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Review

Coagulation–Flocculation Combined with Ozonation for River Water Treatment: Physicochemical Mechanisms, Treatment Performance, and Environmental Implications

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Abstract

River water quality is increasingly threatened by organic matter, emerging contaminants, pathogens, and other pollutants, creating risks to aquatic ecosystems and human health. Coagulation/flocculation effectively removes suspended and colloidal contaminants, turbidity, and particulate-associated organic matter, but is generally less effective for dissolved organic matter and many emerging contaminants. This review synthesizes recent advances in combining coagulation/flocculation with ozonation for river-water treatment. Ozonation complements coagulation/flocculation by oxidizing dissolved organic compounds, transforming micropollutants, controlling color and odor, and contributing to microbial inactivation; however, ozone alone cannot provide comprehensive removal of particulate and colloidal matter, as well as certain dissolved and ozone-resistant contaminants. Treatment sequence is therefore important. Pre-ozonation can modify natural organic matter and enhance subsequent coagulation under appropriate conditions, whereas coagulation/flocculation followed by ozonation can be particularly advantageous when preliminary removal of suspended, colloidal, and coagulable organic matter reduces oxidant demand before oxidation of residual dissolved contaminants. Reported coagulant doses ranged from less than 1 to more than 100 mg/L, while ozone doses were generally approximately 0.5–2 mg/L, reflecting differences in water matrix, coagulant type, treatment configuration, and target contaminants. Economic performance depends on water quality, chemical consumption, ozone generation, treatment scale, and operating conditions. Environmentally, the combined process can reduce discharges of suspended matter, organic contaminants, micropollutants, and microorganisms, thereby lowering pollutant pressure on aquatic ecosystems. Overall, this integrated process represents a complementary treatment strategy for improving river-water quality and supporting more sustainable protection and management of freshwater resources.

Keywords: coagulation/flocculation; ozonation; physicochemical treatment; river water treatment; contaminant removal; water quality; river restoration

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1. Introduction

Rivers are of fundamental importance to human societies and natural ecosystems, providing freshwater for domestic consumption, agriculture, industry, and other essential activities. Beyond their direct societal value, rivers function as dynamic biogeochemical reactors that transport and transform essential elements, including carbon, nitrogen, phosphorus, and silicon, from terrestrial environments toward coastal and marine systems. Through biological and physicochemical processes, river systems also influence greenhouse gas emissions and regulate biogeochemical cycling at regional and global scales [1,2].

Riverine ecosystems also provide a wide range of ecosystem services, including freshwater provisioning, nutrient regulation, habitat provision, flood mitigation, climate regulation, and cultural and recreational benefits [3,4]. Their role in transporting nutrients, particularly nitrogen and phosphorus, is especially important because riverine nutrient inputs influence downstream productivity, eutrophication, and marine biogeochemical processes [5]. Consequently, maintaining river water quality is essential for protecting aquatic ecosystems, preserving water resources, and supporting human well-being.

However, increasing urbanization, industrialization, agricultural intensification, and inadequate wastewater management have placed considerable pressure on river systems worldwide. River waters can receive complex mixtures of municipal and industrial wastewater, agricultural runoff, nutrients, suspended solids, heavy metals, pharmaceuticals, personal care products, and other emerging contaminants. Heavy-metal contamination, in particular, has been identified as a widespread concern in surface-water systems globally [6], while pharmaceuticals and personal care products are increasingly recognized as persistent contaminants that can enter aquatic environments through wastewater discharges [7]. The occurrence of microplastics represents an additional environmental concern because these particles can persist in aquatic systems and interact with other contaminants [8].

The severity and complexity of river pollution are illustrated by numerous highly impacted river systems. In Europe, pharmaceutical contamination has been documented in river environments, including the Western Balkan region and the Vecht River, where the occurrence of pharmaceutical compounds and their potential human-health risks have been investigated [9,10]. In North America, nutrient enrichment associated with agricultural activities in the Mississippi River basin contributes to excessive primary productivity and hypoxic conditions in the northern Gulf of Mexico [11]. The Detroit River and connected Great Lakes environments have also been affected by legacy contaminants such as mercury and persistent organic pollutants, with exposure concerns associated with contaminated fish [12]. These examples demonstrate that river pollution can involve multiple contaminant classes and pathways, making effective water-quality management increasingly challenging.

Similar problems have been reported in Latin American river systems. The Tietê River basin in Brazil has been affected by metal contamination, with several trace elements detected at elevated concentrations in river sediments [13]. In Mexico, heavy-metal contamination has been documented in sediments of the Lerma River, including elements such as arsenic, chromium, and lead [14]. The Atoyac River in Puebla, Mexico, represents another example of a highly impacted river system, with reported contamination by nutrients, organic matter, trace elements, and other pollutants associated with industrial, municipal, and agricultural activities [15]. Collectively, these cases demonstrate the widespread occurrence of complex contaminant mixtures in river systems and the need for effective strategies to improve water quality.

The diversity of contaminants present in river water creates significant challenges for treatment because pollutants differ substantially in size, chemical structure, solubility, reactivity, and environmental persistence. Conventional physicochemical processes, particularly coagulation/flocculation, are widely applied for the removal of suspended solids, colloidal particles, and turbidity. This process destabilizes colloidal particles and promotes their aggregation into larger flocs that can subsequently be separated from the aqueous phase. Coagulation/flocculation can also remove a fraction of organic matter associated with particulate and colloidal phases. However, its effectiveness for dissolved organic matter and many emerging contaminants is generally more limited, creating a need for complementary treatment processes.

Ozonation is an advanced oxidation process that can complement coagulation/flocculation by targeting dissolved organic compounds and selected emerging contaminants. Ozone reacts directly with susceptible organic structures and can also generate highly reactive hydroxyl radicals under appropriate water-quality conditions, promoting the transformation of a broad range of organic pollutants. However, the effectiveness of ozonation is strongly influenced by water-matrix characteristics, ozone demand, operating conditions, and the chemical nature of the target contaminants. In addition, ozonation may generate transformation products that need to be considered when evaluating overall treatment performance.

The combination of coagulation/flocculation and ozonation is particularly relevant for river-water treatment because these processes address complementary fractions of water pollution. Coagulation/flocculation promotes the destabilization and separation of suspended and colloidal particles, turbidity, and particulate-associated organic matter, whereas ozonation provides an oxidation stage for dissolved organic compounds and emerging contaminants that may remain after physicochemical separation. The integrated process can also improve aesthetic water-quality characteristics, particularly color and odor, while contributing to the reduction microorganism's contaminants. From an environmental perspective, this complementary treatment can reduce the pollutant burden transferred to downstream ecosystems, improve the quality of freshwater resources, and decrease potential risks to aquatic organisms and human activities such as recreational water use. Thus, combining separation and oxidation offers a practical strategy for addressing the complex and heterogeneous contamination typically encountered in polluted rivers.

Despite the extensive application of coagulation/flocculation and ozonation in water treatment, information concerning their integrated application to polluted river water remains dispersed among studies conducted under substantially different water-quality conditions, coagulants, ozone doses, and treatment configurations. In particular, a comprehensive assessment of how the sequence of coagulation/flocculation and ozonation influences contaminant removal, ozone demand, treatment performance, and environmental benefits is still lacking. This represents an important scientific and practical gap because river water contains complex mixtures of suspended particles, colloids, dissolved organic matter, micropollutants, color- and odor-causing compounds, and microorganisms that may respond differently to separation and oxidation processes. Therefore, this review synthesizes the available evidence on coagulation/flocculation–ozonation treatment of river water, comparing different coagulants, ozone application strategies, treatment sequences, operating conditions, treatment performance, sludge generation, costs, and environmental implications. Particular attention is given to determining under which conditions the integrated process, and especially the application of coagulation/flocculation prior to ozonation, provides advantages for improving river-water quality and reducing pollutant pressures on freshwater ecosystems.

2. Methodology

2.1. Literature Review and Study Selection

A narrative literature review was conducted using Google Scholar, scientific journal and publisher platforms, and backward citation searching. The search was updated through October 2026, with no lower publication-year restriction. Search terms included combinations of coagulation, flocculation, ozonation, ozone, river water, surface water, natural organic matter, turbidity, micropollutants, pre-ozonation, post-ozonation, simultaneous ozonation, and treatment cost. Publications available in English were primarily considered.

River and surface-water studies constituted the primary evidence base. When river-water-specific information was limited, studies using wastewater, WWTP effluents, industrial effluents, or other non-river matrices were included only as supporting contextual evidence and were identified by matrix type in the tables and discussion.

For each study, data were extracted on water matrix, treatment configuration, coagulant and ozone conditions, relevant operating parameters, target contaminants, and removal performance. Environmental and economic information was also recorded when available. Because experimental conditions differed substantially among studies, reported removal efficiencies were used for contextual comparison rather than direct quantitative comparison.

2.2. Construction of Predominance-Zone Diagrams

Thermodynamic predominance-zone diagrams for aluminum- and iron-containing aqueous systems were constructed using the MEDUSA software version 16. The diagrams were generated to identify the predominant aqueous and solid species as a function of pH and to illustrate the pH ranges in which dissolved Al- and Fe-containing species can undergo hydrolysis, complexation, and precipitation. The calculations were performed at 25 °C and an ionic strength of 0.1 M, selected to represent a high-ionic-strength river-water scenario. Thermodynamic equilibrium data and the corresponding chemical equilibria incorporated into the MEDUSA database were used to calculate the stability domains of the relevant species under the specified conditions. Carbonate and other background-water ligands were not included, since the diagrams were intended as simplified coagulant–water speciation models focused on the intrinsic hydrolysis, complexation, and precipitation behavior of the Al(III) and Fe(III) coagulants.

3. Physicochemical and Thermodynamical Aspects of the Coagulation/Flocculation Processes

The coagulation/flocculation process is relatively simple to implement and can be applied to large volumes of water and wastewater. To provide a clear basis for understanding the process and its application to river-water treatment, the following definitions and physicochemical concepts are considered.

Particles refer to discrete solid materials suspended in the aqueous phase whose physical characteristics, including size, shape, and density, influence their gravitational settling behavior. Particles range from relatively coarse and dense inorganic particulates, such as sand and grit, which can settle rapidly under gravity, to smaller and less dense organic and inorganic particles that may require coagulation and flocculation to enhance their aggregation and subsequent separation [16,17].

Colloids are finely dispersed particles or droplets within an aqueous system, typically ranging from approximately 1 nm to 1 μm in size. Colloidal particles can remain suspended for extended periods because of Brownian motion and electrostatic repulsion associated with their surface charge and electrical double layer. Examples include negatively charged clay and metal-oxide particles, humic substances, and microbial-derived particles or fragments. Colloids can contribute substantially to turbidity and color and can facilitate the

transport of contaminants through adsorption and other interfacial interactions. Because their natural settling is limited, coagulation/flocculation is commonly employed to destabilize colloids and promote their aggregation into larger flocs that can subsequently be removed by sedimentation or filtration [16,18].

Coagulants are chemical agents added to water or wastewater to destabilize colloidal and finely suspended particles, thereby facilitating their aggregation into larger flocs. The principal mechanisms involved in coagulation include charge neutralization, electrical double-layer compression, adsorption, and precipitation followed by enmeshment or sweep flocculation. Common inorganic coagulants include aluminum sulfate and ferric salts, such as ferric chloride. Organic coagulants, including polyamines, are also used. In addition, natural coagulants, such as chitosan and *Moringa oleifera* extracts, have demonstrated potential for water treatment applications [19,20].

Flocculants promote the aggregation of destabilized particles into larger and more readily settleable flocs. An important mechanism is polymer bridging, in which long-chain polymeric molecules adsorb onto the surfaces of particles and connect them to form larger aggregates. Charge patching and other polymer–particle interactions may also contribute to floc formation and stability. Flocculants can be derived from natural materials, such as starch and chitosan, or can consist of synthetic organic polymers, such as polyacrylamide and its derivatives. Modified biopolymers can also be designed to provide specific interactions under different water chemistries [21,22].

Zeta potential refers to the electrical potential at the slipping plane of a particle suspended in a liquid medium. It provides an indirect measure of the electrostatic interactions governing colloidal stability. Particles with relatively high positive or negative zeta-potential values generally experience stronger electrostatic repulsion and tend to remain dispersed, whereas values closer to zero are generally associated with reduced electrostatic stabilization and an increased tendency toward aggregation. Although thresholds such as $\pm$30 mV are commonly used as practical indicators of colloidal stability, the relationship between zeta potential and coagulation efficiency depends on the particle characteristics, ionic strength, pH, and coagulant chemistry. Consequently, coagulation/flocculation generally seeks to reduce the magnitude of the zeta potential sufficiently to destabilize colloids and promote floc formation [23–25].

An important initial step in water and wastewater treatment is the removal of suspended solids through sedimentation. The settling behavior of suspended particles depends on particle size, density, shape, concentration, and the hydrodynamic conditions of the treatment system. Under conditions in which particle–particle interactions are limited, the settling velocity of small, discrete, approximately spherical particles can be described by Stokes' law. However, the settling behavior of aggregated particles and flocs can deviate substantially from that of ideal spherical particles because flocs are porous, irregular, and fractal structures. Experimental and numerical studies have demonstrated that floc settling velocities can differ considerably from those predicted for equivalent compact spheres, with reported ratios of fractal-aggregate to equivalent-sphere settling velocities ranging from approximately 0.16 to greater than 4, depending on the fractal dimension and primary particle size [26].

Following coagulation/flocculation, destabilized particles aggregate to form flocs with complex and heterogeneous structures. Floc density generally decreases as floc size increases because larger aggregates contain increasing amounts of entrained water and have greater internal porosity. Reported effective floc densities are approximately 30–350 kg m^{-3}, although the actual values depend strongly on floc composition, size, structure, and formation conditions. The relationship between floc size and settling velocity is therefore not necessarily monotonic: settling velocity may initially increase as flocs grow,

but beyond a critical size, increasing porosity and decreasing effective density can reduce the settling velocity [27,28].

The sedimentation of discrete particles can therefore be described, under appropriate conditions, using the classical Stokes' law. For coagulated and flocculated particles, however, modified settling relationships that account for floc structure, porosity, effective density, and fractal geometry are more appropriate [29].

1. Stokes' Law

The following is the simplest model used for small, rigid, spherical particles settling in a laminar fluid:

$$V_s = \frac{2}{9}\frac{(\rho_p - \rho_w)\, g r^2}{\mu} \quad (1)$$

where

V_s = settling velocity (m/s)
ρ_p = particle (or floc) density (kg/m^3)
$\rho_{(w)}$ = water density (around 1000 kg/m^3)
g = gravitational acceleration (9.81 m/s^2)
r = particle radius (m)
μ = dynamic viscosity of fluid (Pa·s)

Note that in this model the key factors affecting the settling velocity are the density difference between the particle and water and the particle radius. Water density and viscosity depend on water temperature.

2. Modified Stokes' Law for Flocs (Fractal Model)

Another approach for porous flocs and non-spherical particles is often modeled using fractal dimensions

$$\boldsymbol{V_s} = \frac{1}{18}\frac{g d_f^2 \Delta_p}{\mu} \quad (2)$$

$$\Delta_p = (\rho_p - \rho_w)\left(\frac{d_f}{d_p}\right)^{D_f - 3} \quad (3)$$

where

d_f = floc diameter
d_p = primary particle diameter
Δp = Effective density
D_f = fractal dimension (typically 2.2–2.8)

Predominance Zone Diagrams (also known as speciation or stability diagrams) represent the thermodynamic stability of different chemical species of a particular element as a function of environmental variables such as pH and redox potential (Eh). Each zone in the diagram indicates conditions under which a specific chemical species is the most thermodynamically stable. These diagrams are constructed from equilibrium constants and Gibbs free energy data.

Predominance diagrams are used for designing treatment processes like coagulation–precipitation, oxidation–reduction, and anaerobic digestion, where understanding chemical speciation is essential [30].

Figures 1 and 2 present the predominant speciation diagrams of aluminum and ferric ions at concentrations of 10 and 100 mg/L, in the presence of chloride and sulfate anions. For aluminum, a broad range of pH conditions favors the formation of hydrolyzed Al(III) species and amorphous aluminum hydroxide precipitates, which can contribute substantially to colloid destabilization and particle removal through charge neutralization,

adsorption, and sweep flocculation. A similar behavior occurs with ferric ions (Fe^{3+}), for which hydrolysis produces a range of aqueous hydrolyzed species and, depending on pH and total iron concentration, ferric hydroxide/oxyhydroxide precipitates. These hydrolyzed species and precipitates can promote colloid destabilization and particle removal through charge neutralization, adsorption, and enmeshment within the developing flocs. Supplementary Tables S1 and S2 provide equilibrium constants.

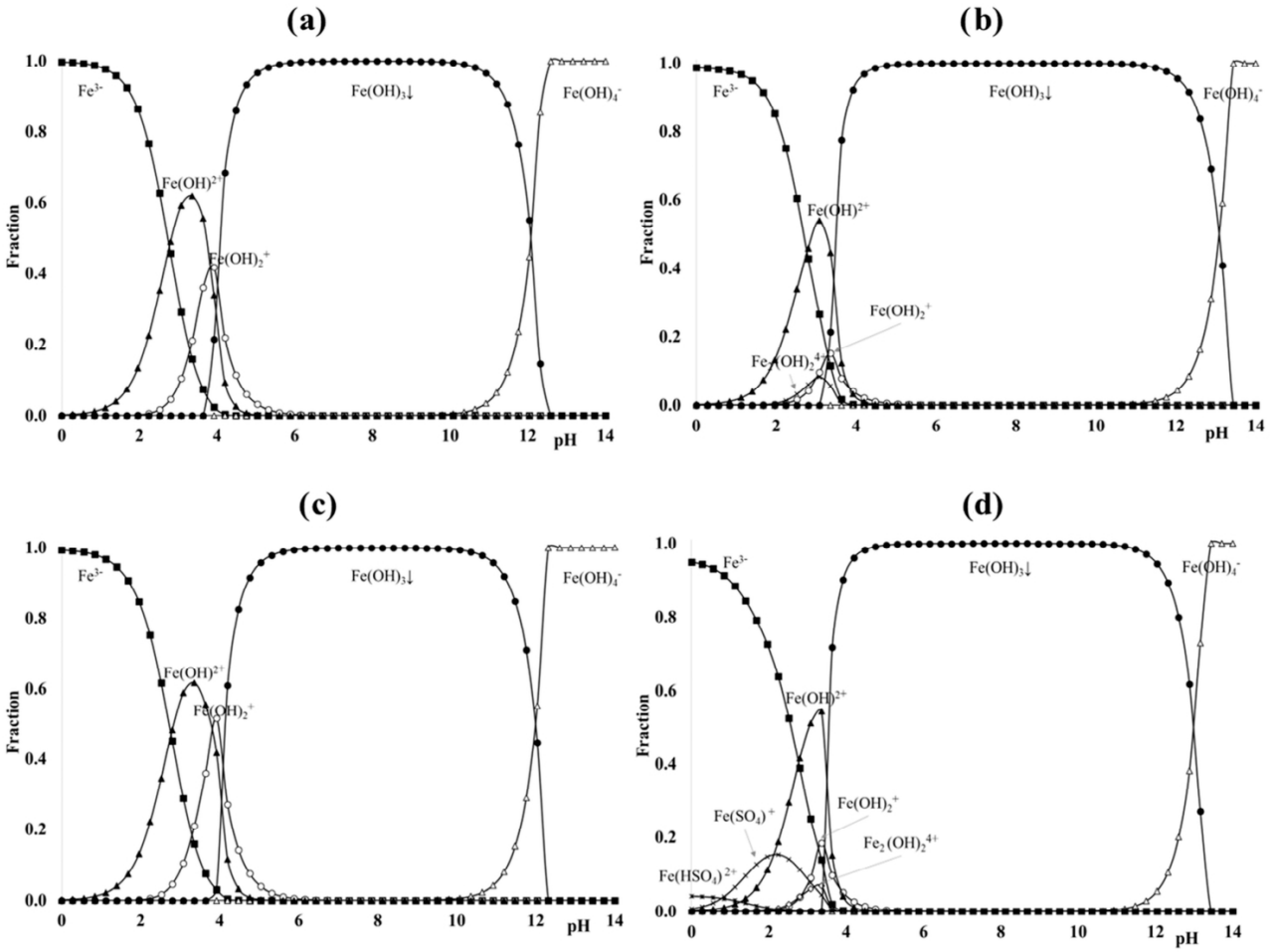


Figure 1. Predominance Zone Diagram of (**a**) ferric chloride at 10 ppm, (**b**) ferric chloride at 100 ppm, (**c**) ferric sulphate at 10 ppm and (**d**) ferric sulphate at 100 ppm.

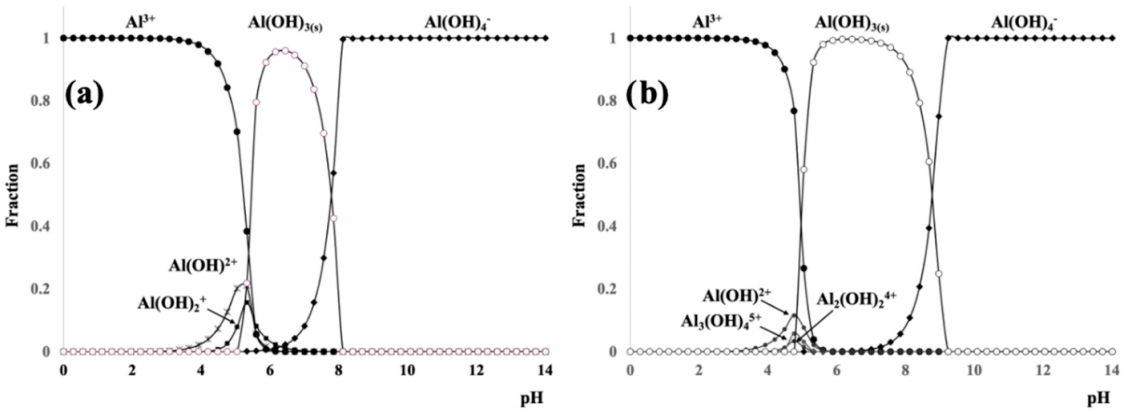


Figure 2. *Cont.*

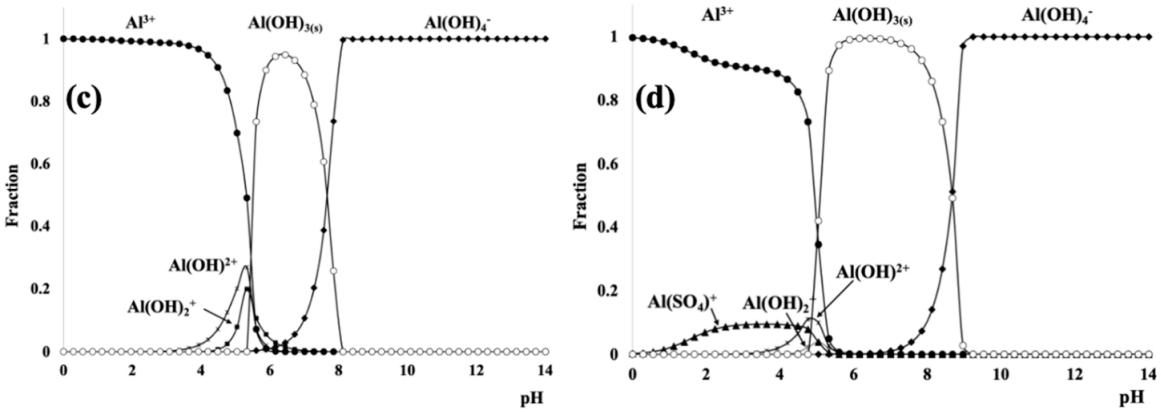


Figure 2. Predominance Zone Diagram of (**a**) aluminum chloride at 10 ppm, (**b**) aluminum chloride at 100 ppm, (**c**) aluminum sulphate at 10 ppm and (**d**) aluminum sulphate at 100 ppm.

4. Ozonation: Chemistry, Mechanisms, and Environmental Functions

Ozone (O_3) is widely recognized as one of the most powerful and versatile oxidants available for water and wastewater treatment, offering high oxidation capacity, operational flexibility, and effective contaminant removal. With a redox potential of approximately 2.07 V, ozone can oxidize a wide range of organic and inorganic contaminants, including micropollutants, natural organic matter, color-causing compounds, metals, and pathogens [31,32].

Operationally, ozone is generally generated on-site using corona discharge or dielectric barrier discharge systems, eliminating the need for the storage and transportation of large quantities of chemical oxidants and reducing the associated safety risks. In addition, ozone generation can be controlled according to treatment demand, since ozone is produced only when required [33].

Following treatment, ozone decomposes relatively rapidly to molecular oxygen and does not leave a persistent chemical residual comparable to that of chlorine-based disinfectants. This characteristic makes ozonation attractive for water treatment applications. Additional advantages include effective removal of taste- and odor-causing compounds [34], as well as high pathogen-inactivation efficiency, including against some chlorine-resistant microorganisms [35].

Ozone (O_3) acts through two primary oxidation mechanisms in aqueous environments: direct oxidation by molecular ozone and indirect oxidation mediated by hydroxyl radicals (•OH). These pathways govern the transformation and degradation of a wide range of contaminants during water and wastewater treatment.

In direct oxidation, ozone reacts selectively with specific functional groups in organic and inorganic molecules, including carbon–carbon double bonds, activated aromatic structures, amines, sulfides, and certain inorganic species. These reactions are generally more selective than hydroxyl-radical reactions and depend strongly on the chemical structure and reactivity of the target compound.

Example reactions:

Simplified ozonation of olefins:

$$RCH = CHR + O_3 + H_2O \rightarrow 2RCHO + H_2O_2 \quad (4)$$

Oxidation of phenol:

$$C_6H_5OH + 2O_3 \rightarrow C_6H_4O_2 + H_2O + 2O_2 \quad (5)$$

Oxidation of sulfides to sulfoxides/sulfones:

$$R_2S + O_3 \rightarrow R_2SO + O_2; R_2SO + O_3 \rightarrow R_2SO_2 + O_2 \quad (6)$$

Oxidation of Fe^{2+} and Mn^{2+}:

$$2Fe^{2+} + O_3 + 5H_2O \rightarrow 2Fe(OH)_{3(s)} + O_2 + 4H^+ \quad (7)$$

$$Mn^{2+} + O_3 + H_2O \rightarrow MnO_{2(s)} + O_2 + 2H^+ \quad (8)$$

Ozone decomposes in water, especially under alkaline conditions or in the presence of catalysts, to form hydroxyl radicals (•OH), which are non-selective and extremely reactive (oxidation potential ~2.8 V).

Key reactions:

Initiation step:

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \quad (9)$$

Radical generation:

$$HO_2^- + O_3 \rightarrow HO_5^- \quad (10)$$

$$HO_5^- \rightarrow HO_2^\bullet + O_3^{\bullet -} \quad (11)$$

Radical equilibrium and propagation:

$$HO_2^\bullet \rightleftharpoons O_2^{\cdot -} + H^+ \quad (12)$$

$$O_2^{\cdot -} + O_3 \rightarrow O_3^{\cdot -} + O_2 \quad (13)$$

Hydroxyl-radical formation:

$$O_3^{\cdot -} \rightleftharpoons O_2 + O^{\cdot -} \quad (14)$$

$$O^{\cdot -} + H_2O \rightleftharpoons {}^\bullet OH + OH^- \quad (15)$$

Attack on organic pollutants:

$${}^\bullet OH + R{-}H \rightarrow H_2O + R^\bullet \quad (16)$$

This cascade of reactions can promote the transformation and, under favorable conditions, partial mineralization of contaminants such as pharmaceuticals, pesticides, dyes, and endocrine-disrupting compounds [36–39].

Several factors influence ozone reactions in aqueous systems. Higher pH generally promotes ozone decomposition and can increase the formation of hydroxyl radicals (•OH). However, natural organic matter (NOM), carbonate, and bicarbonate can act as radical scavengers and therefore decrease the availability of •OH for contaminant oxidation. In contrast, certain transition metals and UV irradiation can promote the formation of reactive species and enhance ozone decomposition and oxidation reactions [40–42].

Table 1 shows that ozonation alone can be highly effective for specific classes of contaminants, particularly chromophoric and odor-causing compounds, and can provide substantial microbial inactivation. However, its capacity to remove or mineralize bulk dissolved organic matter is considerably more limited and depends strongly on the water matrix, ozone exposure, and characteristics of the target contaminants. For example, studies of river-water ozonation have reported TOC removals below 20% in some cases, whereas another study reported approximately 31% DOC removal. Similarly, ozonation of Lerma River water resulted in approximately 19% TOC removal, despite substantial

reductions in color and turbidity. These results indicate that ozone can effectively transform oxidation-sensitive fractions of river-water organic matter and improve specific water-quality parameters without necessarily achieving extensive mineralization.

Table 1. Treatment performance of ozonation alone for river water.

River Water Treated	Conditions	% Pollutant Removal Reduction Obtained by O_3 Alone	Reference
Lerma River, Mexico	O_3; 120 min	19% TOC, 67% True Color	[43]
Han River, Republic of Korea	O_3; 1 mg/L; 5 min	31% Dissolved Organic Carbon >80% UV_{254}	[44]
Han River system (Paldang Reservoir), Republic of Korea	O_3; 1–2 mg/L; 10 min	Reduction of taste- and odor-causing compounds	[45]
Ebro River, Spain	TiO_2-catalyzed ozonation 1.5–3.0 g O_3/g	13% TOC 52% UV_{254}	[46]
Danube River bank-filtration water (Serbia)	O_3; 1.0–1.5 g O_3/m^3	≈20% TOC	[47]
Colorado River, USA	O_3 alone; 2 mg/L; 4 min	>4.5-log E. coli inactivation.	[48]
Ohio River, USA	O_3; 6.26 mg min/L	Total coliform: ~4.1-log inactivation Heterotrophic bacteria: ~3.36-log inactivation	[49]

Therefore, ozone alone should not be considered a universal treatment for the complex mixture of particulate, colloidal, and dissolved contaminants present in polluted river water. Its effectiveness is particularly evident for oxidation-sensitive dissolved compounds and microbial contaminants, whereas particulate and colloidal fractions generally require a complementary separation process, such as coagulation/flocculation.

Environmental significance of ozonation in river-water treatment.

From an environmental perspective, the ability of ozonation to oxidize dissolved organic compounds, reduce chromophoric and odor-causing substances, and inactivate microorganisms can provide important benefits for degraded river systems. Reduction of color and odor can improve aesthetic and recreational water quality, while microbial inactivation can reduce potential exposure risks associated with pathogenic microorganisms. The transformation of selected organic micropollutants may also decrease their persistence and potential biological effects in downstream aquatic environments. Nevertheless, ozonation does not eliminate all contaminant fractions and may generate transformation products that require consideration in environmental assessments. Consequently, the environmental value of ozonation is greatest when it is incorporated into an integrated treatment strategy.

5. Coagulants and Their Role in Integrated River-Water Treatment

This section presents the results reported for the treatment of river water using metal-based, natural, and synthetic coagulants. For aluminum-based coagulants, Table 2 summarizes the principal findings, whereas Table 3 presents reported pollutant-removal efficiencies obtained using ferric sulfate. A comparative analysis of aluminum- and iron-based coagulants for river-water treatment, as summarized in Tables 2 and 3, indicates that both classes of coagulants can provide effective treatment and substantial improvements in water-quality parameters under appropriate operating conditions.

Table 2. Aluminum Sulfate Performance in River Water Treatment.

River Water Treated	Conditions	% Pollutant Removal	Reference
Tello River (Indonesia)	Dose: 68.3 mg/L; pH 6	TSS: 89.6%	[50]
Ba River (Vietnam)	Dose: 60 mg/L; pH 7.45	DOC 37.2% Turbidity: 86.7%	[51]
Oum Er-Rbia River (Morocco)	Dose: 20 mg/L; pH 7.3;	Effective turbidity reduction	[52]
Paraguaçu River (Brazil)	Dose 45–65 mg/L; pH 6.5–7.5	Turbidity: ~90%; Al residuals: <0.1 mg/L	[53]
Yangtze River (China)	Dose: 2.80 mg/L; pH 6.8–7.3	COD: 34.48% NH_3N: 40% Turbidity: 82.82%	[54]
Surface water (Ethiopia)	Dose: 70 mg/L pH: 7.5	Turbidity: 99.16% E. coli: 29.78%	[55]
Surface water (Africa)	Dose: ~428 mg/L pH = 8	Conductivity: 85.6% Turbidity: 98.05% Organic matter: 99.62%	[56]
Surface water (USA)	Dose: 180–200 mg/L pH: 5–5.5	DOC: 58% Color: 80% Turbidity: 15%	[57]

Table 3 provides the pollutant removal in river water using ferric sulphate.

Table 3. Ferric Sulfate/Chloride Performance in River Water Treatment.

River Water Treated	Conditions	% Pollutant Removal	Reference
Kızılırmak River (Turkey)	Iron Sulfate Dose: 10–60 mg/L; pH: 4.5–9.5	Turbidity: 98.84% (pH 4.5) Alkalinity: 99.21% (pH 4.5) TDS: 95.61% (pH 9.5)	[58]
Karoun River (Iran)	Ferric Chloride Dose: 1–4.6 mg/L	Effective turbidity removal	[59]
Wadi El Bey River (Tunisia)	Ferric Chloride Dose: 400 mg/L Ferric Sulfate Dose: 400 mg/L	COD: 30% Color: 55% COD: 20% Color: 55%	[60]
Agricultural drainage water, Sacramento–San Joaquin Delta, California	Ferric Sulfate Dose: 13–31 mg Fe/L	DOC: 72.1% UV_{254}: 82.5%	[61]
Moulin Papon dam (France)	Ferric Chloride: 22 mg/L: pH:4–5	TOC: 78% UV_{254}: 84%	[62]
Volga River (Russia)	Iron Sulfate: 15 mg/L pH: 9	Improved turbidity and color reduction under alkaline conditions	[63]
Surface water Sarasota County United States	Ferric Chloride: 120 mg/L	DOC: 85% Color: 98%	[64]

Aluminum salts, particularly aluminum sulfate (alum), are extensively used because of their effectiveness in removing turbidity and natural organic matter (NOM), with removal efficiencies that can exceed 80% under optimized conditions. However, their performance may decrease at low temperatures, and residual aluminum in treated water is an important

consideration because excessive residual concentrations may have environmental and human-health implications. In contrast, iron-based coagulants, such as ferric sulfate, ferric chloride, and ferrous sulfate, generally exhibit effective performance over a relatively broad pH range and can be particularly effective for the removal of phosphorus and certain heavy metals. These characteristics are consistent with the thermodynamic predominance-zone analysis presented previously. Furthermore, iron-based coagulants can form relatively dense flocs with favorable settling characteristics, potentially enhancing subsequent sedimentation. Despite these advantages, iron-based coagulants may impart a slight coloration to treated water and can generate substantial quantities of sludge [65–68].

Ultimately, the selection between aluminum- and iron-based coagulants should be based on the physicochemical characteristics of the river water, target contaminants, treatment objectives, operating conditions, and downstream environmental considerations. Each coagulant system presents distinct advantages and limitations depending on the treatment conditions. Therefore, site-specific optimization of coagulant type, dose, pH, and subsequent separation conditions is essential for achieving effective river-water treatment.

5.1. Natural Coagulants for River-Water Treatment

The use of natural coagulants such as Moringa oleifera, cactus mucilage, and chitosan in water and wastewater treatment involves several mechanisms, including charge neutralization, polymer bridging, adsorption, and, in some cases, sweep flocculation. These mechanisms collectively destabilize suspended and colloidal particles, facilitating their aggregation into larger flocs that can subsequently be removed by sedimentation or filtration.

Natural coagulants such as the cationic proteins and peptides present in Moringa oleifera seeds can carry positive charges under appropriate pH conditions. These positively charged species interact with negatively charged particles, such as clay minerals, organic matter, and microbial cells, in the water. This interaction reduces electrostatic repulsion and can decrease the zeta potential of the particles, thereby promoting their aggregation. Table 4 summarizes representative studies on the application of natural coagulants for river-water treatment.

Table 4. Natural Coagulants Treating River Water.

River Water Treated	Conditions	% Pollutant Removal	Reference
Tana River (Kenya)	Moringa oleifera seed powder Dose: 0.02 g/L; pH initial ~7.6	Turbidity: 70.6%; clarified to ≤15 NTU	[69]
Worongnge Village River (Indonesia)	Moringa oleifera seed powder Dose: 2 g/L; pH final ~7.2	Turbidity reduced by ~>50% (46 NTU final)	[70]
Tulte River (Ethiopia)	Papaya seed extract Dose: 20 mL; pH 6	Coliform: 96.32% Turbidity: 96.19%	[71]
Simulated 500 NTU river water	Lupin bean extract 50 mg/L; pH 7.0	Turbidity: 86.4%	[72]
Beringin River (Indonesia)	Chitosan Dose: 30 mg/L pH 8.1	Microplastics: 68.3%	[73]
Tamazula River (Mexico)	Chitosan Dose: 5 mg/L	Turbidity: 90.6%	[74]
Karun River (Iran)	Dose: PACl 4 mg/L + Chitosan 0.04 mg/L; pH: 8	Turbidity: 97.14%	[75]
Tietê River (Brazil)	Quaternary ammonium tannate (QAT) Dose: 150 mg/L	Turbidity: 93.21%	[76]

Natural polymers such as chitosan can promote floc formation through polymer bridging, whereby polymer chains adsorb onto multiple particle surfaces and link individual particles together. This mechanism can produce larger and denser flocs, particularly when the polymer has an appropriate molecular weight, charge density, and chain conformation. The effectiveness of chitosan is also strongly influenced by pH because its degree of protonation determines its interaction with negatively charged colloidal particles.

Some natural coagulants can also promote particle removal through adsorption and entrapment within a polymeric network. For example, water-soluble cationic proteins from Moringa oleifera seeds can destabilize negatively charged colloids and promote floc formation [70]. The effectiveness of this mechanism depends on the composition and concentration, as well as the characteristics of the water matrix and the operating conditions. Figure 3 schematically illustrates the principal mechanisms involved in natural-coagulant-assisted coagulation/flocculation.

Synthetic coagulants and polymeric flocculants promote particle destabilization and aggregation primarily through charge neutralization, polymer bridging, and sweep flocculation. Cationic organic polymers and metal-based coagulants destabilize suspended colloidal particles by reducing the electrostatic repulsion that normally maintains their stability in aqueous media. Because many natural colloids carry a net negative surface charge, cationic polyelectrolytes can adsorb onto their surfaces and partially or completely neutralize this charge. For example, polydiallyldimethylammonium chloride (PolyDADMAC) is a strongly cationic polyelectrolyte that readily adsorbs onto negatively charged particles, thereby reducing the magnitude of the zeta potential and promoting particle–particle collisions and aggregation (Table 5 and Figure 4) [77].

Table 5. Synthetic Coagulants Treating River Water.

River Water Treated	Conditions	% Pollutant Removal	Reference
Pasig River (Philippines)	ACH + PolyDADMAC; total dose: 10 ppm; ACH:PolyDADMAC ratio = 4.5; pH 6	Turbidity: 94.6%	[77]
Ganjiang River (China)	PAC Dose: 10 mg/L pH 7.1–7.5	Turbidity: 91.67%	[78]
Nile River (Egypt)	$Al_2(SO_4)_3 \cdot 18H_2O$; 1% Yellow PAC	Turbidity: 84.6%	[79]
Yangtze River (China)	PAC dose: 9.7 mg/L; pH 6.9	Optimized removal of TSS, TOC, and TN	[80]
Danube River	PACl Dose: 1 mmol Al/I; pH 7.7	Textile fibers: 98%	[81]
Polluted River Water (China)	PAC 100 mg/L + dynamic membrane filtration	COD: 70% Total Phosphorus: effective removal	[82]
Tigris River (Iraq)	PACl + polyacrylamide: 40 mg/L each	Turbidity: 99.1%	[83]

In polymer bridging, long-chain polymers such as polyacrylamide (PAM) adsorb onto more than one particle simultaneously, creating interparticle bridges that promote the formation of larger flocs. These flocs may subsequently be removed by sedimentation, flotation, or filtration, depending on their size, density, and the treatment configuration. In contrast, inorganic coagulants such as polyaluminum chloride (PACl) and polyferric sulfate (PFS) undergo hydrolysis in water to produce a range of positively charged monomeric and polymeric hydroxo species. For aluminum-based coagulants, representative hydrolysis

products include $AlOH^{2+}$ and $Al(OH)_2^+$, although the actual species distribution strongly depends on pH and coagulant composition. At sufficiently high dosages and appropriate pH conditions, the formation of amorphous $Al(OH)_3(s)$ or $Fe(OH)_3(s)$ precipitates can promote sweep flocculation, in which suspended and colloidal particles are adsorbed onto or physically enmeshed within the growing metal-hydroxide precipitates. The relative contribution of charge neutralization, adsorption, bridging, and sweep flocculation depends on factors such as pH, alkalinity, coagulant dose, particle surface properties, and water chemistry [66,80].

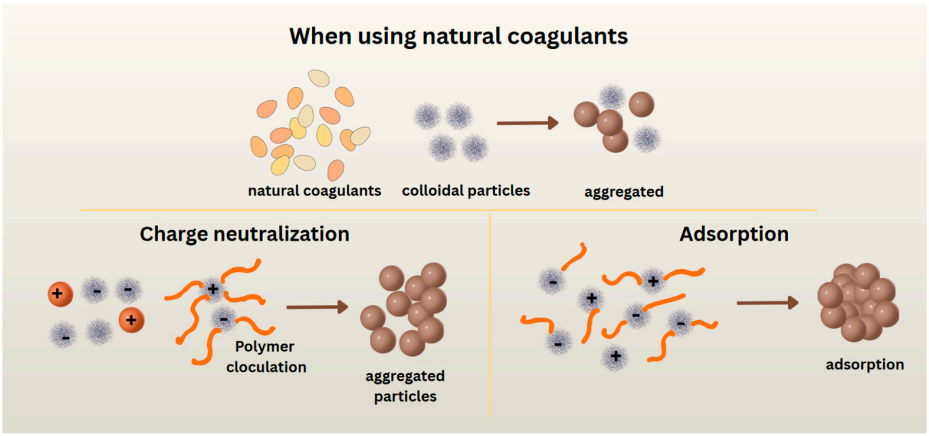


Figure 3. Natural coagulation interactions. Orange/yellow shapes represent natural coagulant components, orange wavy lines represent polymer chains involved in particle destabilization and aggregation, blue-gray spheres represent colloidal particles, brown spheres represent aggregated particles, and "+" symbols indicate positive charges. Colors are used for schematic identification only.

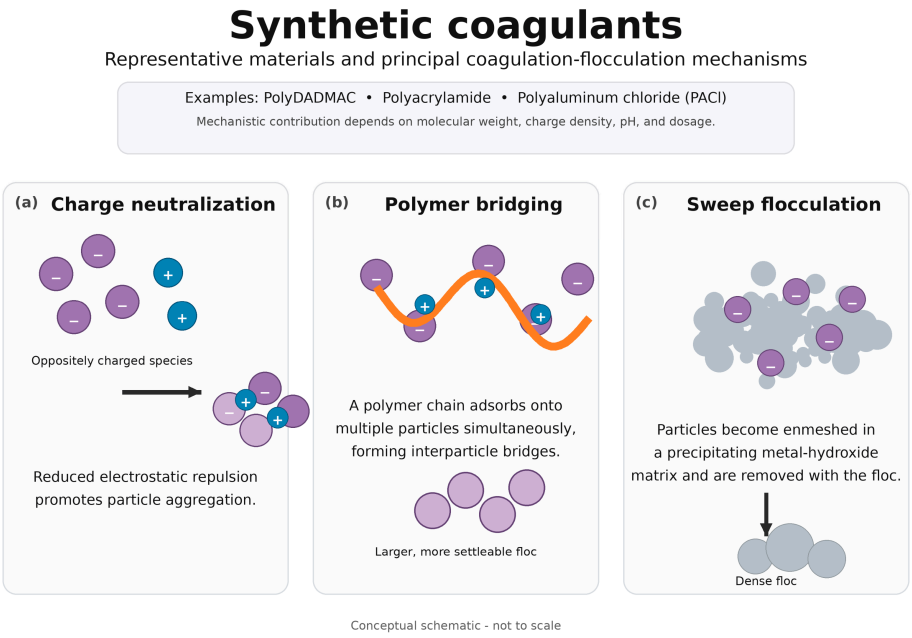


Figure 4. Diagram of synthetic coagulation. (**a**) charge neutralization, where oppositely charged species reduce electrostatic repulsion and promote particle aggregation; (**b**) polymer bridging, where polymer chains adsorb onto multiple particles and form interparticle bridges; and (**c**) sweep flocculation, where particles become enmeshed in precipitating metal-hydroxide flocs. Purple spheres represent negatively charged particles, blue spheres with "+" symbols represent positively charged species, the orange line represents a polymer chain, gray spheres represent metal-hydroxide precipitates/flocs, and arrows indicate the direction of the aggregation or flocculation process. Colors are used for schematic identification only.

5.2. Environmental Significance of Coagulation/Flocculation in River-Water Treatment

Coagulation/flocculation is one of the most practical, adaptable, and technically accessible processes for improving river-water quality because it can be implemented with relatively simple equipment, short treatment times, and operational conditions that can be readily adjusted to changes in raw-water composition. Its main advantage is the effective removal of turbidity, total suspended solids (TSS), colloidal particles, apparent color, particulate organic matter, and a substantial fraction of natural organic matter (NOM). The process is highly versatile because different coagulant families can be selected according to the characteristics of the river water. Metal-based coagulants, such as aluminum sulfate, ferric salts, polyaluminum chloride (PACl), and polyferric sulfate (PFS), are generally preferred when high turbidity, suspended solids, phosphorus, and NOM must be rapidly removed, because hydrolysis produces positively charged species and amorphous metal-hydroxide precipitates that promote charge neutralization and sweep flocculation. Their major advantages are their well-established performance, relatively low cost, rapid action, and broad applicability, although their use may increase sludge production, modify pH and alkalinity, and leave residual aluminum or iron if dosage and operating conditions are not properly controlled. Natural coagulants, including chitosan and plant-derived materials, are attractive when biodegradability, low toxicity, reduced chemical input, and lower production of metal-containing sludge are priorities; however, their performance may be more variable because it depends on raw-material composition, extraction method, storage conditions, and the characteristics of the treated water. In contrast, synthetic organic coagulants and flocculants, such as PolyDADMAC and polyacrylamide-based polymers, can provide high charge density, effective particle destabilization, and strong interparticle bridging at comparatively low doses, often producing larger flocs and reducing the amount of inorganic sludge generated. Nevertheless, careful control is required to avoid overdosing and to minimize concerns associated with residual polymers or unreacted monomers. This diversity of available coagulants is precisely why coagulation/flocculation is so useful for river-water treatment: the coagulant type, dosage, pH, mixing conditions, and treatment sequence can be easily adapted to waters with different levels of turbidity, organic matter, mineral content, and seasonal variability. Although the process is less effective for many dissolved and highly soluble contaminants, it provides a robust first barrier that substantially improves the physicochemical quality of river water [84,85].

6. Effect of Ozonation on the Coagulation–Flocculation Process

This section discusses the effects of ozone application before, during, and after coagulation–flocculation, with particular emphasis on how the point of ozone addition influences contaminant removal and overall treatment performance.

As summarized in Table 6, pre-ozonation can enhance the performance of coagulation–flocculation in river-water treatment by modifying the physicochemical properties of natural organic matter (NOM), colloidal particles, and other oxidizable contaminants. Ozone preferentially reacts with electron-rich and unsaturated moieties in NOM, including aromatic and humic structures, producing smaller and more oxygenated compounds that are generally more hydrophilic and may contain a greater proportion of negatively charged functional groups. Moderate ozone doses, typically in the range of 0.5–1.2 mg O_3/L, improved subsequent coagulation performance by modifying colloidal stability and the interactions between NOM and the coagulant. Improvements were reported for turbidity, color, trace-metal removal, and UV-absorbing organic matter, with reductions of up to 97% for UV-related parameters in some of the evaluated river and surface waters. These effects have been associated with partial oxidation of NOM, changes in particle surface properties, and the formation of flocs with more favorable characteristics for solid–liquid

separation. However, the beneficial effect is strongly dose-dependent. At ozone doses above approximately 2.0 mg O_3/L, extensive oxidation may convert NOM into low-molecular-weight carboxylic acids, aldehydes, and other highly hydrophilic compounds that are less effectively removed by conventional coagulation. Consequently, the removal efficiency of dissolved organic carbon (DOC) and, in some cases, UV_{254} related organic matter during the subsequent coagulation step may decrease. Overall, the results presented in Table 6 indicate that appropriately controlled pre-ozonation can reduce coagulant demand and decrease the formation potential of some disinfection by-products (DBPs), while improving the removal of several water-quality constituents. Nevertheless, the optimum ozone dose depends on source-water composition, NOM characteristics, pH, alkalinity, and coagulant type.

Table 6. Pre-Ozonation + Coagulation in River Water Treatment.

River Water Treated	Conditions	% Pollutant Removal	Reference
North-China surface water	Ozone dose 1.0 mg/L $FeCl_3$: typical jar-test dose; pH neutral	Turbidity & $UV_{(254)}$ removal enhanced; low ozone (1 mg/L) aided coagulation; higher ozone (2 mg/L) reduced UV removal	[86]
South China dam/source water	Ozone Dose 0.85 mg/L $AlCl_3$ 25–150 mg/L; pH 7	NOM removal: $UV_{(254)}$↑ 34.6%, COD(Mn)↑ 18.1%, TOC↑ 15.3% improved; THMFP reduced	[87]
Municipal WWTP effluent (for reuse context)	Ozone Dose 1.2 mg/L; PAC 100 mg/L; pH 7.7	Pre-ozonation + PACl removed ~71% DON, ~66% DOC, ~97% $UV_{(254)}$; DBP formation potential reduced by >40%	[88]
Warta River reservoir (Poland)	Powdered activated carbon (PAC): 100 mg/L; PAX coagulant: 5 mg/L; Ozone: 2 mg O_3/L	Color removal 86–90%; Turbidity 85–90%; DOC/TOC/UV removal improved by 11–12%; Metals removed ~62–66%	[89]
Assiniboine River (Canada)	Ozone applied before coagulation: up to 0.8 mg O_3/mg DOC; $Fe_2(SO_4)_3$ coagulation	Improved DOC removal; reduced ferric sulfate demand; enhanced THMFP removal	[90]

The application of ozonation after coagulation–flocculation can provide an additional polishing barrier for residual dissolved and oxidizable contaminants in river-water treatment (Table 7). The available studies report further reductions in organic-matter-related parameters such as TOC, oxidizability, and UV_{254} after coagulation–flocculation [91]. In addition, pilot-scale treatment of Huangpu River water showed substantial removal of pharmaceuticals, pesticides, and odorants when post-ozonation was incorporated into a treatment train that also included biological activated carbon [92]. Recent studies have shown that post-ozonation can provide additional treatment benefits after coagulation-based processes under different river-water conditions. In Tietê River water, coagulation–flocculation followed by hydrodynamic cavitation-assisted ozonation produced additional COD removal [76], whereas a recent study using high-DOC riverine water showed further transformation of dissolved organic matter when coagulation/softening was followed by ozonation and biologically active filtration [93]. However, because these studies differ in treatment configuration and downstream processes, the available evidence should be interpreted cautiously and does not establish universal superiority of post-ozonation.

Table 7. Coagulation–Flocculation Followed by Ozonation in River Water Treatment.

River Water Treated	Conditions	% Pollutant Removal	Reference
Stradomka River (Poland)	PAX-19 Dose: 3 mg Al/L pH 6.84 Ozone: 1.2 mg O_3/L	TOC: 28–33% OXI: 45–46% UV_{254}: 69–73%	[91]
Huangpu River (China)	Post-ozonation mode: coagulation → sedimentation → sand filtration → O_3 → BAC; O_3 dose: 1.5 mg/L	COD 66%; 27 pharmaceuticals 85%; 25 pesticides 72%; odorants 92%	[92]
Tietê River (Brazil)	Coagulation–flocculation → HC + O_3. PGα21Ca: 300 mg/L or quaternary ammonium tannate (QAT): 150 mg/L; O_3 generator nominal output: 3 g/h; reaction: 1 h (PGα21Ca) or 2 h (QAT)	Coagulation–flocculation: ~93% turbidity. After CF + HC/O_3: COD 47.63% (PGα21Ca) and 40.13% (QAT)	[76]

As summarized in Table 7, the available river-water evidence indicates that ozonation applied after coagulation–flocculation can further improve treated-water quality by targeting residual dissolved organic matter, UV-absorbing compounds, micropollutants, and other oxidizable constituents. However, the reported treatment configurations differ among studies, with some including additional processes such as biological activated carbon or hydrodynamic cavitation. Therefore, the reported removal efficiencies should be interpreted within the context of each treatment train and should not be attributed exclusively to ozonation. Overall, the available evidence supports post-ozonation as a potentially useful polishing step, while direct comparative evidence for river-water applications remains limited.

These effects result primarily from the oxidation of aromatic, unsaturated, and chromophoric structures remaining in natural organic matter (NOM) after coagulation. Ozone can also transform persistent organic micropollutants that are poorly removed by conventional coagulation–flocculation, thereby providing an additional treatment barrier. Although reductions in dissolved organic carbon (DOC) have also been reported in some integrated treatment systems, ozonation generally promotes the transformation of NOM into smaller, more oxygenated, and more biodegradable compounds rather than complete mineralization. In addition to direct reactions with molecular ozone, ozone decomposition may generate highly reactive hydroxyl radicals (•OH), particularly under conditions that favor ozone decomposition or in the presence of catalytic surfaces, thereby extending the oxidation of residual organic compounds. Post-ozonation can also increase the biodegradability of residual organic matter, which may enhance its removal in subsequent biological filtration or other downstream processes. Furthermore, oxidation of aromatic NOM may reduce the formation potential of some chlorinated disinfection by-products (DBPs); however, this benefit depends strongly on source-water chemistry, and bromate or other oxidation by-products may form when bromide or suitable precursors are present. Overall, the results summarized in Table 7 indicate that post-ozonation is a valuable polishing step after coagulation–flocculation, capable of improving color, UV_{254}, residual organic-matter characteristics, and the removal of selected micropollutants.

As shown in Table 8, the simultaneous application of ozonation during coagulation–flocculation can improve both the kinetics and overall efficiency of contaminant removal under appropriate operating conditions. Mechanistically, ozone modifies natural organic matter (NOM) and other oxidizable constituents while coagulation and floc formation are occurring, thereby altering particle surface properties, colloidal stability, and interactions between NOM and the coagulant. Ozonation can partially oxidize high-molecular-weight and aromatic organic matter, introducing oxygen-containing functional groups and increas-

ing the hydrophilicity of some NOM fractions. These transformations may reduce the stabilization effect of NOM on colloidal particles and, depending on water chemistry and coagulant type, favor particle destabilization, aggregation, and floc growth. In parallel, ozone decomposition under favorable conditions can generate hydroxyl radicals (•OH), which contribute to the non-selective oxidation of more refractory organic contaminants that may not be efficiently removed by coagulation alone. Partial oxidation of organic matter may also modify its affinity for metal-hydroxide precipitates and other floc surfaces, enhancing adsorption or incorporation into growing flocs. Nevertheless, these effects are strongly dependent on ozone dose, pH, alkalinity, NOM composition, coagulant type, and mixing conditions, and excessive oxidation may produce low-molecular-weight, highly hydrophilic compounds that are less effectively removed by coagulation.

Table 8. Ozonation Coupled with Coagulation/Flocculation.

River Water Treated	Conditions	% Pollutant Removal	Reference
Arroio Dilúvio River (Brazil)	Coagulant: 52.5 mg/L; pH 10; O_3: 0.5–1.0 mg/L; pre-ozonation: 15 min	Pharmaceuticals removal significant; faster floc formation and turbidity reduction	[94]
Iron-ore effluent	Polymer: 1.15 mg/L; O_3: 1.25 g, 15 min; pH ~7–8	Turbidity: 95% COD: 37%	[95]
Gavshan Dam (Iran)	US/O_3 pretreatment: O_3 3 mg/L; US 80 kHz, 200 W/cm^2; PACl 0.81 mg/L	NOM: 95% Turbidity: 50% TOC:75%	[96]

Studies conducted on water from the Arroio Dilúvio River have reported accelerated floc formation together with improved removal of turbidity and selected pharmaceutical compounds. Similarly, studies on iron-ore wastewater have shown turbidity reductions of up to 95%, accompanied by improved solids settleability. These findings support the beneficial integration of ozonation with coagulation–flocculation, suggesting that the combined process can enhance contaminant removal while also improving floc formation and the settling behavior of suspended solids. As a result, downstream solid–liquid separation processes, such as sedimentation and filtration, may become more efficient [94,95].

Environmental significance of coagulation–flocculation and ozonation treatment sequences.

Considering the three treatment sequences discussed above, no single configuration can be regarded as universally optimal because treatment performance depends strongly on source-water characteristics and treatment objectives. For turbid river waters with high suspended-solids concentrations and high ozone demand, coagulation–flocculation followed by ozonation can often be an advantageous configuration. In this sequence, coagulation–flocculation first removes a substantial fraction of the particulate and colloidal load, including particle-associated organic matter, thereby producing clarified water with a lower oxidant demand. Ozonation can then be applied as a polishing step to target residual dissolved organic matter, color- and odor-causing compounds, selected micropollutants, and microorganisms. This treatment rationale is consistent with U.S. EPA guidance describing ozone as both a disinfectant and an oxidant whose performance depends on water-quality conditions and treatment objectives [97,98]. Nevertheless, direct comparative evidence evaluating pre-ozonation, simultaneous ozonation, and post-ozonation specifically in river-water treatment remains limited. Therefore, coagulation–flocculation followed by ozonation should be regarded as an often advantageous option for turbid, high-ozone-demand waters rather than as a universally superior treatment sequence. Pre-ozonation or simultaneous ozonation may provide advantages under other water-quality conditions, and selection of the treatment sequence should be based on source-water char-

acteristics, ozone demand, NOM composition, pH, alkalinity, coagulant chemistry, and specific treatment objectives.

7. Sludge Production

Despite the central role of coagulation–flocculation in river-water treatment, relatively few recent studies report direct measurements of sludge production, sludge volume, solids concentration, or dewaterability under full-scale or environmentally representative conditions. Nevertheless, available comparisons indicate that both aluminum- and iron-based coagulants can generate substantial quantities of water-treatment residuals, although the resulting sludge differs markedly in structure, water content, settling behavior, and handling requirements. Aluminum-based coagulants, such as aluminum sulfate and polyaluminum chloride (PACl), are widely used because of their relatively low cost and high efficiency for the removal of turbidity, suspended solids, and natural organic matter (NOM). However, aluminum-based sludge is often highly hydrated and may contain more than 99% water in some treatment systems, resulting in low solids concentrations and relatively poor dewaterability. Consequently, additional thickening, conditioning, or polymer-assisted dewatering may be required, increasing treatment complexity, storage requirements, and disposal costs. The environmental relevance of residual aluminum is also important, particularly when sludge is intended for reuse, land application, or disposal under conditions that could favor metal release; therefore, residual-metal content and leaching potential should be evaluated as part of sludge management strategies.

In contrast, iron-based coagulants, including ferric chloride and ferric sulfate, often produce denser and more readily settleable flocs, which can result in sludge with improved thickening and dewatering characteristics compared with aluminum-based residuals. The total dry mass of sludge produced is not necessarily lower and may even be greater in some systems because of the coagulant dose and the formation of iron hydroxide precipitates; however, improved compaction can reduce the volume of sludge that must be stored, transported, or mechanically dewatered. Iron-rich residuals may also offer additional advantages in certain downstream applications because ferric iron can bind phosphate and sulfide, potentially limiting sulfide release and associated odor formation when these residuals are incorporated into wastewater or anaerobic treatment processes. However, these benefits are highly dependent on sludge composition, redox conditions, and the intended management route. Therefore, coagulant selection for river-water treatment should consider not only contaminant-removal efficiency but also the quantity, composition, settleability, dewaterability, and final destination of the sludge generated. Site-specific factors—including treatment objectives, raw-water chemistry, available infrastructure, residual-metal limits, disposal costs, and opportunities for beneficial reuse—should ultimately determine the most appropriate coagulant and sludge-management strategy [99].

8. Estimated Cost of Using a Coagulation/Flocculation + Ozone Treatment

The cost of treating river water using a combined coagulation/flocculation and ozonation process is influenced by many important factors, including the type and dose of coagulant used, ozone generation method, energy consumption, water matrix complexity, and the desired treatment goals. In this analysis, the infrastructure requirements are not considered, only the direct costs of the treatment.

Coagulation/flocculation, in most cases, use aluminum or iron salts and this remains a relatively low-cost and scalable method; however, it is limited in its ability to remove emerging micropollutants and organic precursors to disinfection by-products.

On the other hand, the use of ozone, while highly effective for degrading pharmaceuticals, pesticides, and natural organic matter, significantly increases operational costs due

to high energy requirements for ozone generation and the need for system components made from ozone-resistant materials (e.g., stainless steel, PTFE). Recent advances in ozone-generation technologies may offer opportunities to improve energy efficiency and reduce operating costs [31].

Available cost estimates for ozonation-based treatment are largely derived from wastewater studies and should therefore be interpreted as contextual analogues rather than as direct cost estimates for river-water treatment. Ref. [100] concerns coking wastewater and is therefore considered only as a wastewater analogue. Ref. [101] reported costs of 0.06–0.32 USD/m^3 for single ozonation and 0.32–0.63 USD/m^3 for powdered activated carbon (PAC)-catalyzed ozonation under wet-weather primary wastewater conditions at flow rates of 100–600 MLD. Other studies discussing advanced oxidation and ozone-based treatment processes [32,102,103] provide useful treatment-performance context, but do not establish directly transferable cost estimates for river-water applications. Consequently, the economic performance of combined coagulation/flocculation and ozonation for river-water treatment remains site-specific, and further river-water-specific techno-economic assessments are needed.

9. Environmental Implications and Perspectives

The environmental relevance of integrating coagulation/flocculation with ozonation arises from the complementary functions of both processes. Coagulation/flocculation is particularly effective for removing suspended and colloidal particles, turbidity, apparent color, particulate organic matter, and contaminant fractions associated with solids, whereas its performance toward dissolved and low-molecular-weight organic compounds is generally more limited [104]. Ozonation complements these limitations by oxidizing residual dissolved organic matter and selected micropollutants through direct reactions with molecular ozone and, under favorable conditions, hydroxyl-radical-mediated oxidation [105]. Among the treatment configurations discussed in this review, coagulation/flocculation followed by solid–liquid separation and subsequent ozonation is particularly advantageous for turbid river waters, because the particulate and colloidal load is removed before ozone application, reducing competing oxidant demand and allowing ozone to react more efficiently with residual dissolved contaminants. This sequence can also improve color, odor, and microbiological quality, thereby enhancing both the environmental and aesthetic characteristics of treated river water [106–108].

By reducing suspended solids, particle-associated organic matter, selected metals, pharmaceuticals, and other contaminants, the integrated process can decrease pollutant exposure to aquatic organisms and reduce environmental pressures associated with toxicity, oxygen depletion, bioaccumulation, and interference with biological processes [6,7]. Ozonation also provides an important disinfection barrier against a broad range of waterborne microorganisms, including many bacteria and viruses [108], which is especially relevant for rivers used for recreation or as downstream water sources [109].

Coagulation/flocculation followed by ozonation should nevertheless be considered part of a broader river-management strategy rather than a standalone solution to river degradation. Proper management of coagulation sludge and ozonation by-products is essential because contaminant removal or transformation does not necessarily imply complete mineralization; in particular, ozone can generate smaller oxygenated compounds and, in bromide-containing waters, may promote bromate formation if operating conditions are not adequately controlled [99,105,106]. Despite these considerations, the sequential combination of coagulation/flocculation and ozonation offers a practical approach for improving river-water quality because it couples efficient removal of particulate and colloidal matter with targeted oxidation of residual dissolved contaminants and microorgan-

isms [104,105,108]. When integrated with pollution prevention, wastewater management, water-quality monitoring, and watershed protection, this treatment train can contribute to improved water clarity, lower contaminant and microbial loads, enhanced downstream treatability, protection of aquatic ecosystems, and preservation of freshwater resources.

10. Conclusions

Rivers are essential freshwater resources for human well-being, agriculture, biodiversity, and ecosystem functioning, but their quality is increasingly affected by complex mixtures of particulate, dissolved, chemical, and microbiological contaminants. The literature reviewed demonstrates that coagulation/flocculation and ozonation provide complementary treatment capabilities. Coagulation/flocculation is particularly effective for suspended and colloidal matter, turbidity, color, and particulate-associated contaminants, whereas ozonation can address dissolved organic compounds, micropollutants, chromophoric compounds, odor-causing substances, and microorganisms. Their integration therefore provides broader contaminant control than either process alone, although treatment performance strongly depends on water-matrix characteristics and operating conditions.

The reviewed studies indicate that coagulation/flocculation–ozonation is a technically feasible and adaptable approach that can be integrated into conventional water-treatment schemes. Reported coagulant and ozone requirements vary widely among studies because of differences in water composition, contaminant load, coagulant type, treatment configuration, and treatment objectives. The treatment sequence—pre-, simultaneous, or post-ozonation—can substantially influence performance. In particular, coagulation/flocculation followed by ozonation can be advantageous when suspended, colloidal, and coagulable organic matter contribute significantly to ozone demand, because their prior removal can improve subsequent oxidation of residual dissolved contaminants. Nevertheless, the most appropriate sequence remains dependent on source-water characteristics and treatment objectives. Because the available studies employ heterogeneous experimental conditions, the current literature does not support a universal quantitative synergy factor or direct statistical comparison across all systems. Likewise, the economic performance of the integrated process remains site-specific, and further river-water-specific techno-economic assessments are needed.

From an environmental perspective, the integrated approach is particularly relevant for polluted river segments, where reducing suspended matter, organic contaminants, micropollutants, and microorganisms can improve water quality, decrease downstream pollutant transport, and reduce contaminant pressure on freshwater ecosystems. Improvements in color and odor are also environmentally relevant because excessive color can reduce light penetration and affect aquatic processes, whereas odor reflects deteriorated water quality and can limit water use. Ozonation can further contribute to microbial control and improve the microbiological quality of treated water; however, any subsequent use must comply with the corresponding water-quality and microbiological criteria. Importantly, coagulation/flocculation–ozonation should be considered part of a broader river-management strategy that includes pollution prevention, wastewater control, monitoring, and watershed protection. Overall, the available evidence supports this combined treatment as a practical and complementary strategy for improving degraded river-water quality, reducing pollutant loads, and contributing to the protection and more sustainable management of freshwater ecosystems.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/environments13100567/s1: Table S1: Chemical equilibria and corresponding equilibrium constants (log K) used by the MEDUSA program to construct the species-distribution diagrams for the Fe(III)/Cl^- system using 10 and 100 mg L^{-1}, $FeCl_3$, Table S2: Chemical

equilibria and corresponding equilibrium constants (log K) used by the MEDUSA program to construct the species-distribution diagrams for the Fe(III)/SO_4^{2-} system using 10 and 100 mg L^{-1}, of $Fe_2(SO_4)_3$.

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