Coagulation-flocculation parameters for simultaneous removal of nitrates, nitrites, phosphates, and ammonium from wastewater: A mini review

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Abstract. This mini review delves into the critical need to effectively eliminate nitrates, nitrites, phosphates, and ammonium from wastewater to mitigate environmental pollution and uphold water quality standards. Stemming from various human activities like agricultural runoff, industrial processes, and municipal discharges, these pollutants pose significant risks to both aquatic ecosystems and human health if left unaddressed. The study primarily focuses on the efficacy of coagulation-flocculation as a treatment method, which involves the addition of chemicals known as coagulants to destabilize the pollutants. The review further examines the influence of various parameters such as pH, coagulant dosage, and temperature on the simultaneous removal of these contaminants [1,2]. Through detailed analysis, it elucidates the complex interactions among these factors and their consequential impact on overall removal efficiency. Moreover, it underscores the significance of adopting advanced treatment methods like coagulation-flocculation. Additionally, it emphasizes the ongoing need for further research and optimization to address the evolving challenges of wastewater pollution and water resource management comprehensively. By providing insights into optimizing coagulation-flocculation processes, this review underscores the importance of tailored treatment strategies for comprehensive pollutant removal. ***Keywords*:** Ammonium, Coagulation- flocculation, Nitrate, Nitrite, Treatment.

1 Introduction

Wastewater treatment has become an increasingly urgent environmental priority as population growth, industrialization, and urbanization continue to exert significant pressure on water resources worldwide. The presence of pollutants such as nitrates, nitrites, phosphates, and ammonium in wastewater poses significant challenges due to their detrimental effects on ecological systems and human health. These contaminants, originating from agricultural runoff, industrial discharges, and domestic wastewater, can lead to eutrophication, harmful algal blooms, and contamination of drinking water sources if left untreated.

Conventional wastewater treatment processes, while effective for some pollutants, often struggle to simultaneously remove nitrates, nitrites, phosphates, and ammonium to acceptable levels. However, the coagulation-flocculation process has garnered increasing interest as a promising solution for the overall removal of multiple contaminants from wastewater. Coagulation involves the addition of chemical coagulants, such as aluminum or iron salts, which destabilize colloidal particles and facilitate their aggregation. Subsequently, flocculation promotes the formation of larger, settleable particles through gentle mixing, allowing for their removal by sedimentation or filtration [3,4].

In recent years, research efforts have focused on optimizing coagulation-flocculation parameters to enhance the efficiency of removing nitrates, nitrites, phosphates, and ammonium from wastewater. These parameters include selecting appropriate coagulants and doses, adjusting pH, intensity, and duration of mixing, as well as the presence of coagulant aids or auxiliaries [5,6]. Understanding the interactions between these parameters and their impact on pollutant removal is crucial for designing effective and cost-efficient treatment systems.

This mini-review aims to provide a comprehensive overview of the current state of knowledge regarding coagulation-flocculation parameters for the simultaneous removal of nitrates, nitrites, phosphates, and ammonium from wastewater. By synthesizing recent studies and advancements in this

field, the objective is to identify key factors influencing the efficiency of coagulation-flocculation processes and highlight potential research and optimization avenues.
Ultimately, improving understanding of coagulation-flocculation mechanisms and their application in wastewater treatment can contribute to the development of sustainable solutions to mitigate water pollution and protect the environment and public health.

2 Coagulation – flocculation

The water treatment process of coagulation-flocculation aggregates fine particles, including microbes, colloidal particles such as clays, and organic matter, into larger floc particles, thus facilitating their removal from water by settling. Four fundamental mechanisms are identified for the destabilization of colloidal particles: compression of the double layer (electrostatic coagulation), adsorption and neutralization of charges, particle capture in a precipitate, as well as adsorption and bridging [7].
Coagulation is an essential element of water treatment, allowing for the efficient removal of suspended particles or micro-colloids. This process begins with the destabilization of a colloidal suspension, followed by the aggregation of particles into small clusters or flocs, facilitated by agitation and Brownian motion.
Concurrently, flocculation occurs, enabling the enlargement and uniformization of these flocs through moderate stirring [3], It involves the aggregation of destabilized particles to form small microflocs, which then merge to form larger agglomerates of suspended particles (Figure 1) [4].
To overcome the interaction energy between colloidal particles, there are two possible approaches: the first involves reducing the zeta potential by adding mineral reagents containing multivalent cations, which will be adsorbed onto the colloidal surface, thereby neutralizing the electric charge. This process is generally referred to as coagulation.
The second approach uses organic polymers as flocculation reagents [3]. These polymers allow for the aggregation of colloids not only by reducing the electric charge but also by acting as bridges between colloids. These macromolecular reagents act as a net in which particles are trapped.
The term flocculation is typically reserved to describe this form of destabilization, while the term coagulation is mainly used to describe destabilization of colloidal particles by reducing electric charge. The use of coagulation to treat wastewater is characterized by overall quality indicators such as chemical oxygen demand (COD), turbidity, concentration of suspended solids (SS), and content of organic and mineral substances, primarily aiming to separate suspended solids from water, thereby reducing various impurities [4,5].

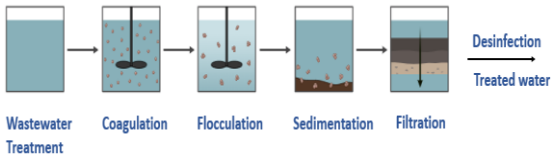

Fig. 1. Coagulation -flocculation process

The water treatment process of coagulation-flocculation aggregates fine particles, including microbes, colloidal particles such as clays, and organic matter, into larger floc particles, thus facilitating their removal from water by settling [6].

2.1 Impact of operating parameters on the coagulation-flocculation process

Operating parameters such as the type of coagulant and coagulant aid, pH, temperature, agitation speed, and duration have all had an impact on the coagulation-flocculation process. Their influence was particularly notable on the efficacy of the coagulant, as well as on these parameters.

2.1.1. Type of coagulant and adjuvant

The selection of coagulants and coagulant aids is of crucial importance in many processes, especially in water treatment, using coagulants such as metal salts like aluminum sulfate or ferric chloride, which are the most commonly used [3-8].
The use of ferric chloride in the treatment of pig wastewater has resulted in a 99% elimination of phosphate and 15% of ammonium. Studies have examined the potential relationship between the use of metal salt-based coagulants and the development of pathogenic diseases [9]. Due to these concerns, research has been conducted to evaluate the effectiveness of natural coagulants [10-13]. The combination of acanthus tribe with moringa and aloe vera has enabled the elimination of 99.12% of nitrate and 99.63% of phosphate [14]. Similarly, the use of cactus as coagulants in water treatment has led to the removal of 80% of nitrites and 99% of ammonium [15].
Regarding coagulant aids, the widespread use of clay minerals as aids in water treatment stems from clay's ability to effectively adsorb organic matter due to its chemically active extended surface [16-19].
The combined use of aluminum sulfate and bentonite has resulted in a 98.2% reduction in phosphate, thereby reducing the amount of aluminum sulfate required. This reduction in the dose of aluminum sulfate helps mitigate its negative effects as a coagulant [20].

2.1.2. Effect of pH and temperature

The effect of pH and temperature on this process is crucial to ensure its effectiveness. Temperature affects the kinetics of the chemical reactions involved in coagulation-flocculation. Generally, an increase in temperature accelerates the coagulation and flocculation reactions, which can improve the efficiency of the process.
Nitrate has undergone significant elimination in various experiments at a pH between 7 to 8 using different coagulants. The use of Ferric chloride with Himoloc DR3000 resulted in an 81% elimination at a pH of 7.66 [21], An acidic pH (7±0.2) can result in the formation of weak HNO_3 ions or the complexation of NO_3^- ions with dissolved aluminum [2]. Similarly, the use of chromium sulfate with cactus juice resulted in a 73% elimination of nitrate, 93% for nitrites, and 83% for ammonium at a pH of 7.7 and a temperature of 15.2°C [22].

2.1.3. Agitation effect and time

Agitation and time can have a significant impact on the coagulation process by influencing particle dispersion, aggregate formation, and the stability of formed aggregates. According to Table 1, rapid agitation typically takes between 1-4 minutes at speeds ranging from 165 to 350 rpm, followed by a flocculation period between 10 to 25 minutes at speeds of 20 to 45 rpm.

Regarding sedimentation, the timing can vary considerably from one study to another. Generally, sedimentation begins after an agitation period and may take at least 30 minutes to manifest significantly. Specific experimental conditions such as particle density and viscosity can also influence the speed and duration of sedimentation [3-23].

Table 1: Impact of Coagulants and Coagulant Aids on the Coagulation-Flocculation Process

Water type	Coagulant type (coagulant+ coagulant aid)	Treatment conditions (coagulation/ flocculation/ setling)	T/pH	Coagulant dose	Elimination rate	Country	Ref.
Coffee wastewater	Acanthus tribe + Moringa + aloe vera	80.73 rpm for 19.23min	20°C/ pH = 8.76	0.750 g of coagulant doses	For nitrate removal of 99.12%, and for phosphate removal of 99.63%	Ethiopia	[14]
Sewage Wastewater Treatment	Cactus	160 rpm for 5 min/ 40 rpm for 25 min/ 30 min	14.7° C/ pH = 12	28 mg/L	99%, 97.87%, 80% and 99% removal of turbidity COD, nitrites and ammonium, respictively	Algeria	[15]
Synthetic water	Aluminum sulfate (SA) + H_2SO_4 treated bentonite (BN)	200 rpm for 3 min/ 45 rpm for 17 min/ 30 min	pH = 2,58	300 mg/L (SA) + 2 g/L (BN)	98,2% removal of PO_4^{3-}	Algeria	[20]
Landfill leachate	Ferric chloride + Himoloc DR3000	120 rpm for 5 min/ 30 rpm for 10-30 min/ 1 h	pH = 7.66	9.5 g/L of coagulant dose, 9.1 ml/L of flocculant dose	The removal efficiencies of color, polyphenols and nitrates were 68.8%, 77.5% and 81.0%, respectively	Morocco	[21]
Effluents from the fish industry	chromium sulfate + cactus juice	120 rpm for 1 min/ 60 rpm for 20 min/ 15 min	15.2 °C/ pH = 7.7	chromium concentration of 176 mg/L + 8 mL cactus juice	COD (94%), BOD_5 (95%), turbidity (96%), suspended matter (91.9%), ortophosphates (17%), nitrates (73%), nitrites (93%) and ammonium (83%).	Morocco	[22]
Wastewater in a high-rate algal pond	Aluminum sulfate + Scenedesmus sp	120 rpm for 1 min/ 25 rpm for 12 min/ 30 min	--	2.5 g/L of Aluminum sulfate + 800 mg/L of microalgae	99% and (> 60%) removal of nitrate and orthophosphate, respictevely	Mexico	[24]

Water type	Coagulant type (coagulant+ coagulant aid)	Treatment conditions (coagulation/ flocculation/ setling)	T/pH	Coagulant dose	Elimination rate	Country	Ref.
Swine wastewater	Ferric chloride	165 rpm for 30 min/ 30 min	22±1° C/ pH = 8.5	2.13 g/L	99% removal of phosphate and 15% removal of ammonium	Canada	[25]
Landfill leachate	Ferric chloride + cationic polyacrylamide	150 rpm for 4.5 min/ 60 min/ 30 min	20˚C/ pH = 3.36	0.87 g/L of coagulantdose, 26 mg/L and of flocculant dose	35%, 40%, 80% and 90% removal of TKN, BOD_5, COD and turbidity, respectively	Tunisia	[26]
Car wash wastewater	Lime	300 rpm for 5 min/ 30 rpm for 30 min/ 30min	pH = 7.38	10 mL of 5% PACl per L + ozonation	100%, 99.2%, 97.3%, 41% and 52% removal of suspended solids, COD, ammonia and nitrate, respectively	Australia	[27]
Wastewater treatment	Ferric sulfate and ferrous sulfate	350 rpm for 60 s/ 30 min	30°C/ pH = 6–6.5	60 mg/L ferric sulfate + 20 mg/L ferrous sulfate	76%, 86%, 50% and 61% removal of PO_4^{3-} , TSS, BOD and COD, respictively	Egypt	[28]
Industrial water	Alum	200 rpm/ 14 rpm for 10 min/ 30 min	25 (+2) °C/ pH = 7.11	60 mg/L of Alum and 2.5 Fenton's mole ratio	89.43%, 72.94 %, 91.06%, 90.96% and 89.85%, removal efficiency of COD, PO_4^{3-}, NH_4^+, NO_3^- and turbidity, respectively	Iraq	[29]
Landfill leachate	Aluminum sulfate	300 rpm for 5 min/ 25 min	24°C/ pH = 5-7	6 g/L of $Al_2(SO_4)_3$	44% and 82% removal of COD and NH_4-N, respectively (SBR 2)	Tunisia	[30]
Car Wash Wastewater	$FeCl_3$	300 rpm for 1 min/ 30 rpm for 20 min/ 30 min	11.4 °C/ pH = 5.61	45 mg/L	92%, 84% and 67% removal of nitrate, nitrite and COD	Australia	[31]
Wastewater treatment	Polyferric chloride	200 rpm for 2 min/ 30rpm for 20min/ 30min	24 ±1°C/ pH = 8.5	28mg/L	77.2%, 94.6% and 20.8% removal of TOC, NH_4^+-N and PO_4^{3-}—P, respectively	China	[32]
Water treatment	polydiallyldimethylammonium chloride (PDADMAC)	300 rpm for 1/ 40 rpm for 10 min/ 30 min	20°C/ pH = 7.53	0.5 mg/L	20% removal of NO_3^- and turbidity removal was 98%	China	[33]

Table 1 illustrates that this study demonstrates the coagulation process is subject to the influence of various coagulants and coagulant aid. It suggests that the choice of coagulant and its associated parameters significantly impacts the efficiency of the coagulation process in removing contaminants from wastewater.

However, several factors beyond the coagulant choice play a role in influencing the process's effectiveness. These factors include pH levels, temperature, mixing intensity and duration, characteristics of the wastewater being treated, and the presence of other substances in the water.

The variations in these factors can lead to different outcomes in terms of contaminant removal efficiency.

3 Conclusion

Wastewater treatment is crucial for preserving our water resources and protecting the environment from pollution. The effective removal of contaminants

such as nitrates, nitrites, phosphates, and ammonium poses a major challenge for conventional treatment systems. However, the coagulation-flocculation process emerges as a promising solution to this issue. By optimizing the parameters of this process, such as the choice of coagulants, doses, pH, and mixing duration, it is possible to significantly improve the removal of these pollutants. This mini-review emphasizes the importance of better understanding these mechanisms to develop sustainable and effective solutions in wastewater treatment, thereby contributing to preserving the quality of our water resources and protecting public health and the environment.

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