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MASTER'S DEGREE THESIS

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Theme

Photocatalytic treatment of produced water over ZnO-CuO/Commercial activated carbon (CAC).

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Dedication

To those who stood by me every step of the way, and were the light that guided me through moments of exhaustion and uncertainty...

To my dear father, my first pillar of strength and life companion.

To my beloved mother, the most precious soul I have, and the heartbeat that never fades.

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Dalila

Dedication

To my beloved family

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ikram

List of abbreviation and symbols

AC: Activated carbon.

BTEX: Benzene, toluene, ethylene, and xylene.

CO_2: Carbon dioxide.

CuO: Copper oxide.

CTC: Carbon tetrachloride.

EAC: Extruded activated carbon.

ELG: Effluent limitations guidelines.

FAO: Food and agriculture organization of the united nations.

FAS: Ferrous ammonium sulfate.

GAC: Granular activated carbon.

H_2O: Water.

H_2S: Hydrogen sulfide.

H_3PO_2: Phosphoric acid.

IN: Iodine number..

Mmcf: Million cubic feet.

·OH: Hydroxyl radicals.

O & G: Oil and grease.

PW: Produced water.

PAC: Powdered activated carbon.

PWW: Produced wastewater.

ROS: Reactive oxygen species.

TW: Treated water.

TiO_2: Titanium dioxide.

UV: Ultraviolet.

WW: Wastewater.

WHO: World health organization.

WO_2: Tungsten trioxide.

ZnO: Zinc oxide.

$ZnCl_2$: Zinc chloride.

List of figures

List of tables

Table of content

Chapter II: Experimental setup

Chapter III: Result and discussion

General introduction

Introduction:

Water scarcity and pollution are among the most pressing environmental issues of the twenty-first century, caused by fast industrialization, population increase, and the effects of climate change. These variables have had a substantial impact on the quality and availability of fresh water supplies, particularly in arid and semi-arid countries. According to the United Nations, by 2025, more than 1.8 billion people would be living in severe water scarcity [1]. Concurrently, the rise of industrial operations, notably in the petroleum industry, has led to in the release of massive amounts of untreated or inadequately treated wastewater such as produced water (PW) into the environment, posing serious hazards to ecosystems and public health [2].

Produced water is a complicated effluent with high concentrations of salts, hydrocarbons, heavy metals, and chemical additions. Its treatment is still difficult due to the limits of traditional treatments such as filtration, coagulation, and biological treatment, which frequently fail to completely eliminate persistent pollutants [3-4].

In response, advanced oxidation processes (AOPs), particularly heterogeneous photocatalysis, present potential, environmentally acceptable options. Photocatalysis uses light to activate semiconductors like ZnO and CuO, producing reactive oxygen species capable of destroying hazardous chemicals [5]. While these materials are abundant and inexpensive, their photocatalytic efficacy is hampered by rapid electron-hole recombination and a small surface area [6]. Supporting metal oxides on activated carbon (AC) improves performance by increasing surface area, boosting pollutant adsorption, and allowing for charge separation. Chemically reactivated activated carbon (RCAC) improves these qualities by increasing porosity and functionalization [7-8].

This study focuses on the photocatalytic treatment of real industrial petroleum effluent with ZnO-CuO photocatalysts supported by commercial and reactivated commercial activated carbon (CAC and RCAC). Three distinct ZnO-CuO weight ratios **(3/7, 4/6,** and **5/5)** were produced and examined using UV-visible light. The study's goal is to determine how effective these systems are at improving critical physicochemical parameters such as pH, electrical conductivity (EC), chemical oxygen demand (COD), total and suspended solids (TDS and TSS), and density, as well as to evaluate how these parameters change over time.

General introduction

The overarching goal of this research is to determine whether carbon-supported ZnO-CuO photocatalysts, particularly those based on RCAC, can provide an efficient and sustainable solution for petroleum wastewater treatment (WW), with potential applications in meeting international water reuse standards [9].

Specifically, the research seeks to answer the following questions:

- ✓ Does the use of RCAC significantly enhance photocatalytic performance?
- ✓ Which ZnO-CuO/CAC ratio provides the highest degradation efficiency?
- ✓ Can this approach bring treated wastewater closer to international benchmarks for safe discharge or reuse ?

The structure of the thesis is composes of 3 chapters a brief description about each chapter as given below:

Chapter I: Theoretical framework and literature review.

Presents the scientific background of WW pollution, conventional and advanced treatment technique, and a detailed review of photocatalysis using ZnO and CuO.

Chapter II: Experimental setup.

Outlines the methodology used for catalyst preparation, CAC reactivation, and the experimental treatment process.

Chapter III: Result and discussion.

Summarizes and analyses results for CAC reactivation, catalyst's efficiency, and treated water quality, with a focus on international standards and future improvements.

Chapter I:

Theoretical framework and literature review

I.1. Produced water (Petroleum water):

Produced water (PW) is the water that clearly exists in underground formations and is co-extracted with oil and gas at some stage in production operations. It is taken into consideration a byproduct of each traditional and unconventional extraction processes, the concentration of components and the volume of produced water vary significantly based on the type and location of the petroleum product as shown in the Table I.1[10]. And due to it's complex, dangerous nature-excessive salinity, poisonous organics, heavy metals, and chemicals-it ought to cautiously dealt with earlier than discharge or reuse.

Table I.1: Produced water volume by field type.

Field Type	Typical produced water volume	Note
Oil reservoirs	High water-to-oil ratio (~9+ bbl water/ bbl oil).	Increases with field maturity.
Gas reservoirs	Lower water volume, avg.~97 bbl water / Mmcf gas.	Wide variability; generally less than oil fields.
Unconventional walls	High initial flow-back then decline.	Horizontal drilling typically reduces water production.

I.1.1. Sources of produced water:

PW originates from numerous sources:

- **Subsurface gas and oil formations,** where hydrocarbons and water are locked together under pressure.
- **Traditional oil and gas reservoirs,** where the holes in the rock naturally contain water.
- **Unconventional sources,** such shale gas deposits, tight sands, and coal bed methane.
- **Water-flooding,** is the process of injecting, into reservoirs during enhanced oil recovery, which subsequently rises to the surface as generated water.
- **Flow-back water -fracturing,** fluid that returns to the surface, is occasionally regarded as a component of generated water in hydraulic fracturing operations [11].

I.1.2. Characteristics and composition:

PW is a complex mixture of organic and inorganic materials that is difficult for the environment to handle. It is much more than just salty water, although it's makeup varies according to the age, production method, and geology of the reservoir, it typically consists of the following:

I.1.2.1. Physical characteristics:

- **Temperature:** high temperatures, often exceeding 100 °C, which affect equipment design.
- **Colour and smell:** the appearance can range from clear to brown or dark due to oil and suspended solids, with potential strong odors from volatile organic compounds or gases like H_2S.
- **Density:** PW is generally denser than freshwater, with density influenced by salinity and dissolved substances.
- **Suspended solids:** comprises sand, clay, corrosion byproduct and biomass.
- **Turbidity:** suspended particles frequently cause high turbidity, which can impede treatment procedures [11].

I.1.2.2. Chemical characteristics:

Include a variety of inorganic salts, particularly high concentrations of major ions like $Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-$ with salinity sometimes exceeding 300,000 mg/L, significantly higher than seawater. Dissolved organic compounds such as oil, grease, BTEX, phenol and fatty acids are present and are often toxic and persistent in the environment. Common dissolved gases include H_2S, CO_2 and methane which can also be hazardous. Heavy metals such as iron, zinc, lead, nickle, chromium and barium can also be found, posing environmental and health risks even in small amounts. Additionally, production chemicals like corrosion inhibitors, scale inhibitors, herbicides and emulsion breakers are frequently included, affecting toxicity and the ability to treat the water [12].

I.1.3. Conventional produced water treatment:

PW from petroleum extraction contains harmful substances as hydrocarbon, heavy metals, high salinity, and potentially radioactive elements, requiring treatment for environmental safety [12]. It is difficult for conventional techniques to effectively handle these contaminants while striking a balance between sustainability and affordability. Conventional treatments methods struggle to mange these contaminants sustainably and cost-effectively (in figure I.1) [13]. These methods are detailed in the table I.2:

Table I.2: Produced water physical treatment technologies [13].

Treatment type	Method	Description	Avantages	Disadvantages
Physical	**Gravity separation / Skimming**	Removes unfastened oil and huge solids primarily based totally on density variations.	Low power consumption; easy operation.	Ineffective for emulsified oils and dissolved contaminants.
	Hydro-cyclones	Uses centrifugal pressure to split oil droplets and suspended solids.	Compact design; excessive float capacity, powerful for large droplets.	Limited elimination for dissolved contaminants; calls for maintenance.
	Sedimenta-tion tanks	Allows coarse debris to settle through gravity over time.	Simple technology; low operational coat.	Ineffective for great debris and emulsified oils.
	Sand / Nut shell filtration	Physical filtration to take away residual suspended solids and varnish water.	Effective sharpening step; easy technology.	Frequent media replacement; constrained elimination of dissolved contaminants.

Table I.3: produced water chemical and biological treatments technologies [13].

Treatment type	Method	Description	Avantages	Disadvantages
Chemical	**Coagulation / flocculation**	Addition of chemicals (e.g., aluminum sulfate) to combination high-quality debris for simpler removal.	Effective at decreasing turbidity and suspended solids.	Generates chemical sludge requiring disposal; chemical costs.
	Dissolved air flotation (DAF)	Injecting microbubbles to help move oil droplets and solids to the floor for removal.	Effectively removes oil droplets and enhances water clarity.	High operational costs, chemical use and sludge generation.
	Advanced oxidation processes (UV / H_2O_2)	Uses ultraviolet mild and oxidants to interrupt down continual natural pollution and disinfect water.	Rapid, non-selective oxidation; powerful disinfection.	High strength consumption; calls for cautious chemical handling.
Biological	**Biological treatment**	Uses microorganisms to degrade natural compounds in produced water.	Sustainable; low chemical use.	Sensitive to excessive Salinity and poisonous compounds; sluggish kinetics.

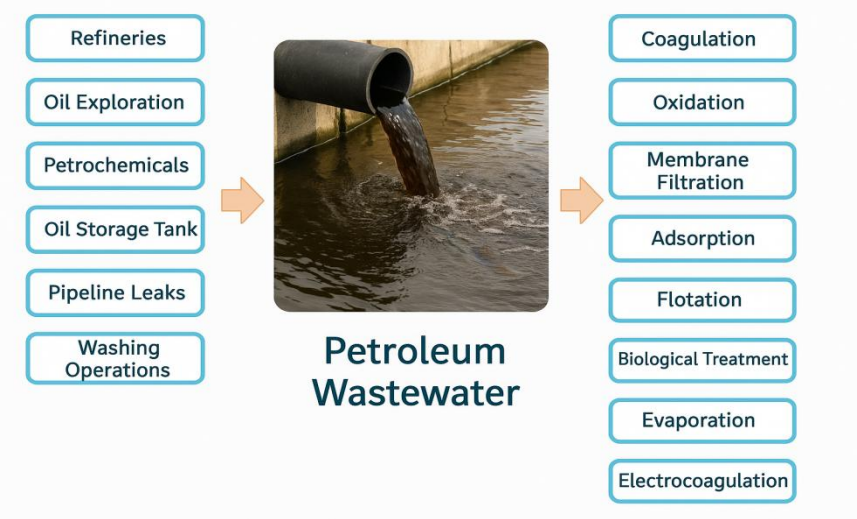


Figure I.1. Conventional and AOPs methods of produced WW.

I.1.4. Environmental requirement and produced water discharge guidelines:

I.1.4.1. Regulating organizations:

- **The U.S environmental protection agency (EPA):** defines national discharge regulations under the clean water act, including ELGs for oil and gas extraction.
- **OSPAR:** regulates offshore discharge in the north east atlantic, with a maximum oil-in-water limit of 40 mg/L.
- **National regulatory authorities:** such as Algeria's ministry of environment and Sonatrach, impose local discharge guidelines and demand permits to comply [14].

Table I.4: Key discharge limites [14].

Parameter	**Maximum allowable limit (Appoximate)**
Oil and grease (O & G)	10 - 40 mg/L (varies by jurisdiction).
Suspended solids	30 - 100 mg/L.
pH	6.0 - 9.0
Hesvy metals	Pb, Cr, Zn < 1 mg/L.
Hydrogen sulfide (H_2S)	Must be removed - highly toxic and flammable.
Total dissolved solids (TDS)	Site - specific, based on discharge location.

I.1.5. Potential reuse of treated produced water:

With superior remedy, PW may be converted from a waste flow right into a precious useful resource in numerous key applications:

I.1.5.1. Hydrogene production:

Treated produced water can be utilized to produce hydrogen through methods like electrolysis or photo-catalytic splitting. Provided it is highly pure, impurities diminish efficiency and damage equipment, thus procedures like as reverse osmosis, deionization are required. This is particularly useful in desert ans oil-rich areas [13].

I.1.5.2. Agricultural irrigation:

After removing contaminants, PW can be reused for both non-food crops and, with advanced treatment, food crops. To avoid soil degradation, salt and heavy metals levels must be monitored on a continuous basis [13].

I.1.5.3. Potable water standards:

PW can be treated to drinking water grade using membrane filtration and reverse osmosis. However, these are energy-intensive and are often saved for emergencies or specialized applications [13].

I.2. Photocatalysis:

An sophisticated oxidation technique called photocatalysis breaks down pollutants in petroleum wastewater by using light-activated semiconductor materials, most often titanium dioxide (TiO_2), but also zinc oxide (ZnO) and tungsten (WO_3). These potocatalysts absorb photons and produce electron-hollow pairs when exposed to light, often ultraviolet or in the case of some materials, visible light as presented in Figure.I.2. These pairs react with oxygen and water in wastewater to produce hydroxyl radicals (·OH) and other unexpected reactive oxygen species (ROS) [15].

These ROS are potent oxidizing agents that can convert a variety of organic contaminants into innocuous byproducts such as mineral salts, carbon dioxide (CO_2) and water (H_2O) by changing them into less hazardous or more stable forms, photocatalysis can also lessen some inorganic pollutants, like heavy metals. because of this, photocatalysis is a strong and adaptable technique for enhancing water quality in industrial and environmental setting [15].

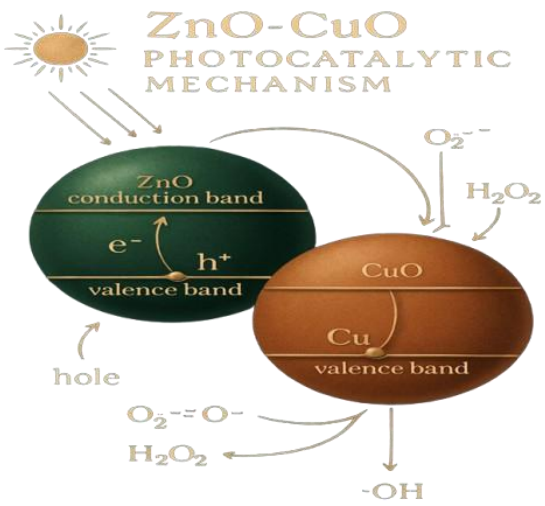


Figure.I.2. Photo catalysis general process.

Photocatalysis is sustainable and effective. After every cycle, the catalyst regenerates itself, enabling continued use. Aligning light energy with the catalyst's band gap is essential to its efficacy. With just light ans catalyst, photocatalysis provides a cleaner alternative to conventional methods for treating pollution while avoiding dangerous chemicals [16].

I.2.1. Factors influencing Photocatalytic efficiency:

A variety of factors affect photocatalytic performance. The kind and quantity of catalyst influence the number of active sites accessible for reactions. The activation energy required depends on the light source and its wavelength, whereas the pH of the solution influences surface charge and reaction rate. High pollutant concentrations can reduce efficiency, and interfering substances-such as other ions or organic matter-can compete for active sites. Furthermore, material factors like surface area, shape, and band gap energy have a substantial impact on total effectiveness [17].

I.2.2. Semiconductor photo-catalysts: mechanisms and applications:

Photocatalytic semiconductors are crystalline materials with a band gap (1.0-3.5 eV) that absorb light and create electron-hole pairs, allowing for redox processes without being consumed. These materials are significant for their ability to harness solar energy in a variety of applications, including environmental cleanup (pollutant

breakdown in air and water), green hydrogen production via water splitting, carbon dioxide reduction into fuels, and medical uses such as surface sterilisation [18].

It has been shown that a variety of semiconductor and nano-hybrid materials, such a $\mathbf{TiO_2}$, $\mathbf{ZnO}$, $\mathbf{SnO_2}$, $\mathbf{CuO}$, $\mathbf{SrTiO_3}$, $\mathbf{Bi_2WO_6}$, $\mathbf{CdS}$, $\mathbf{MoS_2}$, $\mathbf{Ag/Ag_2Te}$,**g-C3N4,** etc., are effective photocatalysts in wastewater treatment through photocatalysis [19].

I.2.2.1. Photo-catalysis mechanism:

The photocatalytic degradation process is schematically shown in Figure.I.3, photons having energy larger than the photo-catalyst's band gap are absorbed by the photocatalyst an electron from it's valance band is ejected into its conduction band, thus an electron / hole (e^-/h^+) pair is created. If the positive charge carrier h^+ remaining in the valance band of the photocatalyst has an oxidation potential above 2.31 V/NHE (normal hydrogen electrode), (potential of the couple $OH\cdot/H^+, H_2O$) at pH = 0, it can oxidize water into ($OH\cdot$) and H^+. If the negative charge carrier e^- remaining in the conduction band of the photocatalyst has a potential below 0.92 V/ENH (potential of the oxygen reduction in O_2^-) at pH = 0, it can reduce O_2 into O_2^-. With an oxidation potential of 2.31 V/ENH at pH = 0, ($OH\cdot$) radicals are energetic enough to break covalent C−C bonds in organic molecules, while O_2^- radicals have a reductive potential sufficient to reduce water into hydrogen peroxide (H_2O_2). Hydrogen peroxide decomposes under UV light into tow ($OH\cdot$) [19]. The photo-generation of ($OH\cdot$) is direct during the water oxidation with h^+, while it is a two-step process during the water reduction with e^-. Consequently, photo-catalytic degradations of organic compounds are more efficiently driven by the oxidative ($OH\cdot$) generation with h^+ [20].

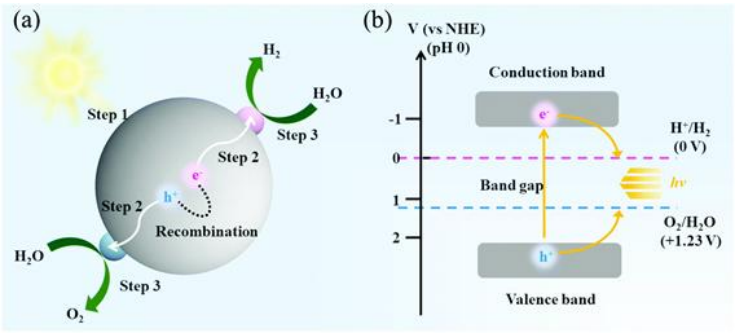


Figure.I.3. Schematic representation of a photocatalytic process mechanism.

The overall mechanism for the photo-catalytic degradationcan be written as follows:

$$\text{Photocatalyst} + h_v \rightarrow \text{Photocatalyst}\,(h^+_{(vb)} + e^-_{(eb)}) \quad \text{(I. 1)}$$

$$H_2O + h^+_{(vb)} \rightarrow H^+ + OH \quad \text{(I. 2)}$$

$$e^-_{(eb)} + O_2 \rightarrow O_2^- \quad \text{(I. 3)}$$

$$O_2^- + HO_2^- + H^+ \rightarrow H_2O_2 + O_2 \quad \text{(I. 4)}$$

$$H_2O_2 + h_v \rightarrow 2\,OH \quad \text{(I. 5)}$$

$$\text{Organic compounds} + OH \rightarrow CO_2 + H_2O + \ldots\ldots \quad \text{(I. 6)}$$

I.2.2.2. Specific properties of the catalysts used in this study (ZnO, CuO):

ZnO and CuO are among the most commonly used semiconductor photo-catalysts, each possessing distinct physical and chemical properties as presented in table I.4, that influence their efficiency in photocatalytic reactions.

Table I.5: Key characteristics of ZnO and CuO.

Property	ZnO (Zinc Oxide)	CuO (Copper(II) Oxide)
Crystal structure	Hexagonal (Wurtzite structure).	Monoclinic structure.
Semiconductor type	n-type.	p-type.
Band gap	~3.2 eV (wide).	~1.2 - 1.9 eV (narrow).
Light absorption range	Ultraviolet (UV).	Visible light.
Chemical stability	Very high, stable under various conditions.	Less stable, may degrade under certain conditions.
Cost	Low.	Relatively low.
Toxicity	Low, environmentally friendly.	Slight toxicity at hig concentrations.
Ease of preparation	Easy to synthesize via multiple methods.	Also easy to synthesize, especially by precipitation.
Photo-catalytic activity	Good under UV light, limited in visible light.	Good under visible light, but less stable.
Electronics	Good electron conductor, but suffers from charge recombination.	Good hole conductor, suitable for p–n junctions.

I.3. Activated carbon as catalyst support:

I.3.1. Definition and types of activated carbon:

Carbon-rich precursors are carbonized and activated to produce AC, a highly porous substance with a large surface area and fine pore structure. It works well for purifying gases and liquids because of its great adsorption ability, which results from physical interactions with target molecules without altering their chemical structure. It can be made from a variety of organic materials, such as peat, wood, and coconut shells [21]. It is frequently customized for certain applications because its qualities vary depending on the source material and production process. Generally,AC is classified into three main types as shown in the table I.5.

Table I.6: Types of AC.

Type	Particle size range	Applications	Key features
Powdered activated carbon (PAC)	5 to 150 Å.	Typically used in liquid-phase adsorption.	Low processing cost and flexible in operation.
Granular activated carbon (GAC)	0.2 mm to 5 mm.	Used in both gas and liquid phases.	Clean handling, longer lifespan, high hardness, reusable.
Extruded activated carbon (EAC)	Cylindrical pellets (1 mm to 5 mm).	Typically used in gas-phase reactions.	Heavy-duty carbon due to the extrusion process.

I.3.2. Properties of commercial activated carbon:

AC is widely utilized across industrial, environmental, and medical applications due to its exceptional adsorptive capabilities. However, its performance is highly dependent on several physical and chemical properties (Table I.6), which vary according to the raw material used and the activation process applied [22].

Table I.7: The key properties that define the quality and suitability of commercially produced activated carbon for specific applications.

Property	Description
Adsorptive properties	Encompasses adsorption capacity, rate, and efficiency; often measured by iodine number, CTC, etc.
Apparent density	Affects the amount of carbon per unit volume, important for system design and capacity.
Ash content	Represents inorganic, non-absorptive material; lower ash indicates higher carbon quality.
pH value	Indicates the potential shift in pH when carbon is added to liquids; varies with treatment.
Particle size	Influences adsorption rate, pressure drop, and filtration behavior.
Moisture content	Ideally between 3- 6 %; excess moisture reduces available surface area and efficiency.
Hardness / Abrasion resistance	Indicates mechanical strength and resistance to breakdown; coconut shell-based carbons are the hardest.
Pore structure	Includes microspores, mesopores, and macropores; determined by raw material and activation method.
Surface area	Typically ranges from 500 to 1500 m^2/g; critical for adsorption performance.

I.3.3. Activation methods: thermal and chemical:

The production of AC mainly relies on two key methods: thermal activation and chemical activation. Each method involves different processing techniques that influence the resulting pore structure, surface area, and the material's performance in targeted applications:

I.3.3.1. Thermal activation: this two-step process involves:

- **Carbonization:** raw materials (e.g., coconut shells, coal) are pyrolyzed at 600-900 °C in an inert atmosphere (argon/nitrogen) to remove volatiles like water and tar, leaving a carbon-rich char [23].

- **Activation:** the char is treated with oxidizing gases (steam, CO_2 or air) at 800-1000 °C to develop porosity via gasification reactions.

$$C + H_2O \rightarrow CO + H_2 \quad \text{(Endothermic)} \qquad \text{(I.7)}$$

$$C + CO_2 \rightarrow 2\,CO \text{ (Endothermic)} \qquad \text{(I.8)}$$

These reactions create a hierarchical pore structure (micro-, mrso-, and macropores) and surface areas of 500 -1500 m^2/g [24].

Advantages:

- ✓ Environmentally friendly (no chemical residues).
- ✓ Produces mechanically robust carbons, ideal for applications requiring abrasion resistance (e.g., water filtration) [24].

I.3.3.2. Chemical activation:

This method uses dehydrating agents (e.g., H_3PO_4, KOH, $ZnCl_2$) to enhance pore development at lower temperatures (200 - 500 °C):

- **Impregnation:** the raw material (e.g., wood, agricultural waste) is soaked in a chemical solution (e.g., 25-85 % H_3PO_4) [25].

- **Heating:** the mixture is heated in an inert atmosphere, promoting dehydration and cross-linking creates a well-developed microporous structure.

- **Washing:** residual chemicals are removed via water/acid washing [26].

Advantages:

- ✓ Higher surface areas (up to 3000 m^2/g) and controlled pore sizes.
- ✓ Faster and energy-efficient compared ti thermal methods.

Table I.8: Comparison between thermal and chemical methods [27].

Aspect	Thermal activation	Chemical activation
Temperature	800 - 1000 °C.	200 - 500 °C.
Activation agents	Steam, CO_2, air.	H_3PO_4, KOH, $ZnCl_2$.
Surface area	500 - 1500 m^2/g.	Up to 3000 m^2/g.
Pore structure	Broad distribution (micro-macro).	Dominantly microporous.
Environmental impact	Low chemical waste.	Requires chemical recovery.

I.3.4. Role in improving photocatalytic performance:

Activated carbon (AC) can improve photocatalytic efficiency when paired with catalysts such as ZnO. Its large surface area and porosity facilitate pollutant adsorption near the catalyst. AC also collects photogenerated electrons, which decreases electron-hole recombination and improves charge separation. Functional groups on its surface enhance interactions with contaminants, making it an important component in sophisticated water and air treatment systems [28].

I.3.5. Iodine number (IN) test as an indicator of adsorption capacity:

The IN (mg/g) quantifies the ability of AC to adsorb tiny compounds such as iodine. A greater iodine value suggests a larger surface area, more micropores, and a better adsorption capability. It is widely used to test the efficacy and adsorption of AC in water and air filtration, particularly for the removal of tiny organic contaminants [29].

I.4. The standards for physicochemical parameters in Produced water:

The oil and gas sector creates produced water, which is a complex wastewater with varying characteristics influenced by factors such as well age, extraction methods, and geological conditions. This water must be treated before it can reused or discharged.

PW is characterized by high salinity, with total dissolved solids exceeding 350.000 mg/L and electrical conductivity over 100.000 $\mu S/cm$. It's pH typically ranges from 5.5 to 9.5; often leaning towards alkalinity. The water contains notable amounts of oil, hydrocarbons, harmful BTXE chemicals, and suspended particles; with density between 1.01 and 1.2 g/cm^3. It has a high chemical oxygen demand often exceeding 10.000 mg/L and includes radioactive isotopes and heavy metals, complicating treatment efforts.

Due to it's hazardous nature, produced water cannot be directly used or discharged and requires advanced treatment methods to meet environmental standard. It may be stored in reservoirs for enhanced oil recovery or disposal while research continues on more effective treatment solutions [30].

Chapter II:

Experimental setup

This chapter present the reactivation of commercial activated carbon (CAC), the synthesis of ZnO-CuO/CAC based photocatalysts, and the evaluation of their performance in treating industrial wastewater under different conditions.

II.1. Mareriel:

In this study, CAC was used as a support material for the preparation of photocatalysts. The activation process was carried out using potassium hydroxide (KOH), and the photocatalysts were synthesized using zinc acetate ($Zn(CH_3COO)_2$) and copper (II) acetate ($Cu(CH_3COO)_2$) . All the chemicals employed in this experiment were of analytical grade.

The industrial WW used in the photocatalytic degradation experiments was collected from the Hassi R'mel oil field, located in Laghouat region (Algeria).

II.2. Reactivation of commercial activated carbon:

CAC was reactivated to enhance its physical and chemical characteristics, notably by increasing its surface area and micro porosity [41], which boosts its effectiveness in adsorption and photocatalytic processes.

The reactivation process involved mixing potassium hydroxide (KOH) with CAC in wieght ratio : 1:4 (1g of CAC for every 4 g of KOH). The mixture was placed in ceramic crucible (Fig.II.1) and subjected to thermal treatment in a tubular furnace (Fig.II.2) at 550 °C for one hour in an inert nitrogen atmosphere, flowing at a rate of 0.5 L/min.

Post reactivation, the RCAC was combined with water in a beaker and stirred for 30 minutes. The mixture was then filtered through filter paper and a funnel, and this washing and filtering process was repeated about four times to achieve the desired pH (= 7). If needed, hydrochloric acid (HCl) was added to ensure the pH reached neutrality. After adjusting the pH, the RCAC was dried in a n oven at 70 °C for one hour and stored appropriately.

All the process steps are represented in figure II.3.

Figure.II.1. Ceramic crucible.

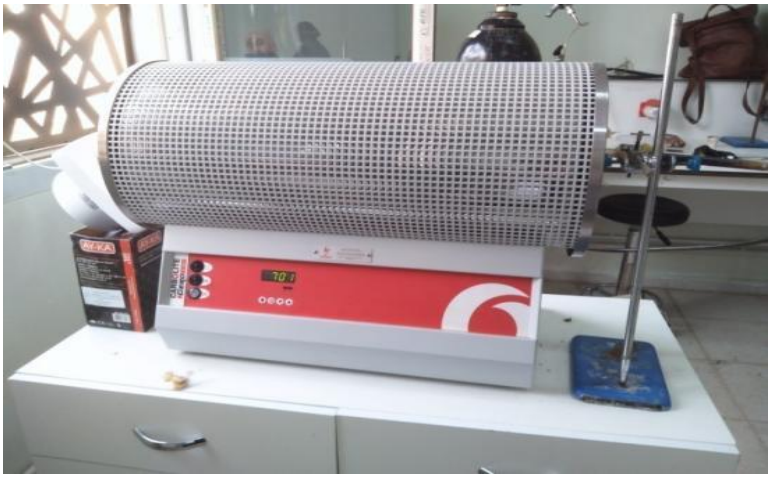


Figure.II.2. Tubular furnace used in the reactivation process of CAC.

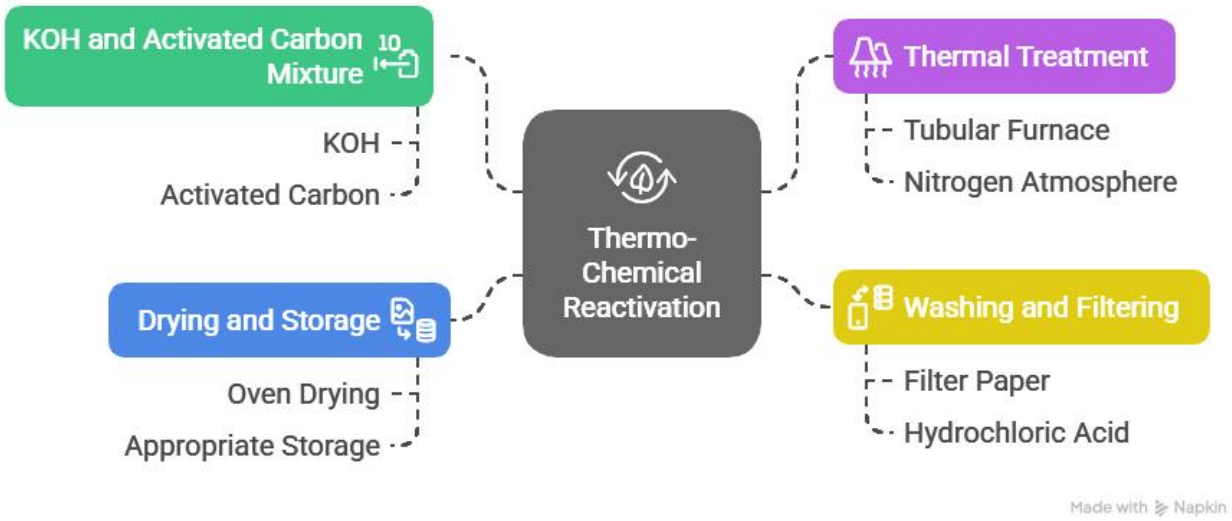


Figure.II.3. Workflow of the thermo-chemical reactivation of CAC.

II.3. Testing the effectiveness and absorbency of RCAC:

II.3.1. Iodine number:

The IN is a key indicator for evaluating the adsorption capacity of activated carbon, particularly for small molecules such as iodine. It is expressed in milligrams of iodine adsorbed per gram of carbon (mg/g) and serves as an indirect measure of micro-porosity and specific surface area. The IN is calculated by determining the amount of iodine adsorbed during a standardized titration process [31].

The iodine number is given by the following formula:

$$IN = \frac{(V_{blank} - V_{sample})}{M} \times N \times 126.9 \times \frac{15}{10} \quad \text{(II.1)}$$

Where:

$\mathbf{V_{blank}}$: Volume of sodium thiosulfate solution (in ml) used for the blank titration.

$\mathbf{V_{sample}}$: Volume of sodium thiosulfate solution (in ml) used for the sample titration.

M : Weight of the sample (in grams) being analyzed.

N : Normality (equivalents per liter) of the sodium thiosulfate solution.

126.69: Conversion factor that relates milli-equivalents of sodium thiosulfate to grams of iodine; it is derived from the molecular weight of iodine (126.9 g/mol) divided by 10.

15/10: A correction or scaling factor.

High IN (typically between 800 and 1,700 mg/g) indicate a well-developed micro-porous structure, enabling effective performance in applications such as water purification and air filtration.

II.3.1.1. Preparation of solutions:

- **Iodine solution:** a 500 ml iodine solution with a concentration of 0.1 mol/L was prepared by measuring 16.6 g of potassium iodide (KI) and placing it in a volumetric flask. After adding 100 ml of distilled water and mixing until clear, 12.7 g of elemental iodine (I_2) was added to the solution and stirred for 1h for complete dissolution as trioxide ions (I_3^-). Finally, 400 ml of distilled water was added while stirring, resulting in a fully mixed solution with a total volume of 500 ml.

- **Sodium thiosulfate solution:** to prepare the sodium thiosulfate solution, 12.41 g of ($Na_2S_2O_3$) was weighted and placed into a 500 ml volumetric flask. Approximately 300 ml of distilled water was added, and the mixture was stirred until fully dissolved. After confirming complete dissolution, distilled water was added to reach a total volume of 500 ml, ensuring the solution was well mixed and homogeneous.

- **Starch indicator solution:** 1 g of soluble starch was dissolved in 100 ml of distilled water and heated with continuous stirring until it reached 90 °C. Stirring continued until starch was completely dissolved, resulting in a clear, homogeneous solution

II.3.1.2. Titration process:

The titration procedure consisted of three successive titrations to measure iodine quantity and assess iodine adsorption by various carbon samples, following a standardized method. Initially, 100 ml of iodine solution was combined with starch indicator and titrated with sodium thiosulfate to determine the V_{blank}. In later titration,

0.05 g of RCAC and CAC were mixed with 15 ml of iodine solution, then filtrated and treated with starch indicator before titration. The experiments were repeated three times for accuracy, recording the sodium thiosulfate amount used to indicate non-adsorbed iodine [32].

II.4. Synthesis of ZnO-CuO supported activated carbon photo-catalysts:

The ZnO-CuO photocatalysts supported on both CAC and RCAC, (ZnO-CuO/CAC and ZnO-CuO/RCAC) were synthesized through a modified impregnation technique (Figure.II.5). Three different weight ratios were represent in Table II.1 for the process: (3/7), (5/5) and (4/6). Each component was measured into separate beakers, mixed with 50 ml of distilled water and magnetically stirred for 30 min. The zinc acetate ($Zn(CH_3COO)_2$)and copper (II) acetate ($Cu(CH_3COO)_2$) suspensions were then gradually added to the CAC and RCAC suspensions while the mixture was continuously stirred and evaporated until nearly dry [33].

Table II.1: Six different photo-catalysts were synthesized in this study [19].

	Representation of photocatalyst	Weight of ZnO (g)	Weight of CuO (g)	Weight of AC (g)	Weight ratio $\frac{(ZnO + CuO)}{AC}(-)$
CAC	3/7 ZnO-CuO/CAC	1.5	1.5	7	0.43
	4/6 ZnO-CuO/CAC	2	2	6	0.67
	5/5 ZnO-CuO/CAC	2.5	2.5	5	1
RCAC	3/7 ZnO-CuO/RCAC	1.5	1.5	7	0.43
	4/6 ZnO-CuO/RCAC	2	2	6	0.67
	5/5 ZnO-CuO/RCAC	2.5	2.5	5	1

II.4.1. Drying: the resulting paste was transferred to an oven and dried at 110 °C for 12 hours.

II.4.2. Calcination: the dried materials were subjected to calcination in a muffle furnace (Fig.II.4) at 500 °C for 3 hours to ensure proper formation of the metal oxide phases and their integration with the carbon support [33].

All this preparation steps are shown in Figure.II.5.

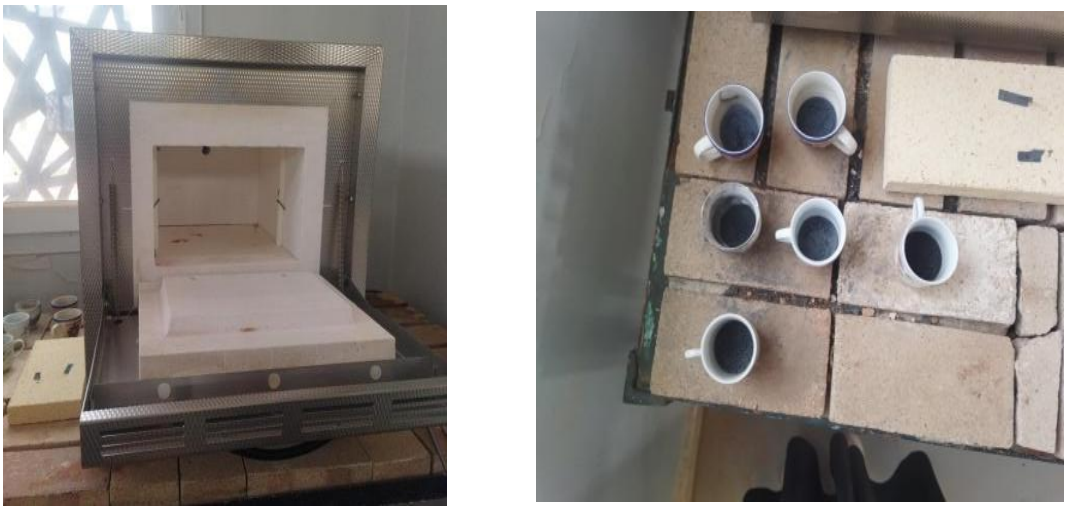


Figure.II.4. Muffle furnace and the photocatalysts samples.

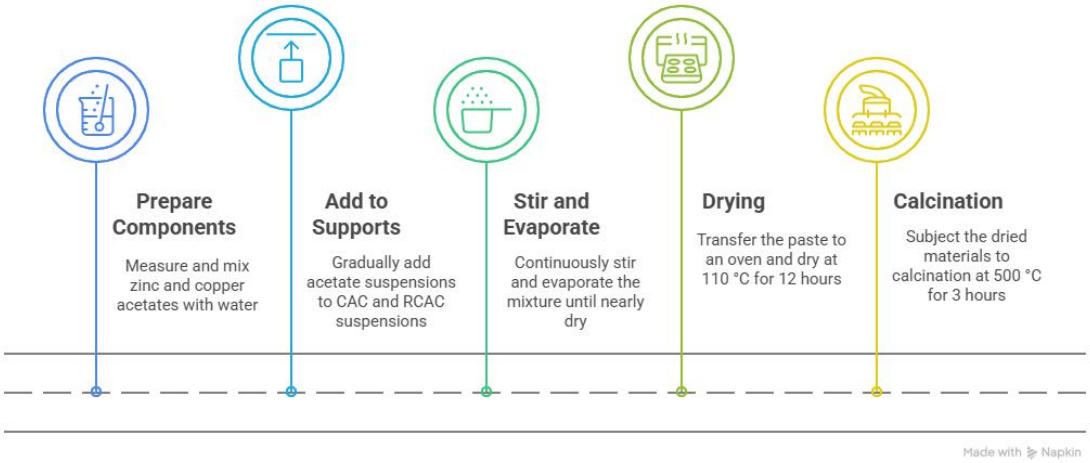


Figure.II.5. Synthesis of ZnO-CuO/AC photocatalysts.

II.5. Photocatalytic degradation experiment:

II.5.1. The preparation of the preliminary experiment for the comparison of catalysts:

Heterogeneous photocatalytic degradation experiment were conducted using industrial wastewater (produced water) obtained from Hassi R'Mel-Laghouat oil well. Prior to the tests, the WW was filtrated with standard filter paper to eliminate suspended solids. The main characteristics of WW were analysed before the experimet such as pH, EC, COD.

The six measured photocatalysts, comprising ZnO-CuO supported on both CAC and RCAC, were evaluated. In each experiment, 0.4 g of catalyst was combined with 200 ml of the filtered industrial PW in an erlenmeyer flask. The mixtures were continuously stirred at 500 RPM for two hours while being illuminated by a 500 W light source that provided strong visible and UV light to boost photocatalytic activity. The experiment took place in multi-position magnetic stirrer (Fig.II.6).

As a final step, the samples were filtrated to remove the catalyst, and the treated water (TW) analyzed to evaluate the effectiveness of each catalyst in removing organic pollutants and improving water quality.the experimental conditions summarized in table.II.2.

Figure.II.6. Experimental instrument for wastewater photocatalytic treatment by ZnO-CuO/CAC.

Samples were collected and analyzed after two hours of photocatalytic treatment to identify the most effective catalyst by assessing the percentage of organic matter removal (DCO) and enhancements in physical properties. A comparison was made among six different types of catalysts.

II.5.2. Time-based dynamic experiment of the optimal catalyst:

Once the most effective catalyst was identified (specifically ZnO-CuO/RCAC at 5/5 ratio), a further experiment was carried out to investigate how treatment efficiency varied over time. Each sample was examined to track changes in indicators such as DCO, EC, TDS and pH, among others. This experiment facilitates the creation of curves that depict the progression of treatment efficiency over time, aiding in the identification of the ideal duration for applying the method in industrial settings. Table.II.3

Table II.2: The preliminary experiment for the comparison of catalysts.

	Catalyser type	Time (min)	Water volume (ml)	Temperature (°C)	Light source (W)	Masse of catalyst (g)	pH
CAC	3/7 ZnO-CuO/CAC	120	200	24.4	500	0.4	4.7
	4/6 ZnO-CuO/CAC	120	200	24.4	500	0.4	4.7
	5/5 ZnO-CuO/CAC	120	200	24.4	500	0.4	4.7
RCAC	3/7 ZnO-CuO/RCAC	120	200	24.4	500	0.4	4.7
	4/6 ZnO-CuO/RCAC	120	200	24.4	500	0.4	4.7
	5/5 ZnO-CuO/RCAC	120	200	24.7	500	0.4	4.7

Table II.3: Time-based dynamic experiment of the optimal catalyst.

	Catalyser type	Time (h)	Water volume (ml)	Temperature (°C)	Light source (W)	Masse of catalyst (g)	pH
RCAC	5/5 ZnO-CuO/ RCAC	0.5	200	26.2	500	0.4	5.77
		1	200	28.7	500	0.4	6.21
		2	200	30.6	500	0.4	6.32
		3	200	32	500	0.4	6.84
		5	200	34.7	500	0.4	7
		12	200	35.8	500	0.4	7

II.6. Physico-chemical parameter :

II.6.1. Potential of hydrogen :

The pH is one of the most critical physicochemical factor in evaluation water quality since it influences various chemical and biological processes in aquatic environments. It is a measure of hydrogen ion concentration that indicates whether water is acidic or basic, with a scale ranging from 0 (very acidic) to 14 (very basic) and 7 representing a natural state, this parameter is dimensionless and in our experiment we use a digital pH (Fig.II.8) meter to measure it [34].

In the context of industrial wastewater, pH is vital for assessing the solubility and movement of heavy metals, chemical stability, and the effectiveness of treatment methods. Acidic conditions (pH < 7) can enhance pipe corrosion and increase the mobility and bio-availability of harmful metals, which might accumulate through the food chain. On the other hand, highly alkaline conditions (pH > 7) may cause the precipitation of specific compounds, impacting treatment efficiency and potentially releasing hazardous substances like ammonia that can harm aquatic life [35].

Additionally, pH affects numerous chemical reactions, including acid-base equilibria, oxidation-reduction processes, and complexation, as well as influencing microbial activity and the behavior of other pollutants. Areas near industrial or mining operations are particularly susceptible, as leachates can modify the pH of nearby water bodies, raising significant environmental and health issues. Consequently, monitoring and regulating pH is vital for maintaining water quality and optimizing wastewater treatment outcomes [36].

Figure.II.7. Digital pH meter.

II.6.2. Electrical conductivity EC:

Electrical conductivity measures the ionic content of produced water from oil and gas extraction, which typically has high EC due to dissolved salts and minerals. High EC poses challenges like scaling, corrosion, and toxicity, making monitoring essential for effective treatment and regulatory compliance. Accurate EC measurement supports the safe reuse of TW in agriculture and industry, aiding freshwater conservation. Advances in sensor technology and real-time monitoring have improved produced water management; enhancing efficiency and sustainability in the oil and gas sector [34].

Figure.II.8. Digital conductivity meter.

II.6.3. Total dissolved solids (TDS):

The aggregate concentration of all organic and inorganic materials dissolved in water in known as total dissolved solids, or TDS these sediments may come from household wastewater, industrial effluents, or natural sources. Untreated or inadequately treated wastewater frequently contains high levels of TDS, which can change the flavor of the water, cause pipe scaling, and obstruct treatment processes.

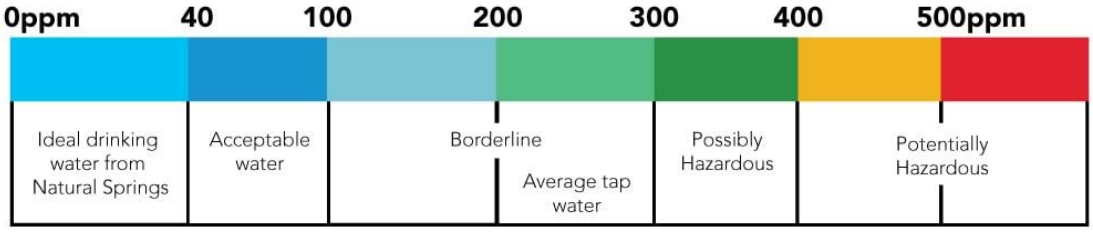


Figure.II.9. Color-coded TDS scale

In this study, "Gravimetric analysis" method was used to determine the concentration of total solids (TS), total dissolved solids (TDS), and total suspended solid (TSS) in an industrial water sample (Fig.II.11) This method involves evaporation and filtration steps to distinguish between the dissolved and suspended fractions of the solids [37].

As show in figure II.10, to clean and dry beakers were first weighed and labeled. A 25 ml portion of the water sample was,added to each beaker. The first beaker was placed in an oven at 103-105 °C until complete evaporation, then let it cooled and reweighed to determine the TS.

The second sample was filtrated using a pre-weighed filter paper, and the filtrate was collected in a separate beaker, evaporated under the same conditions, and reweigh to determine the TDS. The suspended solids TSS were then calculated by subtracting TDS from TS [38].

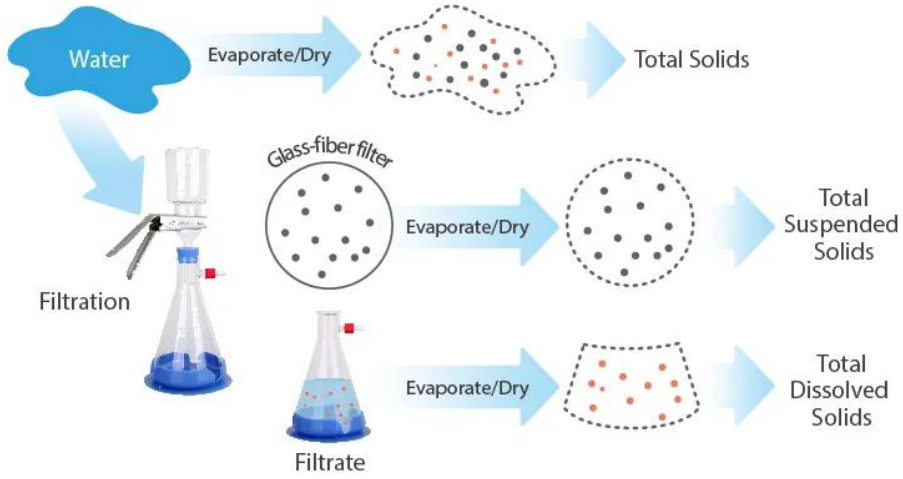


Figure.II.10. Illustration of the gravimetric analysis of water solids (TS, TDS, TSS).

$$\mathrm{TS(mg/l)} = \frac{(W_{TS} - W_{beaker})}{V} \times 1000 \quad \text{(II.2)}$$

$$\mathrm{TDS(mg/l)} = \frac{(W_{TDS} - W_{beaker})}{V} \times 1000 \quad \text{(II.3)}$$

$$\mathrm{TSS(mg/l)} = \mathrm{TS} - \mathrm{TDS} \quad \text{(II.4)}$$

Where:

$\mathbf{W_{TS}}$: Final weight of the beaker after evaporation (mg).

$\mathbf{W_{TDS}}$: Final weight of the beaker containing evaporated filtrate (mg).

$\mathbf{W_{beaker}}$: Initial weight of the empty beaker (mg).

V : Volume of the filtrated water sample (ml).

II.6.4. Chemical oxygen demande (COD):

The chemical oxygen demand is a fundamental parameter used to assess the level of organic and inorganic pollutants in water by measured the quantity of oxygen required for chemical oxidation. High COD values indicate elevated quantities of oxidizable elements, which can dramatically reduce dissolved oxygen levels in natural water bodies, endangering aquatic life. COD is an important indicator of water quality, particularly in monitoring industrial effluents.

In this study, the chemical oxygen demand (COD) of industrial wastewater samples was measured using the "Modified winkler titration method" [39]. This method is based on the oxidation of organic compounds by potassium dichromate ($K_2Cr_2O_7$) under acidic conditions, followed by back-titration of the excess dichromate with ferrous ammonium sulfate (FAS).

II.6.4.1. Reagent preparation:

- ✓ **Potassium dichromate solution (0.25 N):** 6.13 g of $K_2Cr_2O_7$ was dissolved in 500 ml of distilled water, stored in a volumetric flask wrapped in aluminum foil and kept in the dark.

- ✓ **Digestion solution (Ag_2SO_4 , H_2SO_4):** 0.625 g of silver sulfate was added to 125 ml of concentrated sulfuric acid and stirred at 50 °C until completely dissolved, then transferred to a 250 ml volumetric flask.

- ✓ **Ferrous ammonium sulfate (FAS) solution (0.1N):** 4.902 g of Mohr's salt was dissolved in 50 ml of distilled water, followed by the addition of 10 ml of concentrated H_2SO_4. the mixture was then diluted with distilled water to 125 ml and stored in 250 ml flask. Sulfuric acid was added to prevent oxidation.

- ✓ **Ferroin indicator:** 0.4 g of 1,10-phenanthroline and 0.3 g of $FeSO_4.7H_2O$ were dissolved in 10 ml of concentrated H_2SO_4, then diluted to 100 ml with distilled water. Stored the solution dark place.

II.5.4.2. Procedure:

For the analysis , the industrial water samples (before and after photocatalytic treatment) were diluted 201 times by mixing 1 ml of sample with 200 ml of distilled water.

In a clean beaker, 10 ml of the diluted sample was mixed with 5 ml of $K_2Cr_2O_7$ solution and 15 ml of the Ag_2SO_4 , H_2SO_4 digestion reagent. After thorough mixing, five drops of ferrion indicator were added, and the solution was titrated with the FAS solution until the color changed from yellow to a dark reddish-brown, indicating the endpoint. The volume of FAS consumed was recorded and used to calculate the COD value in mg/l of O_2 [40].

Figure.II.11. The sample color changes during the COD procedure.

The Chemical oxygen demande formula:

$$\text{COD (mg/l)} = \frac{(V_{blank} - V_{b.\,sample}) \times N \times 8000}{V_{sample\ used\ (ml)}} \qquad \text{(II.5)}$$

Where:

$\mathbf{V_{blanc}}$: Volume of FAS used for the blank sample (distilled water) in ml .

$\mathbf{V_{b.\,sample}}$: Volume of FAS used for the sample (ml).

$\mathbf{V_{sample\ used\ (ml)}}$: Volume of diluted sample used in the test (typically 10 ml).

N: Normality of FAS solution (eq/l).

8000 : Milli-equivalent weight of oxygen (8) × 1000.

II.7. Limitation of analytical tests:

Due to the limited resources and equipment available in the university laboratory, it was not possible to carry out all the recommended physicochemical analyses for the industrial wastewater samples. Specifically, tests such as Ammonia concentration (NH_3), phosphate content (PO_4^{3-}), biological oxygen demand (BOD_5), nitrate (NO_3^-), nitrite (NO_2^-), total kjeldahl nitrogen (TKN), hydrocarbon percentage, and heavy metal analysis could not be performed.

These parameters are essential for quality and treatment effectiveness. Nonetheless, the lack of required analytical tools (such as spectrophotometres, BOD incubators and ion-selective electrodes) methods employed. Despite these constraints, important factors linked to photocatalytic degradation and fundamental water quality indicators were evaluated to confirm the reliability of the results obtained.

Chapter III:

Result and discussion

III.1. Reactivation of commercial activated carbon (CAC):

Figure III.1 shows the effect of the reactivation process applied to commercial activated carbon (CAC) using potassium hydroxide (KOH) under the following conditions: mass ratio ($\frac{mKOH}{m_{CAC}}$ = 4:1), nitrogen flow rate Q_{n2} = 0.5 L/min, activation time = 60 minutes, and temperature = 550 °C. A thermo-chemical reactivation process was carried out with the aim of improving the adsorption performance of CAC.

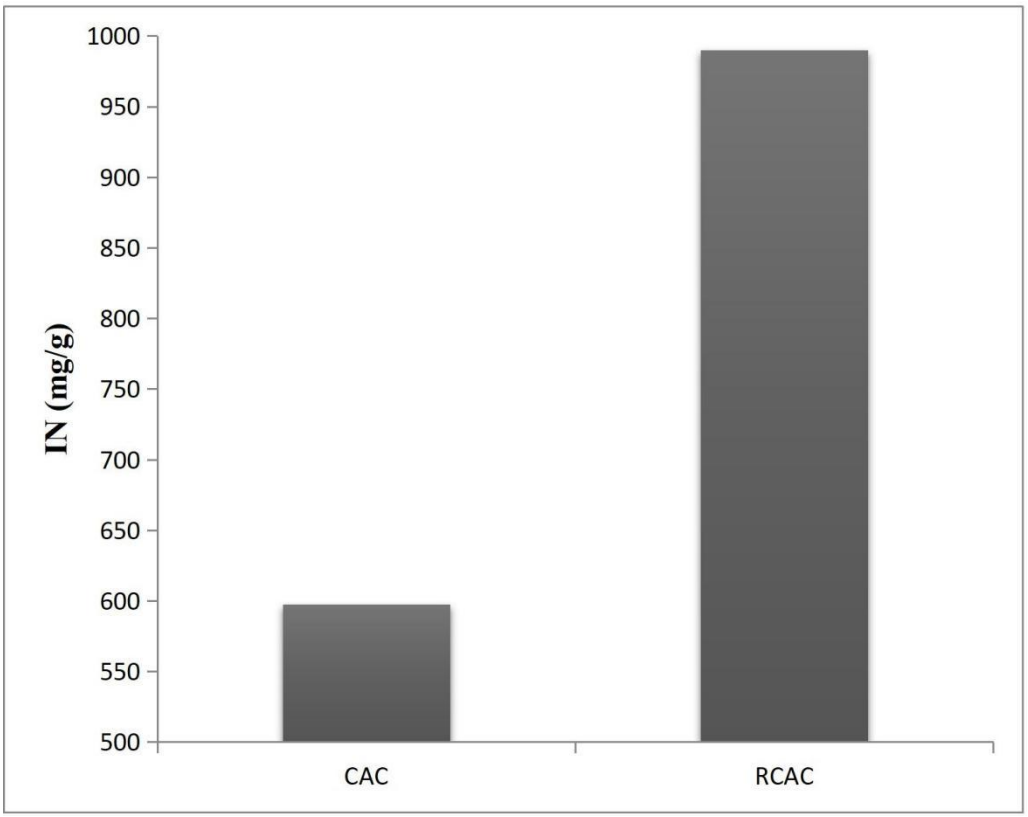


Figure.III.1. Effect of reactivating commercial activated carbon (CAC) ($\frac{mKOH}{mCAC}$ = 4, Q_{N2} = 0.5 L/min, t = 60 min, T = 550 °C).

Among the characterization tests initially planned to assess the improvement in structural and surface properties such as XRD, SEM, and BET isotherms only the iodine number (IN) test could be performed due to limitations in laboratory resources. This test, which evaluates the micro-porosity and the surface activity of the carbon toward small organic molecules, was used as the main indicator of surface activation.

The results revealed that the IN of the reactivated commercial activated carbon (RCAC) reached 989.82 mg/g, which is significantly higher than that of the untreated commercial carbon (597.70 mg/g).

This notable increase indicates a considerable enhancement in adsorption efficiency, especially within the micropore range (pores up to about 2 nm) [41].

Although no structural analysis (e.g., XRD) was performed, the observed improvement in IN is consistent with findings in the literature, where KOH activation is known to chemically etch the carbon framework and induce gasification reactions such as:

$$6\,KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3 \quad \text{(III.1)}$$

These reactions have been reported to result in the development of interconnected micropores and partially enlarged mesopores, which increase the surface area and facilitate the diffusion of adsorbates. Moreover, KOH acts as a strong dehydrating agent during pyrolysis, suppressing tar formation and encouraging the formation of graphitic domains. These graphitic structures are believed to enhance the material's structural stability and electron conductivity, which is particularly advantageous in photocatalytic applications [42].

Based on these insights, it is hypothesized—following patterns observed in published research—that the RCAC could contribute to enhancing the photocatalytic performance of ZnO–CuO systems by improving pollutant adsorption and assisting in charge separation processes. Its improved surface characteristics may reduce electron–hole recombination and increase the efficiency of the system [41-42].

III.2. Photocatalytic treatment of produced wastewater (PWW):

The physicochemical parameters of the industrial wastewater used in this study reveal a high amount of pollution, as shown in the Table III.1. These metrics show increased levels of organic and inorganic contaminants, emphasizing the critical need for an efficient treatment approach to minimize pollution and enhance water quality.

Table III.1: Physicochemical parameters of WW used in this study.

	pH	EC (mS/cm)	Density	TDS (mg/l)	TS (mg/l)	TSS (mg/l)	COD (mg/l)
ww	4.07	33.6	0.8320	378.42	4464.5	86.076	96780

III.2.1. Impact of the photocatalytic treatment on the physico-chemical parameters of the treated water (TW):

III.2.1.1. Evolution and influence of temperature:

Over the course of the 120 minute photocatalytic treatment, the reaction medium's temperature progressively rose from 21 °C to 33 °C, as seen in Figure III.2. The UV/visible irradiation used during the procedure is responsible for this little increase. The system maintained its thermal stability by staying within ideal operating parameters. The influence of temperature on photocatalytic treatment and catalysts is multifaceted, with both enhancing and inhibitory effects by influencing charge dynamics, reaction kinetics, and adsorption-desorption processes.

Moderate heating (≤100 °C) enhances activity by improving charge transfer, accelerating reactions, and increasing molecular collisions. However, excessive temperatures (>70–200 °C) can promote electron-hole recombination and reduce surface adsorption [43].

Optimal temperatures vary by catalyst for exemple : TiO_2 / Pd-TiO_2 performs best around 50 °C, Cu / TiO_2 at room temperature [43], and Au-Al-$CeVO_4$ around 60 °C for H_2 evolution [44]. Practical gains include a 6-fold increase in methyl orange degradation between 38–100 °C [45]. Still, high temperatures can degrade certain catalysts (e.g., Ag/TiO_2 above 55 °C) [43]. Thus, precise temperature control-typically 50-80 °C for liquids and up to 200 °C for gases- is crucial for optimizing photocatalytic performance [44-45].

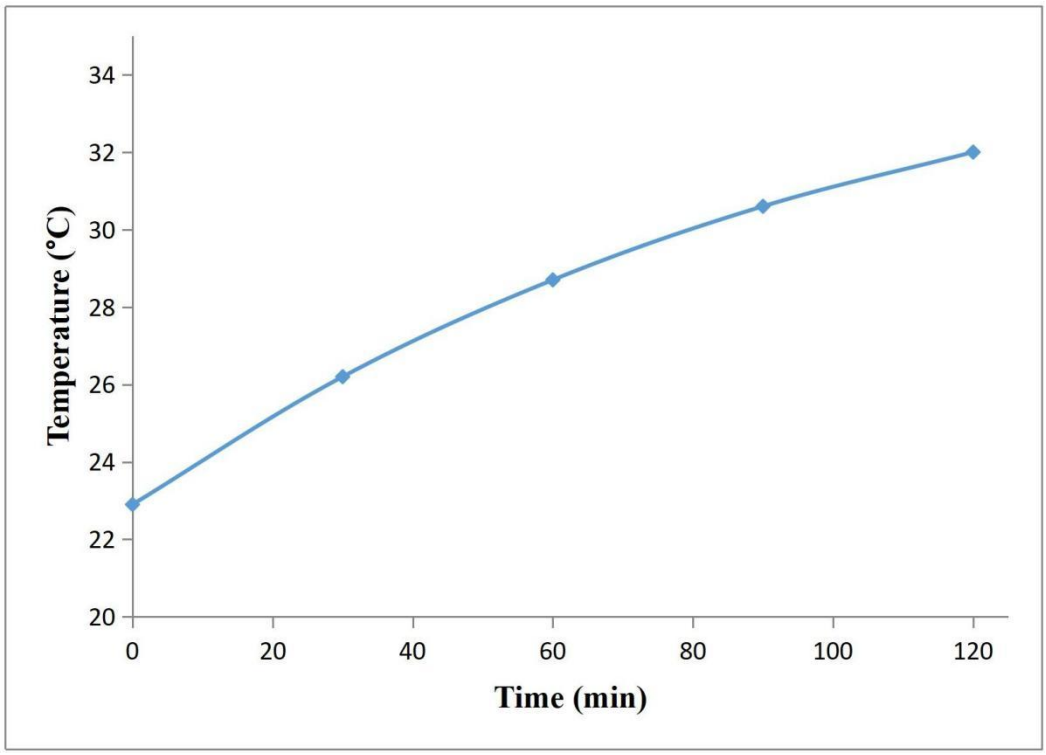


Figure.III.2. Evolution of temperature during photocatalytic treatment over ZnO-CuO/CAC (light source = 500 W, $m_{catalyst}$ = 0,4 g, V_{ww} = 200 mL, t = 120 min).

III.2.1.2. Performance comparison of ZnO–CuO catalysts at different mass ratios supported on CAC vs. RCAC:

III.2.1.2.1. Potential of Hydrogen (pH):

The pH of the wastewater improved notably after photocatalytic treatment, especially with RCAC. For the ZnO–CuO/CAC catalysts, pH values rose from 4.07 to 5.67 (3/7), 6.50 (4/6), and 6.70 (5/5), reflecting partial neutralization.

In contrast, the ZnO–CuO/RCAC samples showed greater enhancement, with pH levels reaching 6.6 (3/7), 6.79 (4/6), and up to 6.84 (5/5), indicating improved buffering capacity and making the treated water more suitable for applications like irrigation.

III.2.1.2.2. Electrical conductivity:

Despite the observed pH improvements, electrical conductivity (EC) remained high across all samples, indicating limited ionic removal. The RCAC-based catalysts showed slightly better performance overall. For instance, 3/7 ZnO–CuO/CAC and 4/6 exhibited EC values around 30 and 29.9 mS/cm respectively, while the 5/5 ZnO–CuO/RCAC sample showed the lowest EC at 29.4 mS/cm, suggesting modest enhancement.

III.2.1.2.3. Water density:

Across all ZnO-CuO ratios, the RCAC-based catalysts consistently yielded lower final water densities than their CAC counterparts. This trend confirms that reactivated carbon not only enhances pollutant adsorption and photocatalytic efficiency, but also contributes to cleaner effluent with lower residual mass content, correlating with improved TSS and TS removal (Figure.III.3.(b); (c)).

III.2.1.2.4. The solids content (TDS, TS, and TSS):

Total Dissolved Solids (TDS) showed modest reductions overall, with RCAC-based catalysts generally performing better, indicating improved adsorption of dissolved pollutants. 3/7 ZnO–CuO/CAC, and 4/6 reduced TDS to 353 and 308.8 mg/L, respectively, while 5/5 ZnO–CuO/RCAC achieved a lower TDS of 359.6 mg/L compared to its CAC counterpart (377.7 mg/L), highlighting RCAC's superior adsorption capacity despite some fluctuations.

Total Solids (TS) results mirrored the TDS trend, with RCAC-based catalysts generally showing better performance and lower residuals. 3/7 ZnO–CuO/CAC, and 4/6 showed TS values of 361 and 376.5 mg/L, respectively, while 5/5 ZnO–CuO/RCAC achieved improved removal with a lower TS of 375.6 mg/L compared to 455.2 mg/L for its CAC counterpart, confirming RCAC's enhanced efficiency.

Total Solids (TS) results mirrored the TDS trend, with RCAC-based catalysts generally showing better performance and lower residuals. 3/7 ZnO–CuO/CAC, and 4/6 showed TS values of 361 and 376.5 mg/L, respectively, while 5/5 ZnO–

CuO/RCAC achieved improved removal with a lower TS of 375.6 mg/L compared to 455.2 mg/L for its CAC counterpart, confirming RCAC's enhanced efficiency.

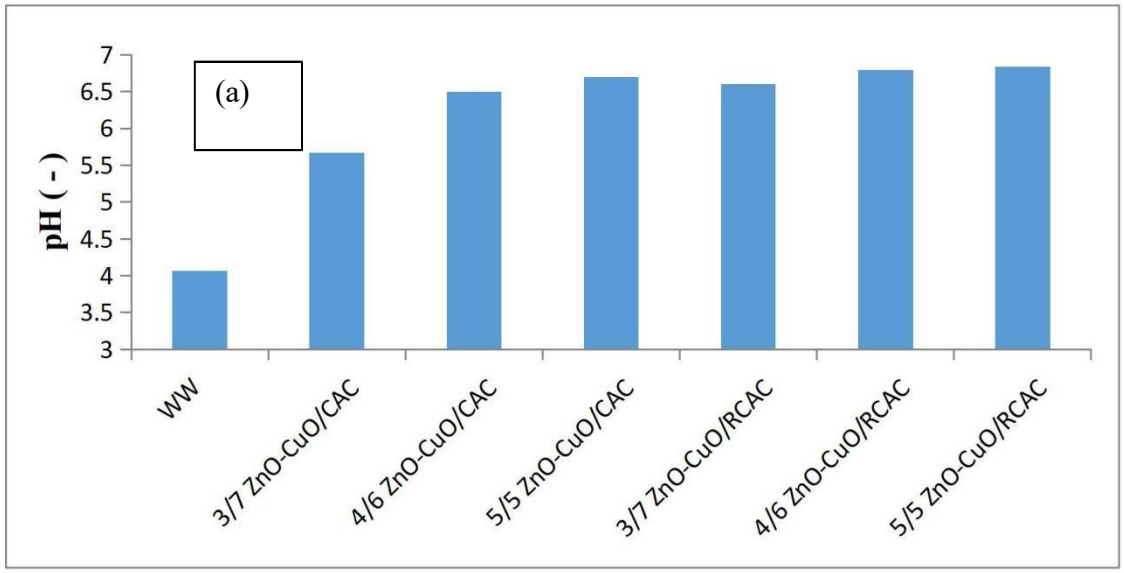
III.2.1.2.5. Chemical oxygen demand (COD):

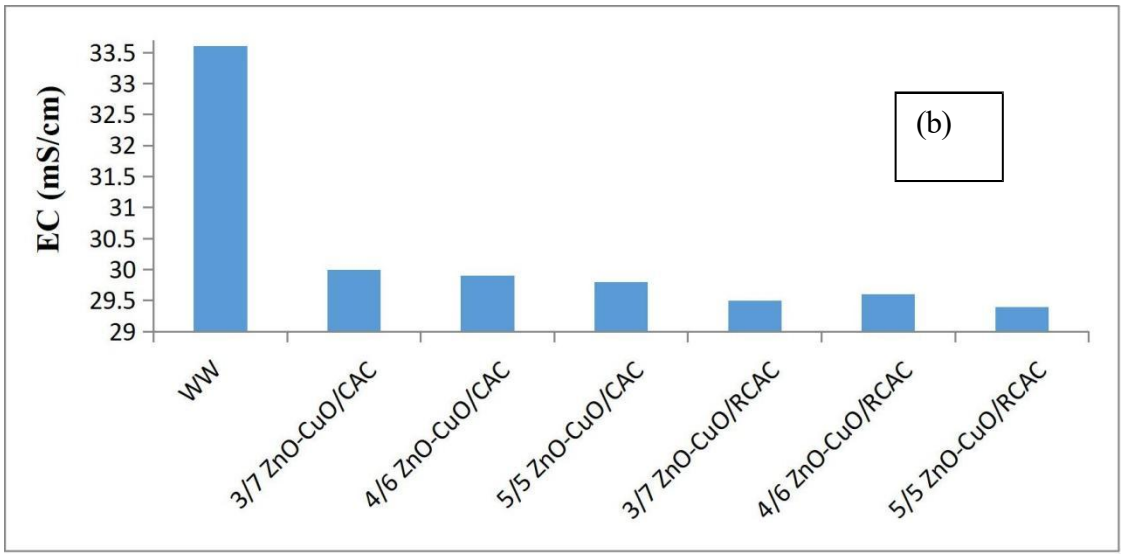
Chemical Oxygen Demand (COD) results highlighted the catalysts' efficiency in degrading organic matter, with RCAC consistently outperforming CAC across all ratios. 3/7 ZnO– CuO/CAC achieved a 21% reduction (76164 mg/L O_2), while the RCAC counterpart improved it to 71340 mg/LO_2 (26%).

The 4/6 ratio showed the weakest performance, with CAC reducing COD to 85812 mg/LO_2 (~11%) and RCAC slightly better at 84204 mg/LO_2 . The 5/5 RCAC catalyst maintained good performance, lowering COD to 74556 mg/LO_2 (~23%).

Across all tested catalyst ratios, the RCAC-based photocatalysts consistently outperformed their CAC counterparts in terms of pH neutralization, TSS and COD reduction, and overall physicochemical enhancement.

These findings affirm the positive impact of thermochemical reactivation in improving surface properties and photocatalytic performance.





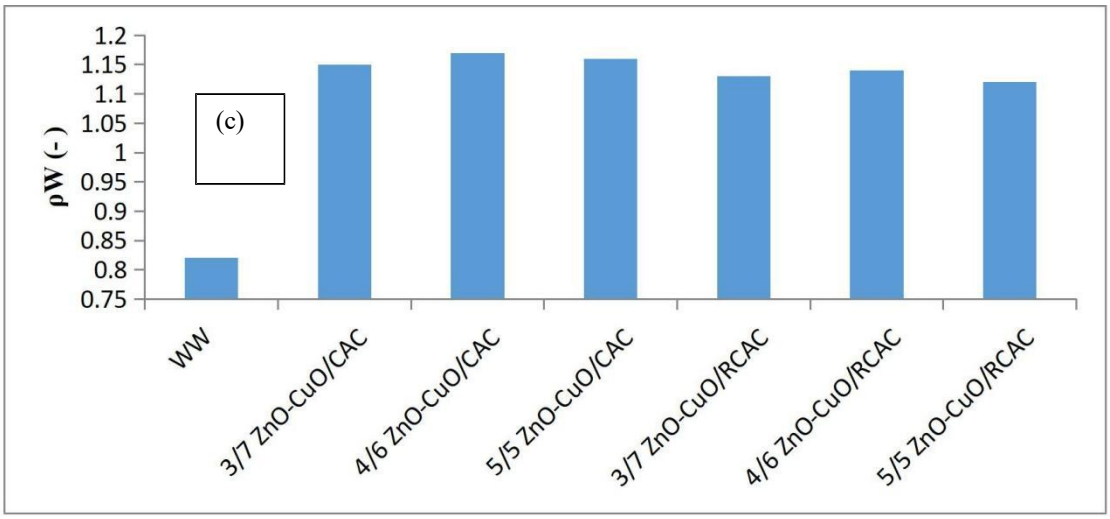


Figure.III.3. Impact of the photocatalytic treatment on the (a) pH,(b) Electrical conductivity, and (c) density of TW

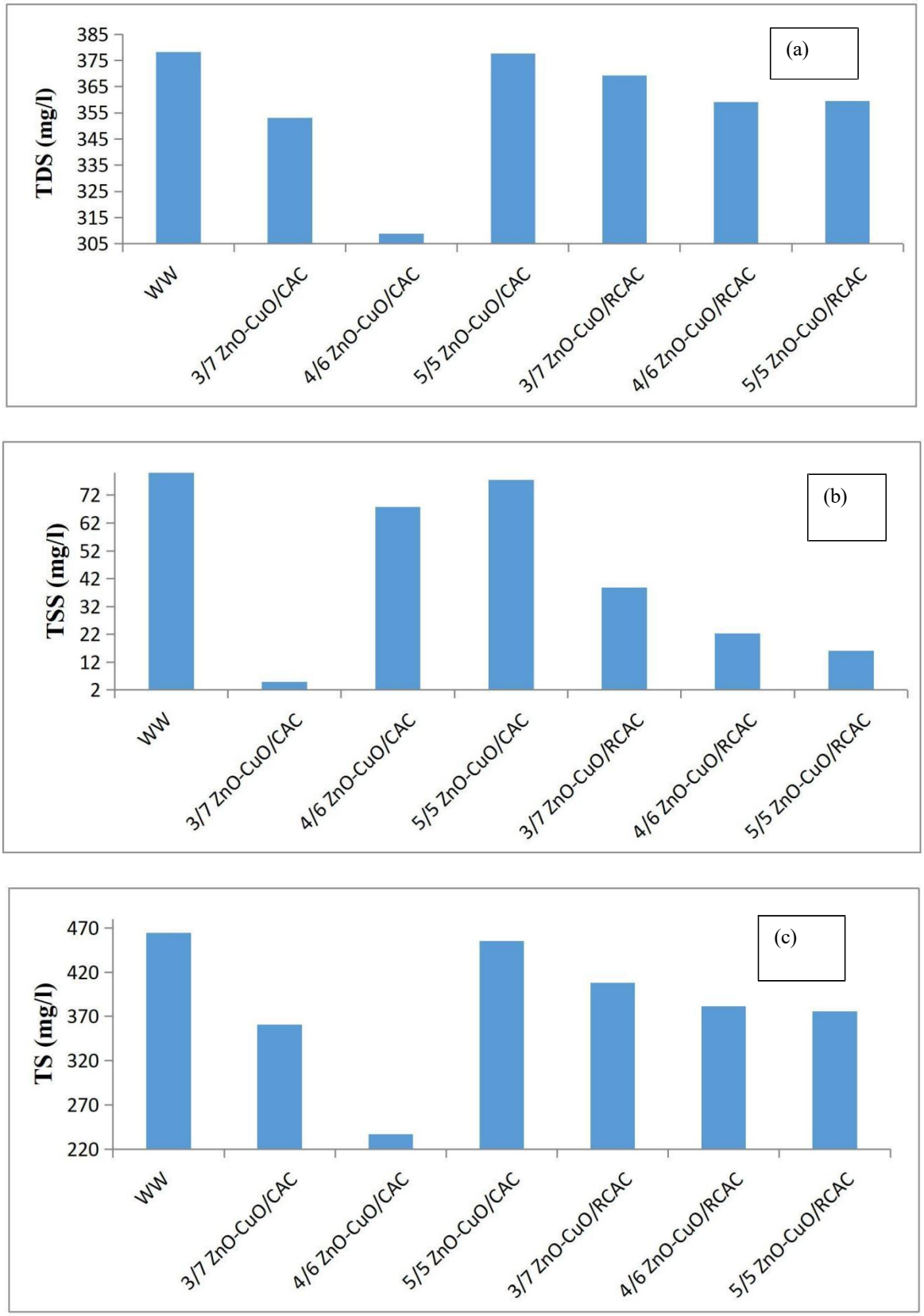


Figure.III.4. Impact of the photocatalytic treatment on the (a) TDS,(b) TS, and (c) TSS of TW.

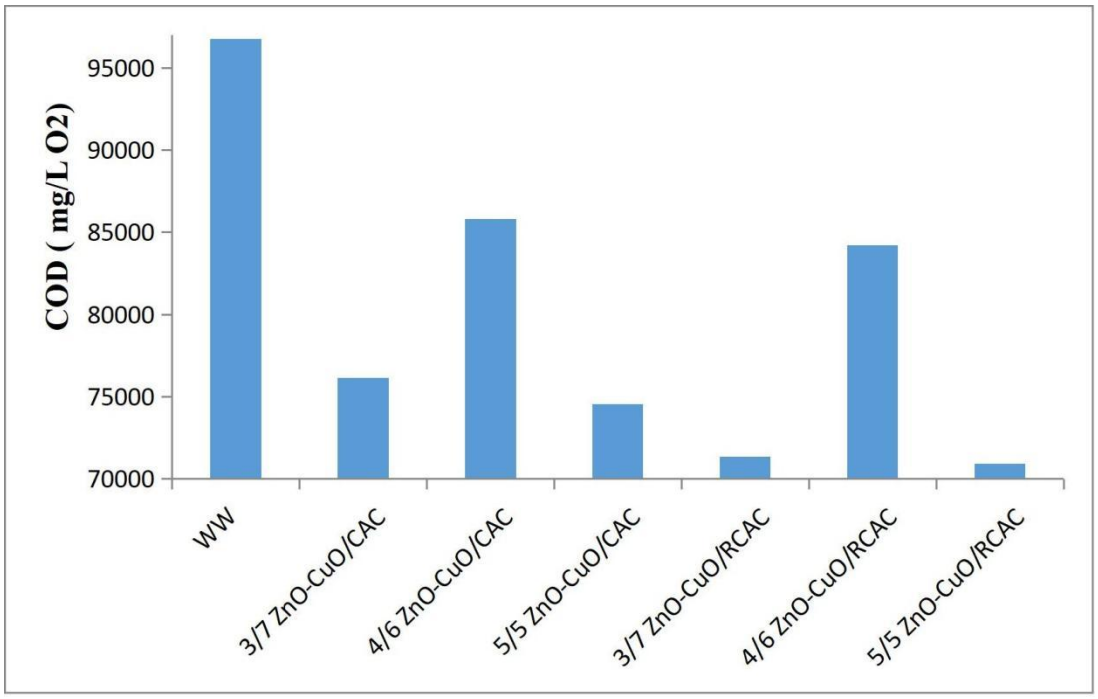


Figure.III.5. The evolution of COD in TW over ZnO-CuO/CAC photocatalyst and WW.

III.2.1.3. Why the 5/5 ZnO-CuO/RCAC catalyst was the best catalyst:

The 5/5 ZnO–CuO/RCAC photocatalyst was selected as the optimal formulation due to its superior overall performance in improving wastewater quality. Among the six tested catalysts, it achieved the most effective pH neutralization, raising the pH to 6.84, which is close to neutral and suitable for environmental discharge and irrigation purposes. It also recorded the highest reduction in Chemical Oxygen Demand (COD), lowering it to 70920 mg/L—a decrease of over 26%—indicating efficient degradation of organic pollutants. Furthermore, this catalyst exhibited the lowest Total Suspended Solids (TSS) at 16.0 mg/L, suggesting improved stability, minimal particle leaching, and effective solid-phase separation. Total Dissolved Solids (TDS) and Total Solids (TS) were also reduced to 359.6 mg/L and 375.6 mg/L, respectively, which were lower than the corresponding values observed for the commercial activated carbon (CAC) version. Additionally, the Electrical Conductivity (EC) dropped slightly to 29.4 mS/cm, reflecting a moderate improvement in ionic pollutant removal.

The 5/5 ZnO–CuO/RCAC catalyst's outstanding performance is mostly due to its balanced semiconductor ratio, which promotes effective p–n heterojunction formation between ZnO (n-type) and CuO (p-type). This configuration enhances charge separation, reduces electron–hole recombination losses, and boosts the generation of reactive oxygen species (ROS), which are essential for the oxidation of organic contaminants [45–46]. In parallel, the reactivated activated carbon (RCAC) contributed a high surface area and improved porosity, greatly enhancing adsorption capacity and catalyst dispersion [46]. This dual function—combining both adsorptive and photocatalytic actions—produced a synergistic effect that led to more effective pH stabilization and greater COD and TSS reduction compared to the other ratios [47].

III.2.2. Effects of photocatalytic treatment duration on treated water (TW) physicochemical properties over 5/5 ZnO-CuO/RCAC:

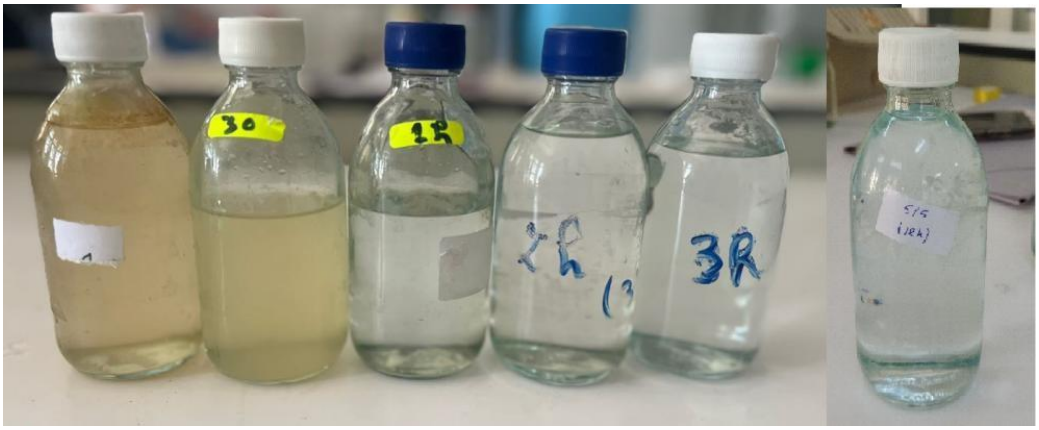


Figure.III.6. The progress of wast water colour after treatment during the time.

III.2.2.1. Water potential hydrogen (pH):

The effects of photocatalytic treatment duration on the physicochemical properties of treated water using the optimized 5/5 ZnO–CuO/RCAC catalyst demonstrate significant temporal dynamics in pollutant degradation. Over a 5 hour period, the pH progressively increased from an initial 5.77 at 30 minutes to a neutral value of 7, after which it stabilized (Figure.III.6.(a)).

This gradual rise in pH reflects the continuous breakdown of acidic contaminants during the early stages of photocatalysis, consistent with the oxidative

degradation mechanisms reported in similar studies. The plateau observed after 5 hours suggests the depletion of readily oxidizable organic pollutants, indicating that the system approaches a steady state where further pH changes are minimal. Achieving near-neutral pH is critical for water reuse, especially in agricultural applications, as it reduces the risk of soil acidification and improves compatibility with irrigation standards. These findings align with other research highlighting that extended photocatalytic treatment enhances water quality by progressively neutralizing acidity and reducing organic load, although treatment efficiency may diminish once easily degradable compounds are exhausted [46]. Overall, the time-dependent evolution of physicochemical parameters underscores the importance of optimizing treatment duration to balance pollutant removal efficiency and operational cost-effectiveness.

III.2.2.2. Electrical conductivity:

The electrical conductivity (EC) of the treated water exhibited a slow but steady decline from 29.7 mS/cm to 24.7 mS/cm over a 12 hour photocatalytic treatment period using the 5/5 ZnO–CuO/RCAC catalyst (Figure.III.6.(b)).

This gradual decrease indicates partial mineralization of ionic species and a corresponding reduction in salinity, reflecting the photocatalyst's ability to break down some dissolved ions and organic compounds contributing to conductivity. However, the relatively high residual EC suggests that ion removal was incomplete, potentially due to the persistence of certain inorganic salts or the formation of intermediate ionic species during photocatalysis, as reported in similar studies. Such findings emphasize that while photocatalytic treatment effectively reduces organic pollutants and some ionic content, it may need to be complemented with additional processes like membrane filtration or ion exchange to achieve comprehensive salinity reduction and meet stringent water reuse standards [47].

This behavior aligns with the broader literature indicating that photocatalysis alone often cannot fully address dissolved ionic contaminants, highlighting the importance of integrated treatment approaches for wastewater reclamation.

III.2.2.3. Water density:

The water density decreased from 1.168 g/cm³ (30 min) to 1.086 g/cm³ (12 hours) **(Figure.III.6.(c))**. This progressive decline corresponds to the elimination of

dissolved organic and inorganic components from the medium. Because density is proportional to solute concentration, its decline corresponds to reported decreases in TDS, TS, and COD, the readings remained within predicted limits, indicating that the treated effluent had become physically stable.

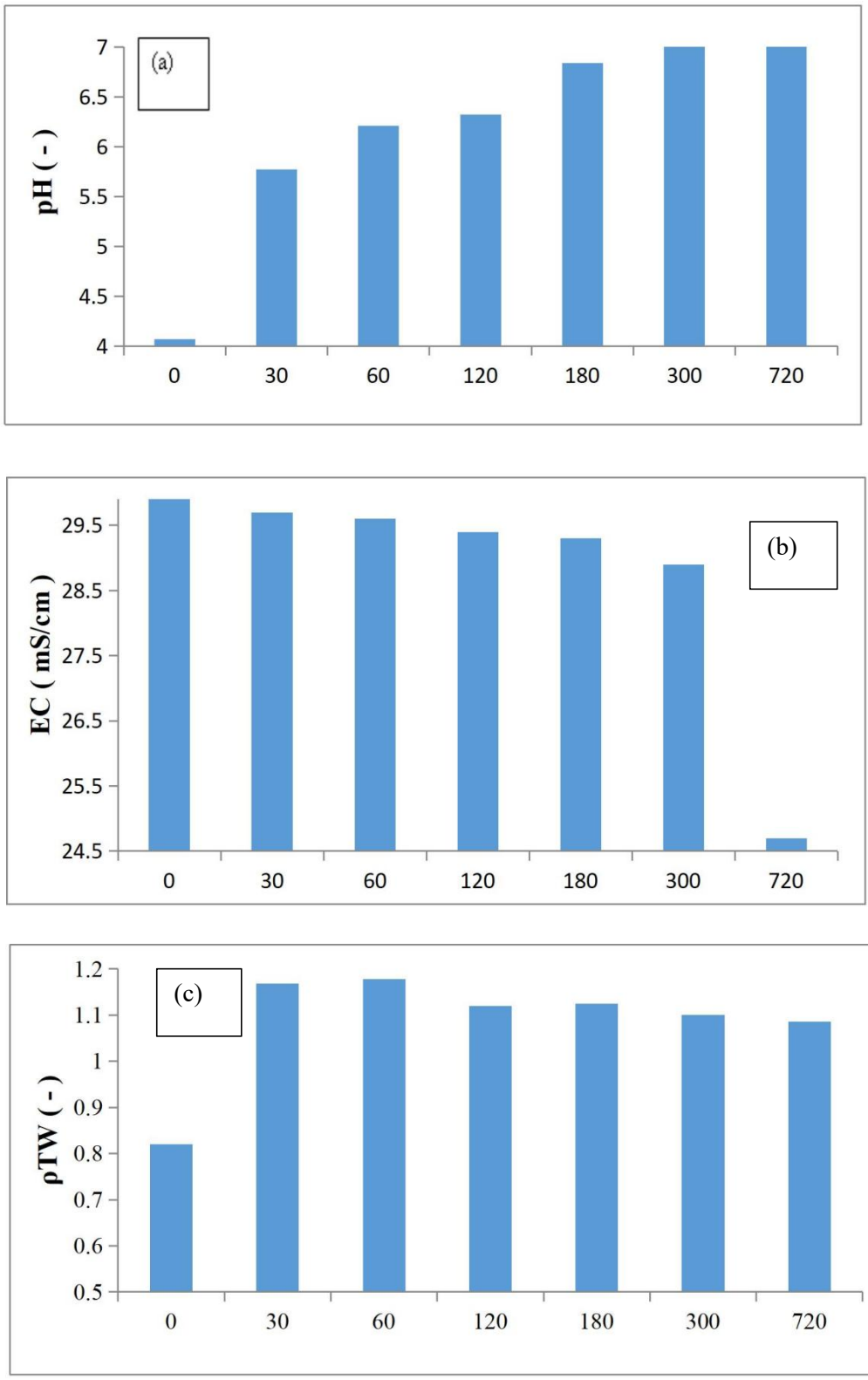


Figure.III.7. Effects of photocatalytic treatment duration on the (a) pH, (b) Electrical conductivity, and (c) density of TW over 5/5 ZnO-CuO/RCAC.

III.2.2.4. The solids content (TDS, TS):

The solids content in the treated water showed significant improvement over the photocatalytic treatment period with the 5/5 ZnO–CuO/RCAC catalyst. Total dissolved Solids (TDS) decreased markedly from 368.6 mg/L to 227.8 mg/L, while total solids (TS) dropped from 385.2 mg/L to 242 mg/L. The most substantial reductions occurred within the first 3 to 5 hours as shown in (Figure.III.7.(a); (b)), coinciding with the phase of highest photocatalytic activity and rapid degradation of organic and particulate matter.

This trend reflects the effective breakdown and removal of easily degradable substances during the initial treatment stage, consistent with observations in similar photocatalytic wastewater studies. After 5 hours, the rate of reduction slowed considerably, indicating that the remaining solids were more recalcitrant or less accessible to photocatalytic oxidation. This plateau effect has been widely reported and suggests that prolonged treatment yields diminishing returns unless combined with other treatment methods [48]. Overall, the results highlight the importance of optimizing treatment time to maximize solids removal efficiency while maintaining operational feasibility.

III.2.2.5. Total suspended solids (TSS):

Total suspended solids (TSS) as seen in (Figure.III.8) exhibited a gradual but consistent decrease from 16.6 mg/L to 14.2 mg/L over the 12-hour photocatalytic treatment using the 5/5 ZnO–CuO/RCAC catalyst. Although the reduction appears modest, the low final TSS values demonstrate the system’s effective removal of particulate matter, which is crucial for reducing water turbidity and enhancing subsequent filtration processes. This trend aligns with previous studies where photocatalytic treatment contributed to the breakdown and aggregation of suspended solids, facilitating their removal [49]. The efficient reduction of TSS not only improves water clarity but also reduces the risk of clogging in downstream treatment units, supporting the practical applicability of this photocatalytic setup for wastewater polishing and reuse. These findings underscore the catalyst’s potential in integrated treatment schemes aimed at comprehensive water quality improvement.

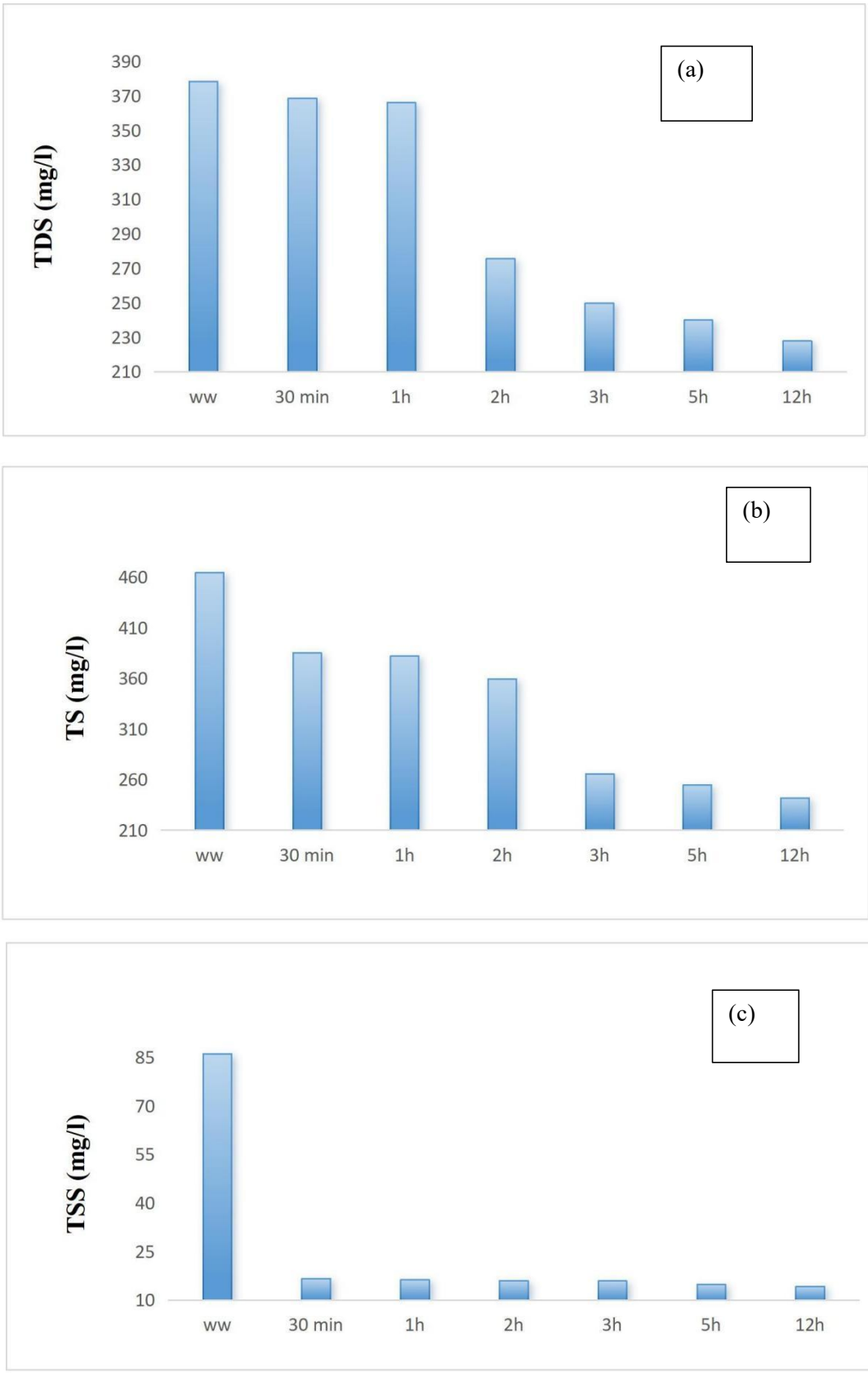


Figure.III.8. Effects of photocatalytic treatment duration on the (a) TDS,(b) TS,(c) TSS of TW over 5/5 ZnO-CuO/RCAC.

III.2.2.6. Chemical oxygen demand (COD):

The most significant observation during the photocatalytic treatment with the 5/5 ZnO–CuO/RCAC catalyst was the substantial reduction in chemical oxygen demand (COD), which decreased from 96,780 mg/L O_2 in the raw wastewater to 42,380 mg/L O_2, after 12 hours (Figure.III.9.), corresponding to a 56% overall reduction. The highest rate of degradation occurred within the first 5 hours, where COD dropped sharply to 64,782 mg/L O_2, indicating that the majority of organic pollutants were either adsorbed onto the catalyst surface or oxidized early in the treatment process. This rapid initial decline is consistent with findings from other studies, which report that photocatalytic systems effectively target readily degradable organic compounds during the early stages of treatment.

After this period, the rate of COD reduction slowed considerably, likely due to the persistence of more recalcitrant or less reactive organic molecules that require longer exposure times or stronger oxidizing conditions to break down. Such behavior is typical in photocatalytic wastewater treatment, underscoring the need for process optimization or integration with complementary methods to achieve deeper mineralization of resistant pollutants. Overall, these results highlight the effectiveness of the 5/5 ZnO–CuO/RCAC catalyst in significantly lowering organic load, particularly during the initial treatment phase[50].

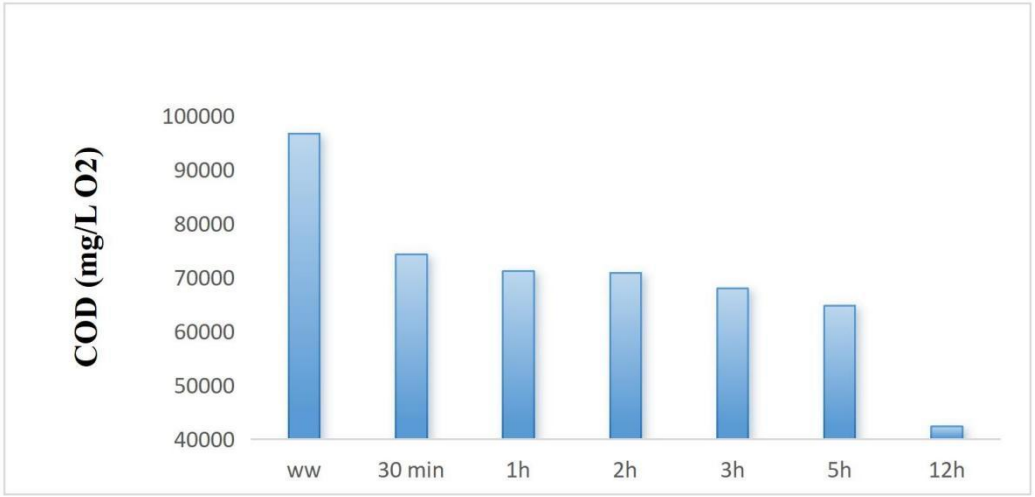


Figure.III.9. The evolution of COD in TW over 5/5 ZnO-CuO/RCAC photocatalyst and WW.

III.3. Parameter initial wastewater (WW), Treated Water (TW) and irrigation standards compliance:

The evaluation of treated water quality after 12 hours of photocatalytic treatment with the 5/5 ZnO–CuO/RCAC catalyst against international irrigation standards (FAO, WHO, and national guidelines) reveals a mixed level of compliance.

Table III.2: Parameter Initial WW Treated Water (TW) Irrigation Standards Compliance.

Parameter	Initial WW	Treated water (TW)	Irrigation standers	Compliance
pH	4.07	7.0	6.0 - 8.5	Compliant.
EC (mS/cm)	33.6	24.7	< 3 (ideal), < 10 (max)	High.
TDS (mg/l)	378.4	227.8	< 500 - 2000	Acceptable.
TSS(mg/l)	86.1	14.2	< 30 - 50	Compliant.
COD (mg/l)	96780	42380	< 250	Very high.

The pH of the treated water reached neutrality (pH = 7.0), which is ideal for irrigation and plant growth, demonstrating the photocatalytic system's effectiveness in neutralizing acidic wastewater, consistent with findings in similar treatment studies. The total dissolved solids (TDS) concentration decreased to 227.8 mg/L, well within the typical irrigation threshold of <500 mg/L, supporting the water's safe reuse for tolerant crops, especially in arid regions where water scarcity necessitates reuse [50].

Total suspended solids (TSS) were also substantially reduced to 14.2 mg/L, complying with reuse guidelines and minimizing risks of irrigation system clogging and poor soil infiltration, as reported in related research. However, despite a significant reduction in electrical conductivity (EC) from 33.6 to 24.7 mS/cm, the final EC remains far above the recommended limit (<3 mS/cm), posing potential risks of soil salinization and reduced crop productivity [51]. This aligns with literature emphasizing that photocatalysis alone often cannot sufficiently reduce salinity, necessitating additional treatments such as ion exchange or reverse osmosis.

Furthermore, although chemical oxygen demand (COD) decreased by over 56%, the final level (42,380 (mg/l O_2)) remains substantially higher than irrigation standards, indicating that while photocatalysis effectively reduces organic load, secondary or tertiary treatments are essential to meet safe reuse criteria .

In summary, the TW meets the required limits for pH, TDS, and TSS, but elevated EC and COD levels highlight the need for further optimization or complementary post-treatment processes to ensure the water's suitability for agricultural irrigation.

III.4. Enhancing the efficiency of photocatalytic wastewater treatment using 5/5 ZnO–CuO/RCAC catalyst:

Optimize the photocatalytic performance of the 5/5 ZnO–CuO/RCAC catalyst, particularly to address the elevated COD and EC levels that remain above reuse standards, several strategic recommendations can be made. Extending the irradiation time beyond 12 hours could facilitate the degradation of more persistent organic pollutants and promote deeper mineralization, as longer exposure often enhances photocatalytic efficiency.

Increasing the catalyst dosage to between 6 and 8 g/L may improve the availability of active sites for pollutant interaction; however, care must be taken to avoid excessive loading that could hinder light penetration and reduce overall activity, a balance highlighted in previous studies.

Enhancing the light source intensity or tuning its wavelength such as employing visible-light activation, solar concentrators, or doping strategies can boost the generation of reactive oxygen species (ROS), thereby improving degradation rates. Improvements in catalyst structure, including dual activation methods or ultrasonic dispersion, can increase porosity and light exposure, facilitating better pollutant adsorption and photocatalytic reactions [51].

Employing hybrid treatment processes that combine adsorption, photocatalysis, and biological steps is recommended to effectively handle complex wastewater matrices, as integrated approaches have shown superior pollutant removal efficiencies. Adjusting the initial pH to a slightly acidic to neutral range (6-8) can favor radical formation and enhance catalyst-solution interactions, optimizing photocatalytic activity [52-53].

Lastly, periodic regeneration of the catalyst is essential to maintain its long-term efficiency and economic viability by preventing deactivation and fouling. Implementing these optimizations can significantly improve treatment outcomes, making the photocatalytic process more effective and sustainable for wastewater reuse applications [54].

Conclusion

Conclusion:

This study addressed the crucial environmental challenge of treating petroleum produced water (PW) by developing an effective, low-cost, and sustainable photocatalytic process. This study, which was carried out in three stages contextual analysis, catalyst synthesis, and experimental validation showed that ZnO-CuO photocatalysts supported on reactivated commercial activated carbon (RCAC) have the potential to improve wastewater quality.

The study found that RCAC considerably improves the photocatalytic performance of ZnO-CuO nanocomposites. The RCAC's iodine number reached 989.82 mg/g, indicating an improvement in its porous structure over CAC. Several photocatalyst compositions were developed and tested under artificial light to determine their effectiveness in treating actual effluent from the Hassi R'mel oil field. The ZnO-CuO/RCAC (5/5) catalyst outperformed the other compositions examined. It achieved:

- ✓ A COD reduction of 56.19%.
- ✓ A TDS reduction by 50.99%.
- ✓ A TSS reduction by 92.7%.
- ✓ A neutralization of pH from 5.6 to 7.0.

These results demonstrate excellent photocatalytic and adsorption activity and reflect the synergy between ZnO-CuO semiconductors and the increased surface area of RCAC. The combination not only promotes oxidative breakdown via reactive oxygen species (ROS), but it also improves pollutant retention via adsorption. Despite the clear improvement in water quality, various limits were identified. Notably, the electrical conductivity (EC) and chemical oxygen demand (COD) levels remained beyond the required limits for irrigation reuse, demonstrating that a single-stage photocatalytic treatment is insufficient for comprehensive purification.

Recommendations to improve the purification rate: to improve water purification efficiency and achieve greater compliance with reuse criteria, the following measures are recommended:

Conclusion

- ✓ **Increase photocatalytic contact time:** extending the treatment period beyond 12 hours may result in more thorough destruction of recalcitrant organic materials.
- ✓ **increase light intensity or use solar energy:** using higher-intensity UV or visible light, or switching to solar photocatalysis, can boost reaction rates and lower energy costs.

- ✓ **To improve surface activity and re-usability,** optimize ZnO-CuO ratios and try alternate carbon supports such mesoporous carbon and thermo-chemical reactivation.

- ✓ **Consider secondary treatments:** adding post-photocatalytic treatments such membrane filtration, ion exchange, or electro-coagulation can reduce persistent ions and boost EC levels.

- ✓ **Evaluate catalyst re-usability and stability:** conduct long-term cycle tests to evaluate the catalyst's stability, degradation rate, and regeneration capacity after repeated applications.

- ✓ **Pilot-scale validation:** to ensure practical application, conduct larger-scale trials in continuous flow systems under field-like conditions.

In conclusion, the ZnO-CuO/RCAC photocatalyst shows great promise as a long-term and efficient treatment for petroleum effluent. Its photocatalytic and adsorptive properties enable significant pollution removal. However, for real-world applications, further investigation and process integration are required to meet demanding reuse or discharge conditions while also promoting environmental protection in oil-producing regions.

Appendix :

Results of the experiment :

Table .1: Results of the preliminary experiment (2 hours) for the comparison of catalysts:

	Catalysts	pH	EC (mS/cm)	Density	TDS	TS	TSS	COD
Commercial activated carbon	**3/7** Zno/CuOC/AC	5.67	30	1.15	353.03	361	4.97	76164
	4/6 Zno/CuO/CAC	6.50	29.9	1.17	308.8	376.5	67.7	85812
	5/5 Zno/CuO/CAC	6.70	29.8	1.16	377.7	455.2	77.5	74556
Reactivated commercial activated carbon	**3/7** Zno/CuO/ RCAC	6.60	29.5	1.13	369.2	408	38.8	71340
	4/6 Zno/CuO/ RCAC	6.79	29.6	1.14	359.2	381.6	22.4	84204
	5/5 Zno/CuO/ RCAC	6.84	29.4	1.12	359.6	375.6	16	70920

Table .2: Results of time-based dynamic experiment of the optimal catalyst:

	catalyst	Time	pH	EC (mS/cm)	Density	TDS	TS	TSS	DCO
Reactivated commercial activated carbon	**5/5** Zno/CuO/ RCAC	**30 min**	5.77	29.7	1.168	368.6	385.2	16.60	74380
		1h	6.21	29.6	1.178	366.1	382.32	16.22	71340
		2h	6.32	29.4	1.12	275.6	359.6	16	70920
		3h	6.84	29.3	1.125	249.7	265.6	15.9	67980
		5h	7	28.9	1.10	240	254.8	14.8	64782
		12h	7	24.7	1.086	227.8	242	14.2	42380

Appendix

Table .3: The volumes of sodium thiosulfate consumed during the three trials for each tested sample.

Sample type	Test 01 (ml)	Test 02 (ml)	Test 03 (ml)	Average volume (ml)
Blank solution	11,6	11,6	11,6	11,6
RCAC	9,3	8,8	8,9	9
CAC	10	10,1	10	10,3

Table .4: the calculated iodine number (IN) values.

	CAC	RCAC
Iodine number (mg/g)	597,70	989,82

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عنوان المذكرة :لمعالجة الضوئية للمياه المنتجة باستخدام /ZnO-CuO الكربون المنشط التجاري(CAC) .

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ملخص: يتناول هذا البحث دراسة معالجة المياه الصناعية الحقيقية بإستخدام تقنية التحفيز الضوئي، عبر استخدام مزيج من أكسد الزنك (ZnO) و اكسد النحاس (CuO)المدعوم على الفحم النشط، سواء التجاري أو المفعل كيميائيا-حراريا. الهدف الأساسي هو تقييم تأثير كل من نسبة المحفز و مدة المعالجة على إزالة الملوثات. تم إختبار ثلاث نسب وزنية مختلفة (3/7، 4/6، 5/5) من ZnO-CuO على نوعي الفحم. شملت التحاليل الفيزيائية و الكيميائية للماء المعالج : درجة الحموضة ،(pH) الموصلية الكهربائية، المواد الصلبة الكلية و المعلقة، الكثافة، و الطلب الكيميائي للأكسجين .(COD) أظهرت النتائج أن المحفز ZnO-5/5 Cuالمدعوم على الفحم المفعل (RCAC) هو الأكثر فعالية، خاصة في خفض COD و تعديل pH نحو القيمة المحايدة. إلا أن بعض المعايير كـ EC و COD بقيت أعلى من الحدود المسموحة بها، مما يستدعي تحسينات إضافية. تؤكد هذه الدراسة إمكانيات التحفيز الضوئي المدعوم بالفحم النشط كمقاربة فعالة لتحسين نوعية المياه الصناعية.

كلمات مفتاحية:التحفيز الضوئي ،ZnO-CuO ،الفحم النشط، المياه الصناعيةCO.، RCAC،

Memory Title: Photocatalytic treatment of produced water over ZnO-CuO/Commercial activated carbon (CAC).

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Abstract: This study focuses on the photocatalytic treatment of real industrial wastewater using binary metal oxides ZnO and CuO supported on activated carbon (both commercial and reactivated). The objective is to evaluate the effect of catalyst composition and treatment time on the degradation of pollutants. Three different weight ratios ZnO–CuO (3/7, 4/6, and 5/5) were tested with both CAC and RCAC supports. The physicochemical parameters monitored include pH, electrical conductivity, total and suspended solids, density, and chemical oxygen demand (COD). Results showed that the 5/5 ZnO–CuO/RCAC catalyst achieved the highest removal efficiency, especially in COD reduction and pH stabilization. However, some parameters, such as EC and COD, remained above reuse thresholds, highlighting the need for further researches . This research confirms the potential of combining photocatalysis with porous carbon materials to improve wastewater quality.

Keywords: Photocatalysis, ZnO–CuO, activated carbon, wastewater, COD, RCAC.

Titre du mémoire: Traitement photocatalytique de l'eau produite sur ZnO-CuO/ Charbon actif commercial (CAC).

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Résumé : Ce travail porte sur le traitement photocatalytique d'eaux usées industrielles réelles en utilisant un système à base d'oxydes métalliques binaires ZnO et CuO, supportés sur du charbon actif (commercial et réactivé). L'objectif principal est d'évaluer l'impact de la composition du catalyseur et du temps de traitement sur la dégradation des polluants. Trois rapports massiques différents de ZnO–CuO/CAC (3/7, 4/6, 5/5) ont été testés avec les deux types de support. Les paramètres physico-chimiques analysés incluent le pH, la conductivité électrique, les solides dissous et en suspension, la densité, ainsi que la demande chimique en oxygène (DCO). Les résultats montrent que le catalyseur 5/5 ZnO–CuO/RCAC est le plus efficace , notamment pour la réduction de la DCO et la neutralisation du pH. Toutefois, certains paramètres comme la CE et la DCO restent supérieurs aux normes de réutilisation, indiquant la nécessité des recherches supplémentaires. Ce travail confirme l'efficacité potentielle des matériaux photocatalytiques combinés au charbon poreux pour le traitement des eaux industrielles.

Mots clés: Photocatalyse, ZnO–CuO, charbon actif, eaux usées, DCO, RCAC.