^{2+} concentrations**, the generation of $\bullet\text{OH}$ is insufficient, leading to lower degradation rates.
 - ✓ -At **high Fe^{2+} concentrations**, excess Fe^{2+} can **scavenge $\bullet\text{OH}$ radicals**, reducing their availability for attacking pollutants

- **Nature and concentration of the electrolyte:** Adding a supporting electrolyte salt to the solution facilitates the flow of current by increasing the conductivity of the solution according to the expression for total conductivity:

$$\gamma_{\text{sol}} = \sum z_i \cdot C_i \cdot \lambda_i \text{ (S/m)}$$

- **Treatment duration:** Treatment duration (or reaction time) significantly influences the efficiency of pollutant degradation
 - ✓ **Longer treatment time** generally allows for more generation of hydroxyl radicals ($\bullet\text{OH}$), which are the main oxidizing agents.
 - ✓ This can lead to **greater breakdown of complex organic pollutants** into smaller, less harmful molecules or complete mineralization (conversion to CO_2 and H_2O).

II.2.4 Advantages and Limitations of the Electro-Fenton Process

In recent years, the Electro-Fenton (EF) process has emerged as one of the most widely applied approaches among electrochemical advanced oxidation processes (EAOPs). However, it is important to consider both the advantages and limitations of the EF method[50]. The **Table II 1** represent some of advantages and drawbacks of the process:

Table II 2. Advantages and drawbacks of E-fenton process[50]

Advantages	Drawbacks
✓ Utilization of a low-cost and readily available catalyst source ✓ In-situ generation of both H_2O_2 and Fe^{2+} enhances $\bullet\text{OH}$ production in solution, thereby improving process efficiency ✓ Employment of inexpensive cathode materials for hydrogen peroxide generation via the oxygen reduction reaction (ORR).	✓ The formation of Fe^{3+} complexes during the process poses challenges for their removal at the end of treatment, ✓ The EF process operates optimally under acidic conditions (pH 2.8–3.5), necessitating a final neutralization step to ensure environmentally acceptable effluent discharge, ✓ Hydrogen evolution at the cathode can compete with the oxygen reduction reaction, thereby reducing the efficiency of H_2O_2 generation.

II.2.5 Recent Studies on Electro-Fenton Applications

Recent advancements have focused on addressing several limitations that hinder the large-scale industrial implementation of the Electro-Fenton process. These include the use of heterogeneous catalysts such as pyrite (EF-pyrite), integration with biological treatments (bio-EF), and the incorporation of solar energy (solar photo-EF, discussed in a separate chapter). Significant progress has also been made in the development of more efficient electrode materials.

II.3 Electrocoagulation process: coagulation process assisted by electrochemistry

Electrocoagulation (EC) is an electrochemical process that employs a low electric current to remove heavy metals from aqueous solutions. It is also effective in treating wastewater containing tannins, dyes, dissolved metals, and suspended solids. In wastewater, many pollutants remain dissolved due to their electrical charges. The EC process introduces oppositely charged ions, which neutralize these particles, leading to their destabilization and subsequent precipitation in a stable form.

Electrochemical treatment methods are known for being rapid, straightforward, cost-effective, environmentally friendly, and easy to operate. Additionally, the treated water is typically clear, odorless, colorless, and suitable for reuse, with minimal sludge production and no risk of introducing secondary pollutants[51].

II.3.1 Principle of Electrocoagulation

Electrocoagulation operates based on redox reactions—oxidation occurs at the anode, where the sacrificial electrode dissolves, and reduction takes place at the cathode, producing hydrogen gas. This process generates in-situ coagulants, eliminating the need for added chemicals.

When direct electric current is applied, metal ions are released from the anode, while hydroxyl ions and hydrogen gas form at the cathode. These metal ions interact with hydroxyl ions to form metal hydroxides, which act as effective coagulants, enabling the destabilization and aggregation of contaminants see **Figure II 3**. Thus, electrocoagulation offers a chemically minimal and efficient alternative for water and wastewater treatment[52], [53].

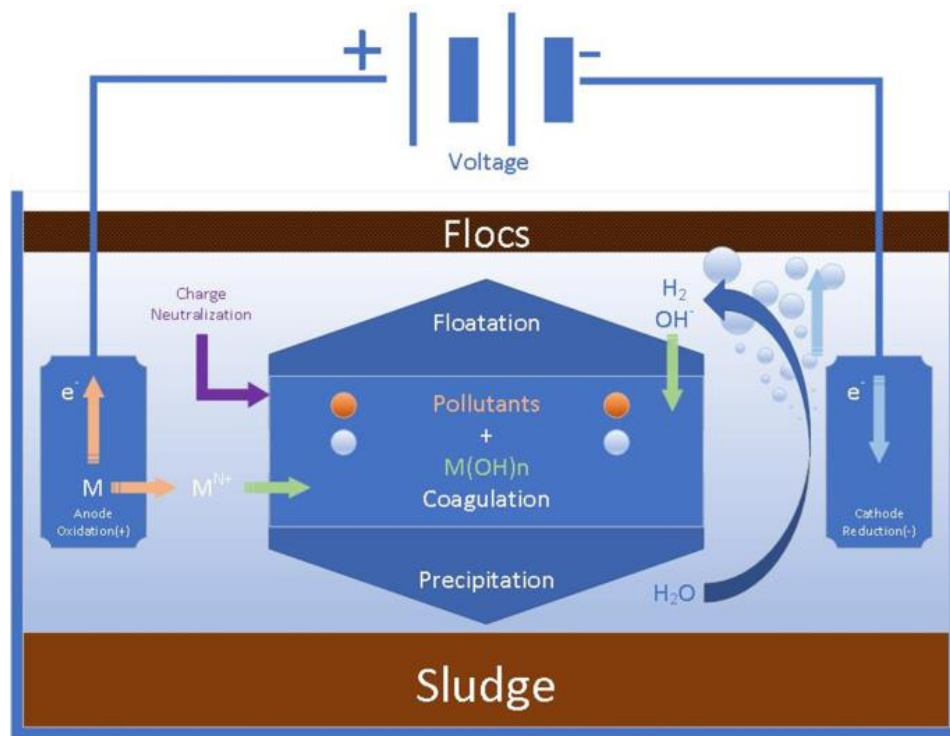


Figure II 4. Electrocoagulation process[54].

II.3.2 Mechanisms of In-Situ Coagulant Formation

The electrocoagulation (EC) process involves seven key steps [55]:

- ✓ Generation of metal cations at the anode,
- ✓ Formation of hydroxyl ions at the cathode,
- ✓ Creation of metal hydroxides through their interaction,
- ✓ Oxidation of toxic contaminants into less harmful forms,
- ✓ Charge neutralization of contaminants,
- ✓ Adsorption and removal of these neutralized particles via sweep coagulation,
- ✓ Flotation of flocs to the surface by hydrogen gas produced at the cathode.

Overall, the EC mechanism relies primarily on three main phenomena: adsorption, coagulation, and flotation see **Figure II 3**.

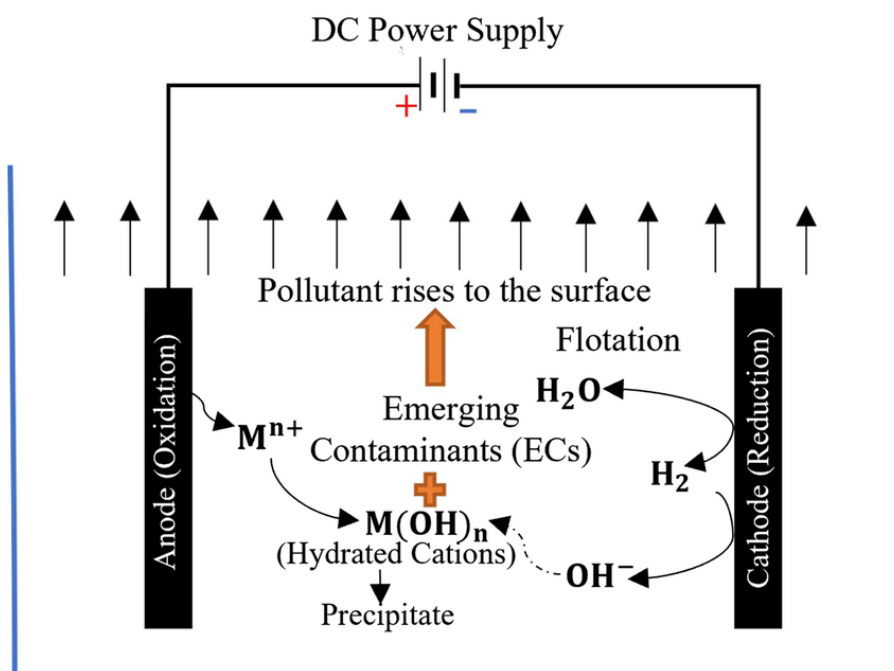


Figure II 5. Typical EC setup and pollutant removal mechanism during EC process[56]

II.3.3 Influence of Operating Parameters

The efficiency of the electrocoagulation (EC) process is significantly influenced by various operating parameters such as Type and nature of electrodes used, Current density and applied voltage, Medium pH, Reaction time and concentration of metallic ion.

Recent studies have provided insights into how these parameters affect treatment outcomes across different wastewater types[57].

❖ Type and nature of electrodes used

In each electrochemical method, the electrode material has a significant influence on how the effluents are treated. It must be nontoxic, affordable, and widely available for the remediation of potable water[58].

The choice of electrode material plays a crucial role in the performance of electrocoagulation (EC) systems. While a wide range of materials such as Al, Fe, Zn, Mg, and others have been explored, aluminium and iron are the most commonly used due to their low cost, wide availability, and good solubility. Aluminium electrodes often demonstrate better efficiency in removing certain pollutants like oil, owing to the superior adsorption capacity of aluminium oxides.

Iron, however, remains a popular choice for its affordability. Both materials can be used in various forms, including plates and industrial scraps like millings or cuttings. In some

applications, combining aluminium and iron electrodes (hybrid configurations) has shown improved performance across a broader pH range[59].

❖ Medium pH

The pH of the wastewater influences the solubility of metal hydroxides formed during electrocoagulation, affecting the removal of contaminants. In dye wastewater treatment, high removal efficiencies (up to 99%) were achieved across a pH range of 3 to 10, indicating the process's robustness to pH variations[5].

❖ Current density and applied voltage

Current density is a critical factor in the EC process, directly impacting pollutant removal efficiency and energy consumption[60].

Current density (CD)—the electric current applied per unit area of the electrode—plays a pivotal role in the electrocoagulation process. It influences the rate of coagulant generation, bubble formation, pollutant destabilization, and energy consumption[61].

▪ Positive effect:

- **Increased Coagulant Generation:** Higher current density accelerates the dissolution of metal electrodes (typically Al or Fe), increasing the availability of metal hydroxide flocs that adsorb and destabilize dye molecules.
- **Improved Dye Removal Efficiency:** A 2023 study on Disperse Yellow 3 dye reported up to 99% color removal at a current density of 10 mA/cm² using aluminum electrodes.

▪ Negative effect:

- **Higher Energy Consumption:** Energy usage (kWh/m³) increases linearly with current density, which may reduce the cost-effectiveness of the process.
- **Electrode Passivation:** Excessive current density can cause passivation (oxide layer formation) on electrodes, reducing their effectiveness.
- **Sludge Overproduction:** Higher metal dissolution rates produce more sludge, increasing post-treatment handling costs.

❖ Reaction time and concentration of metallic ion

The duration of electrolysis affects the extent of pollutant removal and energy usage. In the treatment of high-loaded greywater, extending electrolysis time improved COD, turbidity,

and color removal. However, longer durations also increased energy consumption, necessitating a balance between treatment efficiency and operational costs[62].

II.3.4 Advantages and Limitations of the Electrocoagulation Process

Advantages:

- No need for additional chemicals, reducing the risk of secondary pollution.
- Simple, electrically controlled equipment makes EC easy to operate and manage.
- Effectively removes fine colloidal particles, yielding clear, colorless, and odorless water.
- Produces minimal, easily settled sludge relative to capital cost.
- Gas bubbles from electrolysis enhance pollutant removal by flotation[63].

Drawbacks:

- Sacrificial anodes require regular replacement due to dissolution in the solution.
- Salt may need to be added to improve conductivity in some cases.
- High electricity demand can hinder process scalability in areas with limited power supply.
- Cathode passivation from oxide film formation can reduce EC efficiency[63].

II.3.5 Industrial Applications and Recent Studies

Electrocoagulation (EC) has emerged as an effective and versatile technique for treating various types of industrial wastewater. Recent studies have explored its applications across multiple industries, highlighting its efficiency in removing contaminants and its potential for integration with other treatment methods.

Industrial Applications of Electrocoagulation

- ❖ **Agro-Based Industries:** EC has been applied to treat wastewater from agro-industrial processes, including dairy, sugar, pulp and paper, and olive oil production. Studies have demonstrated that EC can effectively remove organic content and color from these wastewaters, with removal efficiencies exceeding 80%. The process's performance depends on parameters such as electrode materials, electrolysis time, current density, and electrolyte support[64].
- ❖ **Instant Coffee Production:** Research has evaluated the environmental and economic aspects of using EC to treat wastewater from instant coffee manufacturing. By optimizing operating parameters like electrode type, current density, and stirring velocity, significant reductions in color, chemical oxygen demand (COD), and total organic carbon (TOC) were achieved[65].

- ❖ **Electroplating Industry:** EC has been utilized to remove heavy metals such as chromium (Cr) and zinc (Zn) from electroplating wastewater. Using iron electrodes, removal efficiencies of 99% for Cr and 79% for Zn were achieved under optimal conditions (pH 9, 30 minutes of treatment). The process demonstrated low energy consumption, making it economically viable for industrial applications[65].
- ❖ **Oil-Contaminated Wastewater:** Studies have investigated the treatment of oil-contaminated wastewater with high levels of inorganic substances and suspended solids using EC. The process effectively reduced turbidity and pollutant levels, showcasing its applicability in treating complex industrial effluents[66].

Recent Studies and Advancements

- ❖ **Hybrid Systems:** Combining EC with other treatment methods, such as advanced oxidation processes (AOPs), has shown enhanced pollutant removal and cost reduction. These hybrid systems leverage the strengths of each method to achieve higher treatment efficiencies[67].
- ❖ **Parameter Optimization:** Research has focused on optimizing EC parameters—like electrode material, current density, and pH—to maximize treatment efficiency for specific industrial wastewaters. Such optimizations are crucial for tailoring the EC process to different wastewater characteristics[68].
- ❖ **Economic and Environmental Assessments:** Studies have evaluated the cost-effectiveness and environmental impact of EC systems, considering factors like energy consumption, electrode usage, and sludge generation. These assessments help in determining the feasibility of EC for large-scale industrial applications[69].

II.4 Comparison of Both Processes and the Interest in Their Alternation

The following section provides a comparison of both processes and highlights the potential benefits of alternating between them.

II.4.1 Performance Criteria: Efficiency, Cost, Environmental Impact

The **Table II 2** presents the performance criteria for both processes.

Table II 3. Performance criteria for EC and EF

Criteria	Electrocoagulation (EC)	Electrofenton (EF)	Ref
Efficiency	Moderate Removal Efficiency: EC is effective in removing suspended solids, heavy metals, and some organic compounds. For instance, in treating landfill leachate nanofiltration concentrate, EC achieved 57.4% COD removal and 45% TOC removal.	EF excels in degrading recalcitrant organic pollutants. In the same study, EF achieved 69.4% COD removal and 60.2% TOC removal.	[70]
Cost	Lower operating costs due to reduced chemical use and sludge handling.	Lower operating costs due to reduced chemical use	[70]
Environmental Impact	Reduced chemical usage and sludge production; potential for renewable energy integration.	Minimal Chemical Usage, reducing the risk of secondary pollution	[71]

II.4.2 Complementarity Between Electro-Fenton and Electrocoagulation

The integration of Electrocoagulation (EC) and Electro-Fenton (EF) processes has garnered significant attention in recent years for its efficacy in treating complex industrial wastewaters. This hybrid approach leverages the strengths of both methods to achieve enhanced pollutant removal, cost-effectiveness, and environmental sustainability.

1. Sequential Treatment for Enhanced Efficiency

Electrocoagulation (EC) effectively removes suspended solids, heavy metals, and colloidal particles through in-situ generation of coagulants.

Electro-Fenton (EF) excels in degrading recalcitrant organic pollutants via hydroxyl radicals produced from hydrogen peroxide and iron catalysts.

By applying EC as a pre-treatment, the bulk of particulate matter is removed, reducing turbidity and organic load. This facilitates the subsequent EF process to focus on degrading dissolved organic compounds, leading to higher overall treatment efficiency[72].

2. Synergistic Effects on Pollutant Removal

The hybrid EC-EF system exhibits synergistic effects, where the combined processes achieve higher pollutant removal efficiencies than the sum of their individual performances. This is attributed to the complementary mechanisms of coagulation and advanced oxidation[73].

3. Reduction in Sludge Production and Chemical Usage

Integrating EC and EF processes can lead to a reduction in sludge volume and chemical consumption compared to traditional treatment methods. The in-situ generation of coagulants in EC and the catalytic nature of EF minimize the need for external chemical additives[73].

II.4.3 Hypothesis of Alternating Both Processes for Optimized Treatment

Alternating Electrocoagulation and Electro-Fenton treatments enhances the overall efficiency of wastewater purification by leveraging the strengths of each process at different treatment stages—resulting in improved removal of both particulate and dissolved pollutants, reduced chemical consumption, and lower environmental impact.

Sequential EC-EF for Textile Wastewater:

Research on simulated textile wastewater showed that pre-treating with EC followed by EF led to substantial improvements in pollutant removal compared to individual processes.

The EC step effectively reduced turbidity and heavy metals, setting favorable conditions for the EF process to degrade remaining organic compounds [74].

Operational Strategy

- **EC as Pre-treatment:**
 - Removes suspended solids, colloids, and heavy metals.
 - Reduces turbidity, enhancing light penetration and reaction kinetics in subsequent EF treatment.
- **EF as Post-treatment:**
 - Degrades dissolved organic pollutants through hydroxyl radical generation.
 - Improves biodegradability of effluent, facilitating downstream biological treatment if necessary.

Implementing an alternating EC-EF treatment strategy offers a promising approach to address complex wastewater challenges. By tailoring operational parameters to specific wastewater characteristics, this combined method can achieve superior treatment outcomes compared to standalone processes[74].

III. CHAPTER III: EXPERIMENTAL RESULTS AND DISCUSSION

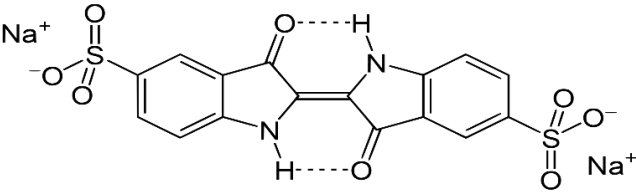
III.1 Materials and methods

III.1.1 Dye data used (indigotin, indigo carmine; E132)

This dye is a synthetic dye (specifically, azo or similar dyes; although indigotin does not contain an azo bond $-N=N-$, it is often associated with this category for its similar properties). It is the sodium sel of 5,5'-indigodisulfonic acid, is an organic salt derived from indigo by aromatic sulfonation. It is also a pH indicator. Its chemical formula is $C_{16}H_8N_2Na_2O_8S_2$ and molecular weight $M = 466.35 \text{ g/mol}$. It is in the form of purple bluish powder.

Indigotine has a pH close to neutral, is well soluble in ethanol and has a solubility of 10 g L^{-1} in water at 25°C (less soluble than all food colours). It is also a redox indicator, varying to yellow during reduction. It is a dye that has good resistance to reducing agents, poor oxidation and heat stability. This dye is still used for staining nylon sutures, food and drugs, it is also used as a biological colorant and as a nitrate and chlorate detection reagent.

Table III 1. Some data on the dye studied (E132; indigotin).

Indigotine	
Name UICPA	5,5'-Disodium indigosulfonate
Appearance	Bluish purple powder
Gross formula	$C_{16}H_8N_2Na_2O_8S_2$
Molecular weight	$466,353 \pm 0,026 \text{ g/mol}$
T° fusion	$>300^\circ\text{C}$
T° boiling	$>340^\circ\text{C}$
Solubility	10 g/ L in water at 25°C ; highly soluble in ethanol

Various factors, such as temperature and pH, influence the degradation of the E132 dye (indigotin or indigo carmine). It has the property of absorbing part of the light spectrum in the visible, their chemical structure, which includes chromophore groupings (aromatic or heterocyclic nuclei with conjugated double bonds) for colouring and auxochromic groupings to ensure the solubility of the dye in water or create effective bonds with chemical groupings of the surface to be dyed, promotes their absorption. It may be transformed into simpler

products or change colour, low molecular weight, several organic acids and inorganic ions, which could have an impact on food safety and product quality [75].

Most dyes are often not biodegradable. To remove dyes, different methods have been developed: physical and chemical treatment such as ozonation [76], [77], coagulation-flocculation [78], adsorption on activated charcoal [79]. Different authors [80], [81], [82] have succeeded in developing photocatalytic methods, however these are generally expensive because of the use of rather expensive catalysts. In our study, we opted to eliminate this indigotin dye (E132) by a combined system of electro-Fenton and electrocoagulation (EF/EC).

III.1.2 Preparation of solutions and analysis of the dye

A commercial food colorant with code "E132" was used in this study. Blue-violet colour, intended for colouring food products for the manufacture of flavoured yoghurts, flavoured industrial cheeses, ice creams, confectionery, jams, seasonings, soups etc. With a view to optimisation, the colorant was prepared at an initial concentration of 0.5M in bi-distilled water.

The spectrum corresponding to this dye is obtained by spectroscopy in the visible on a device (Jenway 7315 spectrophotometer). The pH measurement was performed on a pH meter (Hanna 211Microprocessor) while the conductivity was measured on an instrument (Hanna EC215Conductivity Meter). The measurement of dye turbidity was carried out on a turbidimeter: Phywe System GMBH 2100N, Germany).

III.1.3 Equipment and operating conditions for electro-Fenton/electrocoagulation treatment

The experimental assembly of the combined electro-Fenton/ electrocoagulation system (EF/EC) **figure III.1** and **photoIII.1** consists of a glass electrochemical cell (Becher) in which are placed two parallel flat electrodes between which circulates the dye to be treated (static system) and a bubbling pump with air that allows the passage of air (O₂) inside the beaker. This reactor is easy to implement and use. The two electrodes are approximately equal to 10 cm in length and 2 cm in width, an area of 20 cm² each. The inter-electrode distance is 1 cm, chosen low to limit not only the ohmic drop but also to avoid clogging.

Several factors were tested, namely the nature of the electrodes, the nature of the cathode, the current density, the type and nature of the carrier electrolyte and the initial

concentration of dye, on a synthetic sample of powdered dye at an initial concentration of 0.5M. The solution is constantly stirred with a magnetic shaker to reduce the overvoltage in the electro-Fenton/electrocoagulation reactor. The sample is filtered using special filters that remove all the flocs formed in order to perform reliable measurements of absorbances, thus, it is opted to check the pH on a spot basis. The rate of reduction in staining at the end of the experiment is calculated according to (Eq: III.1):

$$TR(\%) = (Abs_0 - Abs_final) / Abs_0 * 100\% \quad (III. 1)$$

Abs _0- Abs _final: Absorbance successively before and after EF/EC

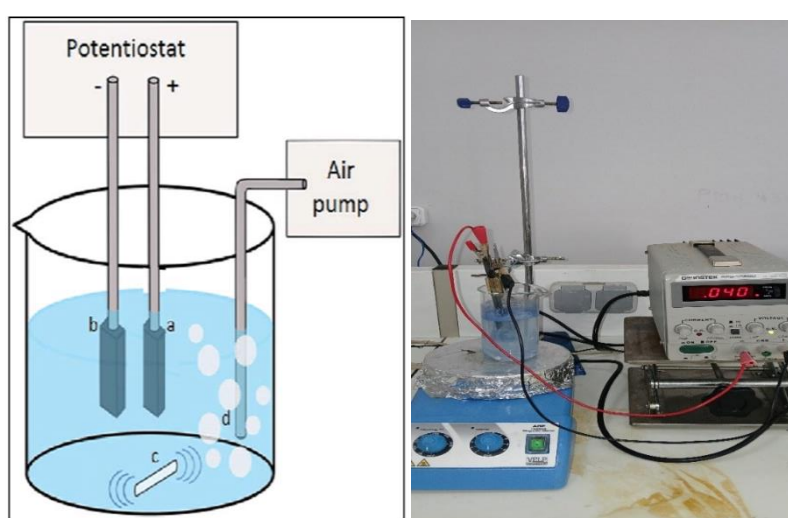


Figure III 1. EF/EC Experimental Setup, photo III 1. Experimental Setup Kherabi Abla 2025

III.2 Results and discussion

III.2.1 Analytical data on the dye being studied (E132)

As mentioned earlier, one dye was studied. **Table III.2** gives some physico-chemical characteristics of the dye. It can be seen that for a concentration of 0.5 M used, the dye absorbs and can be distinguished by a value of $\lambda_{max}(nm)$. The corresponding absorption spectrum in the visible is shown in **figure III. 2**. Given the lack of basic structure of the dye, and in view of the pH values, it is then obvious that the turbidities found are low and comparable to those found in drinking water. The conductivity values found in aqueous solution are not far from drinking water.

The stability or preservation tests of the dye over time (sample of 0.5M dye kept in an amber bottle in the dark and opened once/ 3 days for analysis of absorbance) showed good

stability as no change in initial absorbance was observed in the dark and no change in pH **Figure III.3** during the shelf life of 21 days. It should be noted that small variations were recorded in light, whether for absorbances or pH values.

Table III 2.Some characteristics of the dye studied

Color	Blue
$\lambda_{\max}(\text{nm})$	608
pH₀	6.58
Turbidity(NTU)	09
Absorbance	0.1822
Concentration (M)	0.5
Initiale conductivity ($\mu\text{S}/\text{cm}$)	330

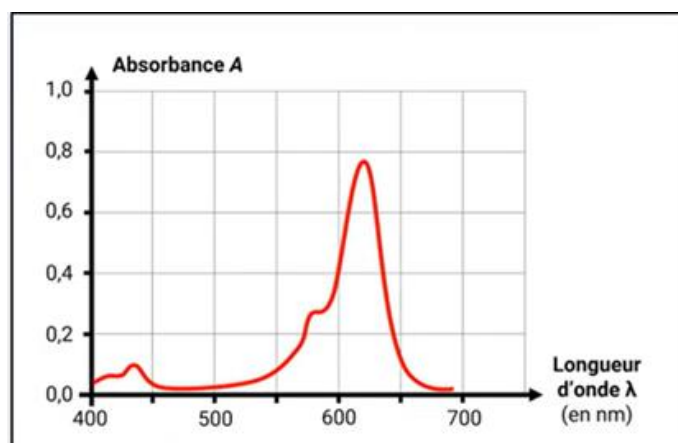


Figure III 2. Spectrum of the dye studied

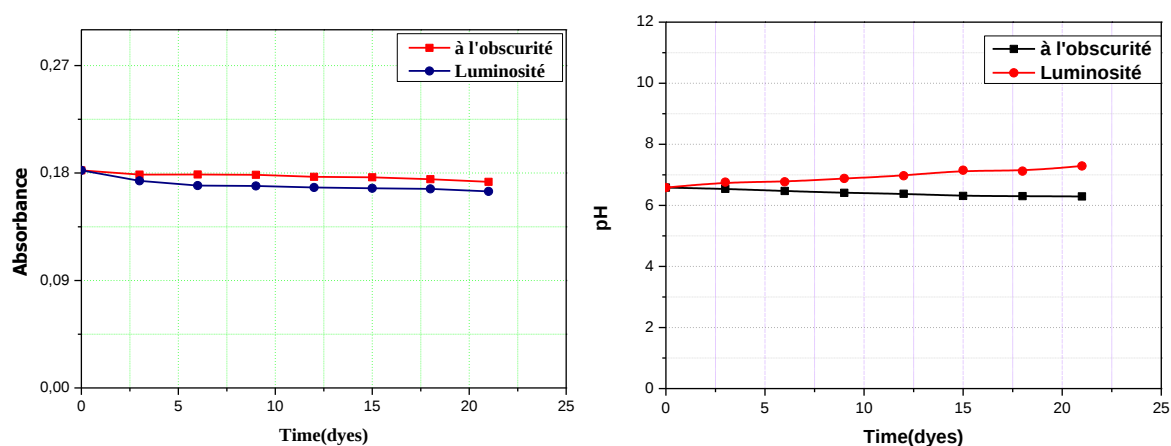


Figure III 3.Stability or preservation tests for dyes over time

III.2.2 Establishment of the calibration curve for the dye under study

The calibration curve for the colorant studied was established identically from a 0.5 M stock solution diluted with bi-distilled water to make daughter solutions at 5, 10, 20, 30, 40 and 50 mg/L. All prepared dye solutions are analysed in visible spectrometry at the maximum wavelengths already optimized namely $\lambda_{\text{max}}=608$. The calibration curve of the dye, corresponding to Absorbance = f (concentration (M)), shows **Figure III. 4** of good correlation coefficient substantially equal to the unit.

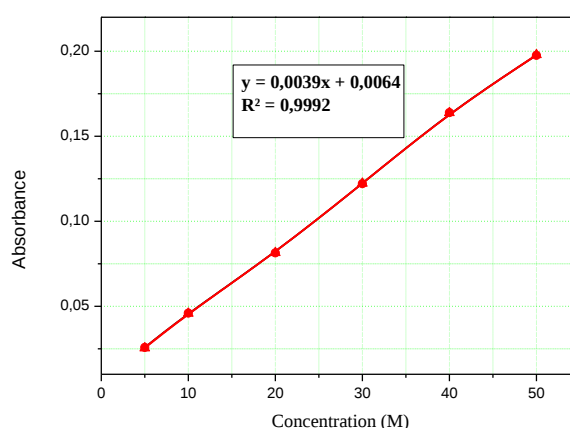


Figure III 4. Calibration curve of the dye studied

III.2.3 Results of FE/CE water dye removal optimization

The water sample to be treated was made in a synthetic medium (dye plus distilled water). The combined electrochemical treatment system adopted is electro-Fenton and electrocoagulation (EF/EC) in static mode (advanced oxidation/electrocoagulation). The system optimization envisaged is necessary; it requires the study of a number of parameters influencing the efficiency of treatment by both processes. For this, and to better optimize this combined EF/EC system, we examined parameters such as the nature of the electrodes then the nature of the cathode only, the current density, the type and concentration of the carrier electrolyte and the initial colorant concentration. Some factors were monitored to better understand the mechanisms and phenomena involved in the reactor, such as pH and the amount formed in hydrogen peroxide H_2O_2 . The COD analysis and mass loss at the sacrificial anode are parameters to be checked at the end of the process, as they are important parameters that may limit the use of this combination of processes.

1. Effect of electrode nature and cathode nature on dye removal efficiency by EF/EC

The objective of this section is to study the influence of the nature of the electrodes on the removal efficiency of staining by a combination of two processes, namely electro-Fenton and electrocoagulation. The electro-Fenton process and related processes (Fenton, photo-Fenton etc.) work optimally with large amounts of catalyst (Fe^{2+}) and hydrogen peroxide (H_2O_2), as well as pH values around 3. [83, 84].

While for electrocoagulation, the best efficiency yields were observed with current densities that promote the formation of large quantities of coagulants in the solution to be treated, pH close to neutrality, as well as other conditions such as inter electrode space, carrier electrolyte concentration and the nature of electrodes [85]. In the case of treatment by the proposed EF/EC system, several factors may affect the removal efficiency of pollutants by this system. Among these factors the nature of the electrodes, it is for this reason that we have chosen to study its impact on the color removal performance.

In order to evaluate the effectiveness of treatment by combining two EF and EC processes, new electrodes were used in the experiments. Five consecutive tests were carried out with five types of electrodes under experimental conditions of: current density 6 mA/cm^2 , flow rate = 200 rpm, inter-electrode space = 1 cm, NaCl electrolyte support at 0.5 M, Initial pH at 3. The results are shown in **Figure III.5**

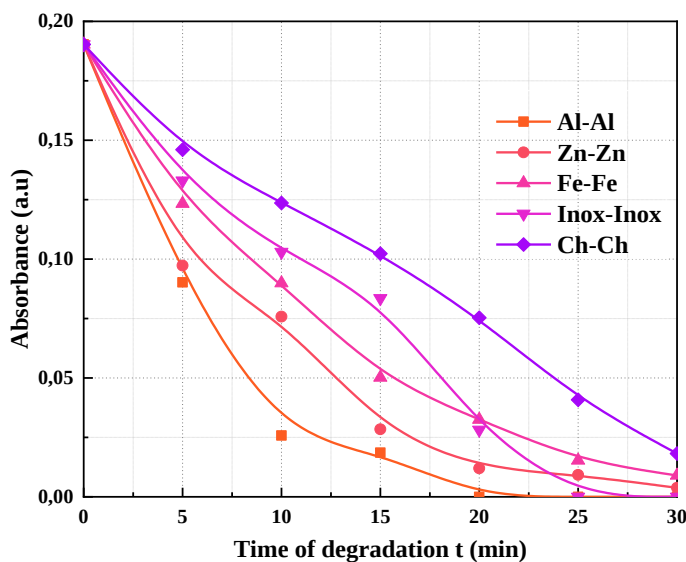


Figure III 5. Evolution of the absorbance of the dye studied as a function of time with different types of electrodes (current density = 6 mA/cm^2 , inter-electrode space 1 cm, NaCl support electrolyte at 0.5 M; $T = 24^\circ\text{C}$; Agitation = 200rpm, electrolysis time = 30 min; initial pH = 3)

From the results of this influence, it can be seen that the absorbance decreases over time for different types of electrodes. All electrode pairs applied led to a decrease in the intensity of staining, the fastest kinetics observed after 20 min of electrolysis by aluminum

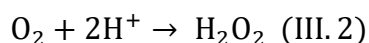
alloy electrodes and about 25 min with stainless steel electrodes. While electrodes made of iron alloys reduce the fine coloration of the dye studied but at the same time generate a yellow coloration in the solution, which is usually due to the oxidation of Fe^{2+} into Fe^{3+} , and the formation of some soluble complexes based on iron such as $[\text{Fe}(\text{H}_2\text{O})]^{3+}$.

The results in **Figure III.5** show well the removal efficiency of dye with electrodes made of aluminum alloys, this efficiency is explained by the fact that the oxidation of this type of electrodes produces in solution quantities of Fe^{2+} . Since this category of electrode consists of several metals such as : Cu, Fe, Mg, Mn, Si and Zn as shown in the table below.

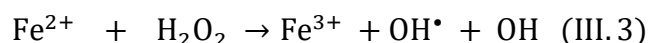
Table III 3. Typical composition of the aluminium alloy electrodes used.

Element	Al	Cu	Fe	Mg	Mn	Si	Zn
Percentage (%)	93.15	4	0.7	0.7	0.7	0.5	0.25

At acidic pH (= 3), the formation of Fe^{2+} and the in situ generation of H_2O_2 in solution causes the initiation of catalytic oxidation processes (**Eq: III.2**):

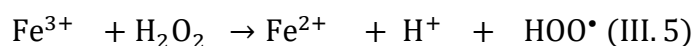
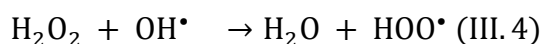


Ferrous ions (Fe^{2+}) react with hydrogen peroxide formed in the medium (**Eq: III.3**):



At these pH (acid) levels, the generation of hydroxyl radicals ($\bullet\text{OH}$ and $\text{HOO}\bullet$) in the solution is considerable. These radicals have a very strong oxidant power, degrade the colouring molecules into CO_2 and H_2O . Mineralization is complete if conditions are optimal, such as the amount produced in catalyst Fe^{2+} and H_2O_2 in solution, and pH stability (acidic pH).

The degradation of "indigotine" dye by electro-Fenton only is slower for higher pH close to neutrality and slightly basic (**6, 7, 8 and 9**) compared to acidic pH, this can be explained by the nature of the oxidant formed with its concentration in the medium. Indeed, at these pH values, the formation kinetics of oxidant agents such as ($\bullet\text{OH}$) and ($\text{HOO}\bullet$) is practically zero, because the formation of these radicals is related to the concentration of H_2O_2 in the medium which is negligible within this pH range [86]. Furthermore, for pH values above 4, ferric ions precipitate as hydroxide. Below pH 2.5; reaction efficiency decreases due to the formation of ferrous complexes (**Figure III.5**), increased rate of H_2O_2 -trapping of $\bullet\text{OH}$ (**Eq: III.4**) and inhibition of iron ion regeneration (**Eq: III.5**).



These results are in agreement with those obtained by several heights [87], or they found that the best colorant removal efficiency by this advanced electro-Fenton oxidation process was observed at a pH equal to 3.

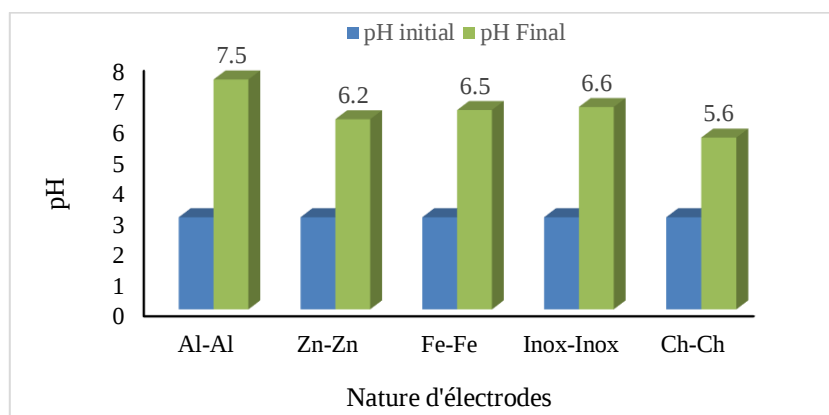


Figure III 6.Initial and final pH measurements during treatment by combining EF/EC with different types of electrodes.

During the EF/EC process without pH fixation (preliminary tests), the pH of the medium changes; **Figure III.6** shows that the observed differences between initial and final pH are particularly noticeable for acid initial pH fading tests (3). Observation of the evolution of final pH, suggests that the combined EF/EC system, like other electrochemical processes, has a certain buffer capacity related to the balance between production and consumption of OH^- . This prevents sudden changes in pH, particularly in low acidic environments [88]. In the case of EF/EC using aluminum alloy electrodes, the increase in pH is one of the major advantages because the rise in pH promotes the formation of white precipitates or flocs thanks to the aluminium (Al^{3+}) already produced in solution, which accelerates the reduction of staining.

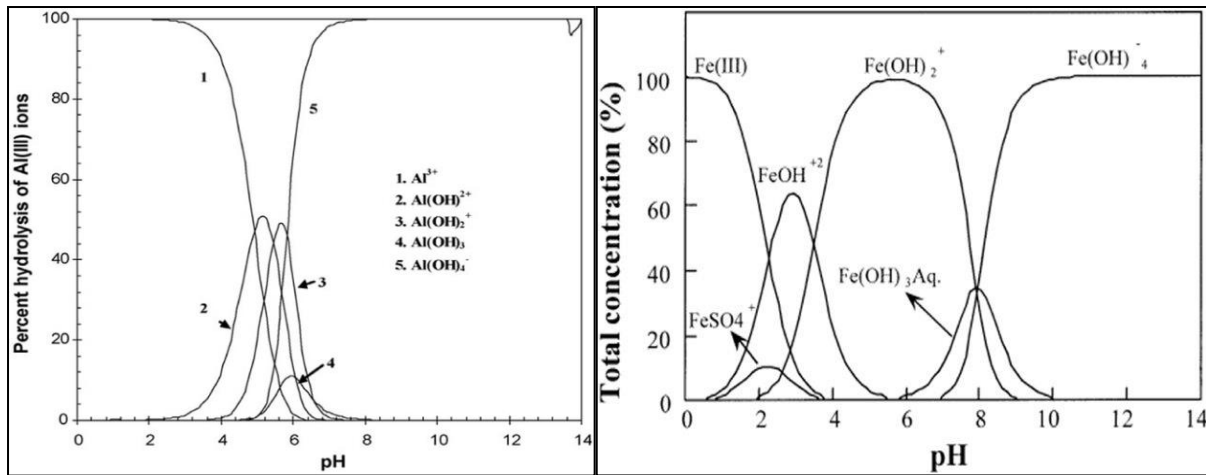


Figure III 7. Speciation of Fe and Al species as a function of pH at $T = 25^\circ\text{C}$.

Figure III.7 shows the speciation curves for aluminium and iron. Indeed, the kinetics of formation of aluminium and iron complexes increases with the increase in pH. Therefore, the combination of two methods such as electro-Fenton and electrocoagulation significantly improves the removal efficiency of water staining. Because throughout the pH range (3 to 8), several mechanisms are at work, either by radical oxidation of the dye; or by precipitation of the dye molecules into insoluble flocks [89].

In another series of manipulations, we have procedures to test the effect of the nature of the cathode, thus several cathodes were examined such as: (Al-Zn; Al-Al; Al-Fe; Al-inox; Al-Ch). The results are presented in **Figure III.8**.

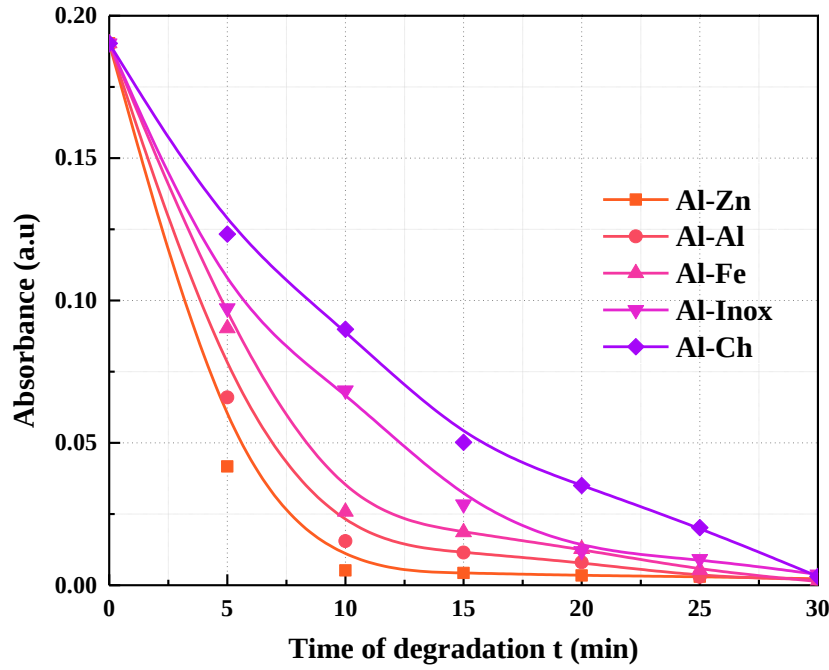


Figure III 8. Evolution of the absorbance of the dye studied as a function of time with different types of cathode (Current density = 6 mA/cm², Inter electrode space 1 cm, NaCl support electrolyte at 0.5 M; T ~ 24°C; Agitation = 200 rpm electrolysis time = 30 min; initial pH = 3).

The type of cathode plays an essential role in the amount of H₂O₂ produced in solution, therefore, this choice directly influences the concentration of radicals generated in the same solution. The results in the figure show that the electrode pair (Al-Zn) gives the fastest elimination kinetics of staining, this may be due to the standard potential difference of the two electrodes which are (E°Al³⁺/Al is -1.66 V; E° Zn²⁺/Zn is 0.7618). The table below **Table III.4** shows the standard potentials of the electrodes used:

Table III 4.Standard potential of the electrodes used:

Cathod	Al	Zn	Fe	Inox (304/316)	Ch
E°	-1.66	-0.7618	-0.44	+ 0.4	/

In water treatment by electrochemical processes, the standard potential guides the choice of electrodes or experimental conditions (pH, catalyst) to promote the production of HO. Indeed, in the combined process using EF/EC with an acid pH, discoloration begins with advanced oxidation of EF. Therefore, they require us to produce H₂O₂ on site by partially reducing dissolved oxygen (**Eq: III.6**), but without creating water molecules [90] (**Eq: III.7**).





According to Figure III.8, it should be noted that the decrease in color begins with oxidation by the radicals formed in solution (which destroy the coloring molecules), and then, as the pH increases, there will be the formation of flocs composed mainly of aluminum and to a lesser extent of iron, which ultimately leads to the total disappearance of color.

2. Effect of current density on EF/EC dye removal efficiency

Current density is one of the most important operating parameters that affect the efficiency of electrochemical processes such as electro-Fenton, electrocoagulation, electro-sorption etc. Thus it can affect the combined EF/EC processing system [91, 92, 93, 94]. In the case of FE, this factor can determine the concentration of the Fe^{2+} catalyst, the speed and size of the bubbles produced at the electrodes, the amount of hydrogen peroxide H_2O_2 , and subsequently the amount of hydroxyl radical ($\bullet\text{OH}$) formed in solution.

On the other hand, current density can determine the amount of hydroxide formed, the speed and size of the bubbles produced at the electrodes, the mixing rate in the EC cell and other redox processes [95], thus the combined EF/EC system is based on the catalytic effect of Iron and more precisely of Fe^{2+} , and the kinetics of formation of the insoluble complexes based on iron or aluminium $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$. It seemed necessary to optimize the study by determining the optimal density for the treatment used. The pH of the medium is adjusted using a solution of hydrochloric acid (HCl) at a concentration of 0.1 M. This choice is justified by the fact that it already exists in the laboratory. In preliminary experiments, four values of current densities in the range 3 to 15 mA/cm^2 (3, 6, 10 and 15 mA/cm^2) were applied for aluminium alloy electrodes at a free pH solution equal to 3 (without pH fixation), an inter-electrode distance equal to 1 cm, an electrolysis time of 30 min. The results are illustrated in **Figure III.9**.

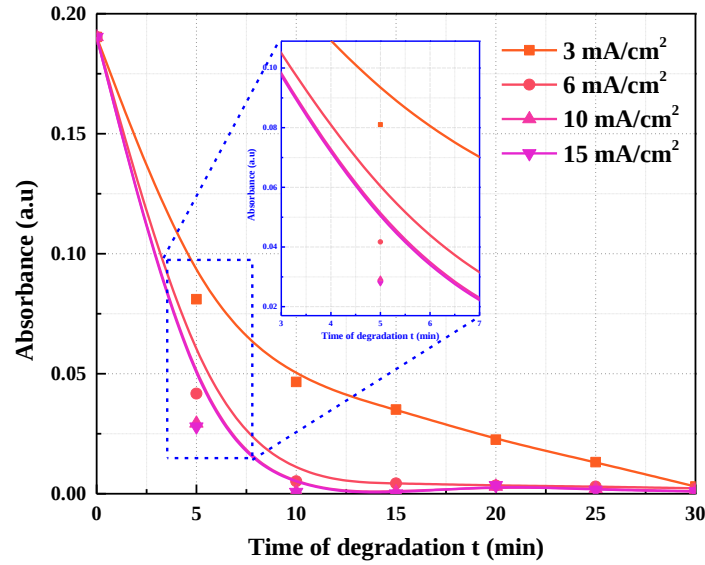
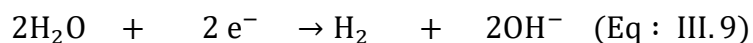
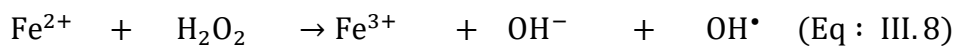


Figure III 9. Evolution of the absorbance of the dye studied as a function of time with different current densities (Al-Zn electrodes; 1 cm inter electrode space, 0.5 M NaCl carrier electrolyte; $T \sim 24^\circ\text{C}$; Agitation = 200 rpm electrolysis time = 30 min; initial pH = 3).

It is clear that the absorbance decreases over time for all four current density values. All applied current densities led to a decrease in the intensity of staining, the fastest kinetics observed after 15 min of electrolysis by an aluminum alloy electrode with a current density of 10 and 15 mA/cm², and about 30 min with the same electrodes at a current density of 3 mA/cm². It can be noted that the efficacy of EF/EC combination treatment becomes relevant if the mechanisms associated with EF are verified in acidic medium. Therefore, with pH increase, these processes will be supplanted by other phenomena mainly associated with electrocoagulation. Thus with the increase in pH these mechanisms will be replaced by other phenomena mainly related to electrocoagulation [96].

Figure III.10 shows the initial and final pH values of different current densities tested, showing that the final pH values increase slightly when the current density increases, which can be explained by the high production and low consumption of hydroxides in solution. In electro-Fenton, there is an in situ generation of H₂O₂ from O₂ and H⁺, which reacts with the ferrous ions Fe²⁺ to produce hydroxyl radicals (•OH) (Eq: III.8) and reduction of water at the cathode (Eq: III.9). This change in pH can affect the solubility of metals, the creation of coagulants and the overall effectiveness of treatments, which highlights the need to monitor and, if necessary, adjust this factor.



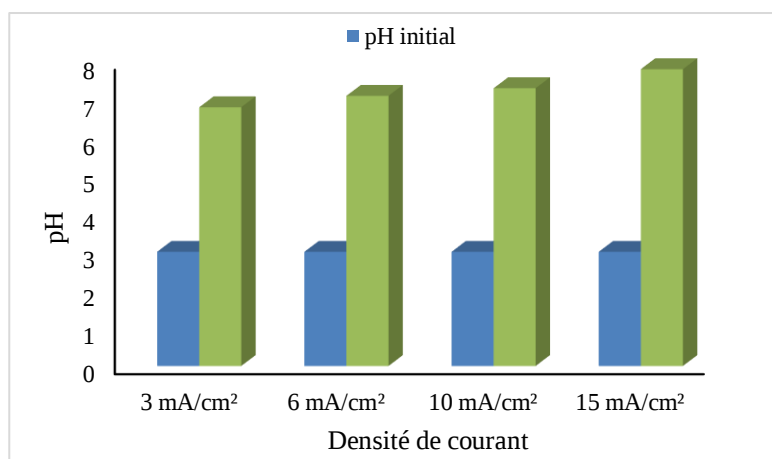


Figure III 10. Initial and final pH measurements when treated with a combination of FE/EC with different current densities.

It is important to note that the current density is directly related to the current intensity and applied potential. The voltage applied as current density is mainly responsible for the electrolytic oxidation of the electrode and then ensures the production of Fe^{2+} and Al^{3+} in solution, leading to the destabilization of dye molecules and the formation of radicals. Finally, the quantity produced in Fe^{2+} or Al^{3+} is directly related to the increase of the current density, knowing that for EC, the experimental quantity actually produced is higher than that calculated theoretically [97].

3. Effect of the type and concentration of the carrier electrolyte on colorant removal efficiency by EF/EC

In electrochemical processes such as electro-Fenton (EF) and electrocoagulation (EC), the nature and concentration of the carrier electrolyte is essential because it affects the conductivity of the medium, the speed of electrochemical reactions and, the removal efficiency of pollutants such as pesticides and dyes [98, 99]. Indeed, the conductivity of the medium justifies the feasibility of the combined EF/EC system in terms of energy consumption time and processing cost [100]. For this, we have chosen to study this factor of nature and concentration of carrier electrolyte with the use of the following electrolytes: NaCl, KCl, MgO and Na_2SO_4 , on the treatment efficiency by combination of EF/EC. Experiments were conducted at an acid pH of 3, current density of 10 mA/cm², 1 cm inter electrode space, Al-Zn electrodes and an initial dye concentration of 0.5M. The results are illustrated in **Figure III.11**

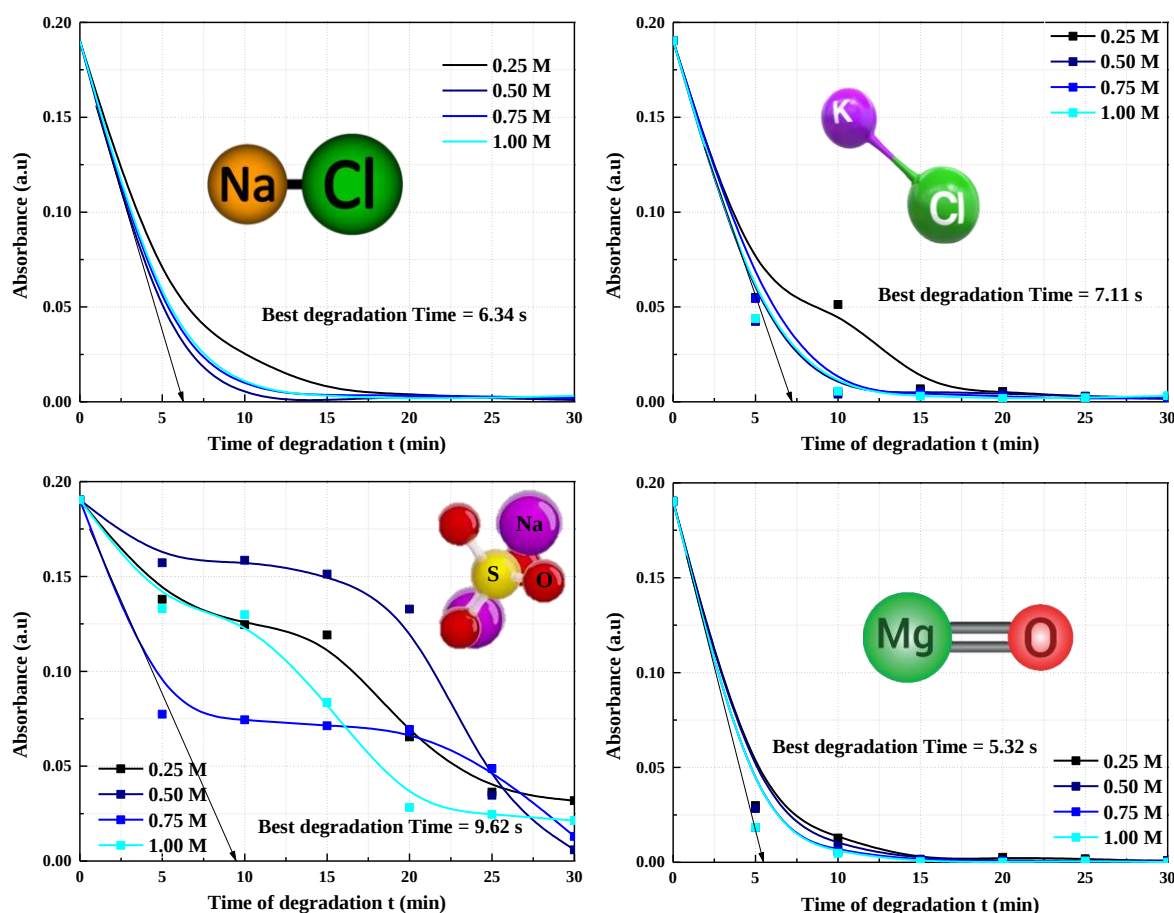


Figure III 11. Evolution of the absorbance of the dye studied as a function of time with different support electrolytes (current density = 10 mA/cm^2 ; inter-electrode space 1 cm, electrodes Al/Zn; $T \sim 24^\circ\text{C}$; agitation = 200 rpm electrolysis time = 30 min).

The results of this influence show (**Figure III.11**) that MgO with different concentrations gives better results in terms of colour removal (elimination rate > 99%), as well as better kinetics than other electrolytes such as KCl, NaCl and Na_2SO_4 . The choice of carrier electrolyte and its concentration are of paramount importance. Indeed, each electrolyte has advantages and disadvantages, like MgO which works as a basic buffer, helping to maintain the pH balance during the process, specifically in the electro-Fenton which tends to acidify the medium initially and then to make it alkaline. This helps to extend the duration of optimal pH (approximately 3), which is critical for stability and efficiency of the hydroxyl radical ($\bullet\text{OH}$) in the electro-Fenton process [101]. Thus, the hydroxides ($\text{Mg}(\text{OH})_2$) can be formed from the Mg ions² released in the solution, these hydroxides play the role of a natural coagulant, promoting the agglomeration and sedimentation of colloidal particles and dyes, which optimizes the efficiency of electrocoagulation with increasing pH. While, NaCl can lead to the generation of active chlorine (Cl_2), which may play the role of secondary oxidant.

However, this can lead to the production of unwanted halogenated by-products. Sodium sulphate (Na_2SO_4). Sodium sulphate : generally preferred for its neutral character, it has no noticeable interference with reactive species and guarantees an effective conductivity [102].

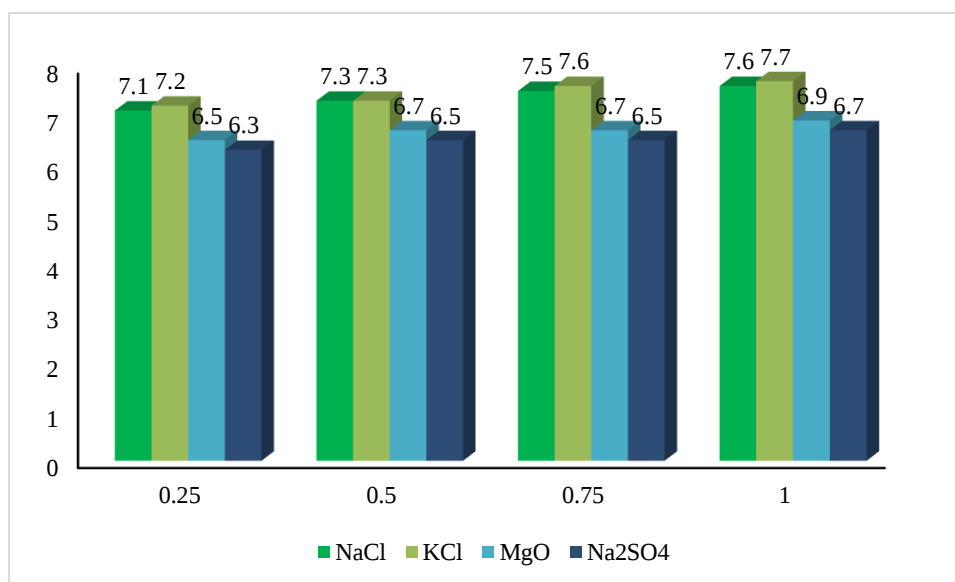


Figure III 12. Final pH measurements during treatment by combination of FE/CE with different carrier electrolytes and their concentrations.

Figure III.12 clearly shows that the final pH values obtained via KCl and NaCl are significantly higher (from 7.1 to 7.7), while for MgO and Na_2SO_4 the final pH values were lower than those observed with KCl and NaCl (from 6.1 to 6.9). In conclusion, the nature of the electrolyte affects not only conductivity but also degradation or coagulation processes [103]. It is for these reasons that we consider the MgO electrolyte for the examination of the next initial dye concentration parameter.

4. Effect of the initial dye concentration on FE/CE removal efficiency

The initial colorant concentration represents the number of colorant molecules present in the solution, which is an important factor to consider when optimizing EF/EC treatment for the removal of dyes from water. During the EC/EF process, H_2O_2 and coagulants are generated in situ by anodic dissolution (Al or Fe). If the amount of dye is increased while maintaining a stable current or processing time, the radical concentration ($\bullet\text{OH}$) and the amount of coagulant generated may be insufficient to oxidize and trap all dye molecules [104, 105]

In general, manufacturers sometimes throw away liquid effluents rich in dyes, which is why we examined the impact of this factor on the efficiency of the combined EF/EC treatment, to further study this crucial parameter, we chose to evaluate four concentrations: 0.25, 0.50, 0.75 and 1 M on the efficacy of the combined treatment by EF/EC. The tests were carried out under conditions of initial pH acidic at 3, current density of 10 mA/cm^2 , electrode spacing of 1 cm, Al-electrodes Zn using a MgO carrier electrolyte at a concentration of 0.5 M. The results are illustrated in **Figure III.13**

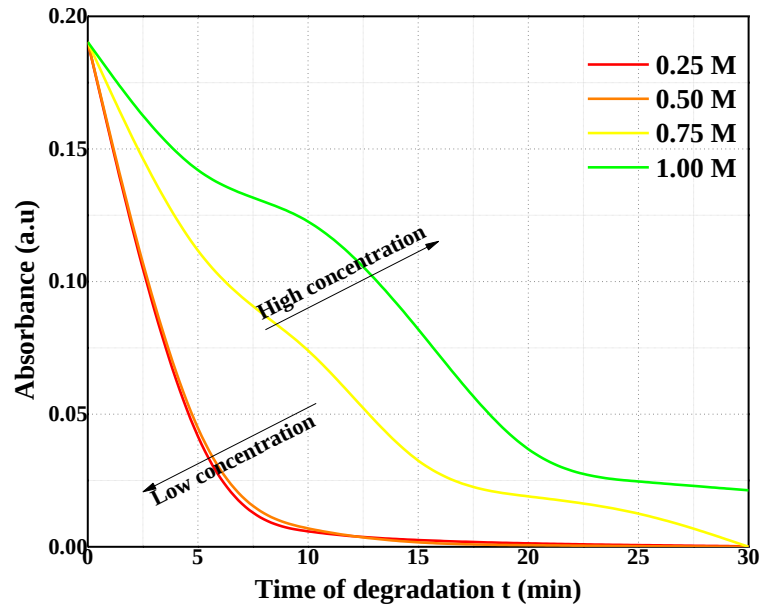


Figure III 13: Evolution of the absorbance of the dye studied as a function of time with different concentrations of the electrolyte of (current density = 10 mA/cm^2 , 1 cm inter electrode space, MgO support electrolyte at 0.5 M; Al/Zn electrode; $T = 24^\circ\text{C}$; Agitation = 200 rpm electrolysis time = 30 min)

Figure III.13 shows that the removal efficiency decreases as the initial dye concentration increases, for a fixed treatment time and current density. This is explained by the lack of radicals that oxidize the colouring molecules. In addition, the surfaces of the formed flocs can be quickly saturated (site saturation) by the colored molecules, which limits adsorption or flotation drive to the surface. In addition, a high concentration of dye can also increase the viscosity of the solution or decrease the ion mobility, this phenomenon slows down the electrochemical processes involved and reduces the turbulence conducive to flake-dye contact. In the same vein, it is important to note that increased opacity and density caused by high intensity of staining may affect the efficiency of flotation separation, especially by limiting the coalescence and ascension of H_2 bubbles produced at the cathode [106].

The illustrations in **Photo III 1** demonstrate the effectiveness of the combined FE/CE process. It should be noted that the volume of floating slurry tends to increase with the increase in conductivity of the medium, either by increasing the concentration of the carrier electrolyte or by changing the electrolyte in question, especially when the initial concentration of the dye is high.



Photo III 2 . *Après élimination de la couleur par EF/EC à différentes concentrations de MgO.Kherabi Abia 2025*

Conclusion

This study used a combination Electro-Fenton and Electrocoagulation (EF/EC) technology to examine the degradation of the synthetic dye Indigotine (E132). In order to improve the dye removal effectiveness from aqueous solutions, the study concentrated on optimising critical operational parameters, such as electrode materials, current density, electrolyte type and concentration, and initial dye concentration.

Because of their advantageous electrochemical characteristics and the production of reactive species such hydroxyl radicals ($\bullet\text{OH}$) and coagulants (Al^{3+}), the results showed that electrodes composed of aluminium alloys, especially the Al-Zn pair, had the best decolorisation efficiency. The ideal current density, which balanced therapeutic effectiveness and energy consumption, was found to be 10 mA/cm^2 . MgO was the most successful electrolyte among those tested; it improved coagulation and served as a pH buffer. The study also emphasised the significance of pH management, showing that electrocoagulation was favoured by near-neutral pH while the Electro-Fenton process was best suited to acidic circumstances ($\text{pH} \approx 3$).

When compared to individual procedures, the combined EF/EC system performed better, attaining high decolorisation rates ($>99\%$) and showing promise for use on an industrial scale. To increase sustainability and cost-effectiveness, however, issues including electrode passivation, sludge generation, and energy use need more research.

In summary, this study offers a potential approach to treating wastewater tainted with artificial dyes by shedding light on the synergistic effects of EF/EC for dye removal. To optimise the procedure for practical uses, future studies should investigate scalability, long-term operating stability, and the incorporation of renewable energy sources.

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Summary:

The removal of indigotin synthetic dye (E132) using a combined electro-Fenton/electrocoagulation (EF/EC) procedure is examined in this paper. The experimental setup, which included a static electrochemical reactor with parallel electrodes and air bubbling, allowed for the optimisation of a number of parameters, including the cathode and electrode characteristics, current density, carrier electrolyte type and concentration, and dye initial concentration. According to the results, the highest fading efficiency (>99%) can be attained using MgO electrolyte, aluminium alloy electrodes, and an acid pH of about 3. The method, which combines effective coagulation with sophisticated oxidation, shows promise for treating coloured water.

Keywords: Indigotin (E132), Synthetic dye, Electro-Fenton (EF), Electrocoagulation (EC), Water treatment, Advanced oxidation, Discoloration

Résumé :

Ce travail examine comment enlever le colorant synthétique d'indigotin (E132) en utilisant une méthode qui combine l'électro-pentone et l'électrocoagulation. L'appareil utilisé, qui est un réacteur électrochimique avec des électrodes parallèles et des bulles d'air, a aidé à améliorer plusieurs facteurs : le type d'électrodes et de cathode, le courant, le type et la quantité d'électrolyte, et la concentration initiale du colorant. On peut atteindre une efficacité de fondu très élevée (plus de 99 %) en utilisant des électrodes en aluminium, un pH acide d'environ 3 et un électrolyte de MgO, comme l'indiquent les résultats. Ce procédé est une bonne méthode pour nettoyer l'eau colorée, car il utilise une oxydation avancée et une coagulation efficace.

Les mots clés : Indigotine (E132), Colorant synthétique, Électro-Fenton (EF), Électrocoagulation (EC), Traitement des eaux, Oxydation avancée, Décoloration

ملخص :

يبحث هذا العمل في التخلص من صبغة الإنديجوتين الاصطناعية (E132) من خلال عملية مشتركة بين الفنتون الكهربائي والتخثر الكهربائي (EF/EC). النظام التجريبي، الذي يتكون من مفاعل كهروكيميائي ثابت مع أقطاب كهربائية متوازية وفقاعات هواء، جعل من الممكن تحسين العديد من المعلمات: طبيعة الأقطاب الكهربائية والكاثود، وكثافة التيار، ونوع وتركيز الإلكتروليت الحامل، والتركيز الأولي للصبغة. يمكن تحقيق أقصى قدر من كفاءة التلاشي (>99%) باستخدام أقطاب سبائك الألومنيوم، ودرجة حموضة حمضية تبلغ حوالي 3، وإلكتروليت MgO، كما أكدته النتائج. وتعد هذه العملية طريقة واعدة لمعالجة المياه الملونة، لأنها تجمع بين الأكسدة المتقدمة والتخثر الفعال.

الكلمات المفتاحية: إنديجوتين (E132)، الصبغة الاصطناعية، الفنتون الكهربائي (EF)، التخثر الكهربائي (EC)، معالجة المياه، الأكسدة المتقدمة، تغيير اللون