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Review

Application of Natural Coagulants for Pharmaceutical Removal from Water and Wastewater: A Review

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Abstract: Pharmaceutical contamination threatens both humans and the environment, and several technologies have been adapted for the removal of pharmaceuticals. The coagulation-flocculation process demonstrates a feasible solution for pharmaceutical removal. However, the chemical coagulation process has its drawbacks, such as excessive and toxic sludge production and high production cost. To overcome these shortcomings, the feasibility of natural-based coagulants, due to their biodegradability, safety, and availability, has been investigated by several researchers. This review presented the recent advances of using natural coagulants for pharmaceutical compound removal from aqueous solutions. The main mechanisms of natural coagulants for pharmaceutical removal from water and wastewater are charge neutralization and polymer bridges. Natural coagulants extracted from plants are more commonly investigated than those extracted from animals due to their affordability. Natural coagulants are competitive in terms of their performance and environmental sustainability. Developing a reliable extraction method is required, and therefore further investigation is essential to obtain a complete insight regarding the performance and the effect of environmental factors during pharmaceutical removal by natural coagulants. Finally, the indirect application of natural coagulants is an essential step for implementing green water and wastewater treatment technologies.

Keywords: natural coagulation; chemical coagulation; pharmaceuticals; *Moringa oleifera*; green treatment technology

1. Introduction

The discharge of pharmaceutical waste into the environment poses a threat to both humans and environmental systems. The disposal of these contaminants without proper treatment has resulted in pharmaceuticals being widespread in ecosystems [1]. The presence and accumulation of these emerging compounds harm the ecosystem. Human drugs such as ibuprofen and acetaminophen are continuously accumulating in the environment, resulting in pollutants in water bodies and causing harmful effects [2]. In addition, the mineralization rate of pharmaceuticals such as diclofenac and ibuprofen through photocatalysis is low, resulting in the accumulation of these compounds in the environment [2].

The effluent of wastewater treatment plants is the typical source of pharmaceutical compounds, since the conventional wastewater treatment methods are not designed to remove these micropollutants [3]. Therefore, these harmful chemicals accumulate and contaminate soil, rivers, oceans, and groundwater [4].

Recently, several studies reported the efficiency of the coagulation-flocculation treatment method for pharmaceuticals' removal, especially in rich organic wastewater [1]. Coagulation-flocculation consists of two steps: (1) the tendency of colloidal particles to form large flocs by destabilization, and (2) settling these large flocs by precipitation. The removal of pharmaceuticals directly by means of the coagulation process is not reported in the literature. The mechanism of pharmaceuticals' removal by coagulation process is indirect by using colloidal particles as a vehicle for pharmaceuticals [3,5,6].

For many years, chemical-based coagulants such as aluminum sulfate (alum) and polyaluminum [7,8] have had different environmental effects by producing highly toxic sludge. In addition, the consumption of water contaminated by the residual chemical coagulants may cause neurodegenerative diseases [9]. Thus, the transition towards natural-based coagulants for water and wastewater treatments has gained increasing attention in recent years [10].

Natural coagulants can be produced from natural sources such as plants and animals. Many studies reported several natural sources for extracting natural-based coagulants [11,12]. Natural resources that possess a higher molecular weight may contain a more extended polymer that increases these natural coagulants' efficiency [13–15]. These sources have been extensively studied to treat different types of wastewater, such as textile wastewater, dairy wastewater, and domestic wastewater [16,17]. In addition, coagulants can also be obtained from animal waste such as banes and shells [18]. The main challenge of using natural coagulants in general, especially animal-based coagulants, is their continuous availability for large-scale treatment [18].

Natural coagulants perform better at a wide pH range [19–21]. In addition, using natural coagulants does not change the pH of water compared to chemical coagulants. In addition, natural coagulants positively affect the ecosystem and the environment [10,22,23]

The application of natural coagulants has been reported in many studies for domestic and industrial wastewater [24]. However, fewer studies investigated the performance of natural coagulants for emergency pollutant removal. In addition, fewer reviews discussed the use of natural coagulant for pharmaceuticals removal. In line with the aforementioned gaps. These reviews present and discuss the recent natural coagulation method for pharmaceutical removal from water and wastewater. A comprehensive comparison between natural coagulants and chemical coagulants is also presented. Finally, this review highlights the required future research to overcome the shortcomings of using natural coagulants.

2. Fundamental of Coagulation Processes

The coagulation process is used wildly in water and wastewater treatment, as it is effective for removing suspended solids, turbidity, organic matter, oil, chemical oxygen demand (COD), and color [25]. The coagulation process is mainly conducted by adding a coagulant that allows small agglomerate particles (unsettleable fine particles) to form larger flocs that can settle. Coagulation and flocculation are interlinked. Coagulation is the clustering process under high-speed mixing, whereas flocculation is the settling process under gentle mixing. Generally, colloidal particles are negatively charged particles. Thus, coagulation is a chemical process that involves neutralizing these particles in water and wastewater, whereas flocculation is a physical process involving the formation of flakes from neutralized particles during the coagulation process. Thus, large flocs form during coagulation, and they aggregate and settle during flocculation [26].

Generally, the coagulation process depends on operating conditions such as settling time, mixing rate, coagulant type, and dosage. These factors determine the quality of the produced water. In addition, the coagulant dosage must be suitable for a decent suspension of particles, and the mixing speed should be high. The other coagulant properties, such as life span and quality, determine the coagulant's stability during storage. Following the coagulation-flocculation, the large flocs sink through gravitational settling; this process depends on the settling rate of the particles [27].

The colloidal particles' sizes range from 0.001 to 1.0 µm due to them being negatively charged and the small size being suspended in water. Four mechanisms are used to destabilize these fine particles using a coagulant; charge neutralization, polymer bridging, sweep flocculation, and double-layer compression (Figure 1).

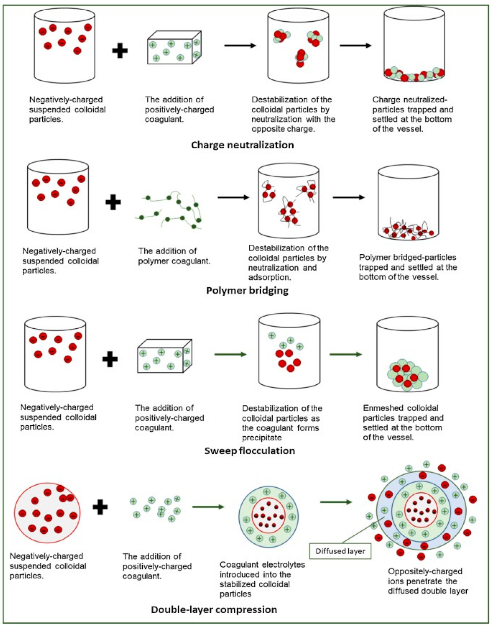

Figure 1. Coagulation mechanisms diagram showing charge naturalization, polymer bridging, sweep flocculation, and double-layer compression, copied with permission from Ref. [10], Copyright, 2021, Elsevier.

In the charge neutralization mechanism, the oppositely charged ions are used to attract colloidal particles, and coagulants added to the wastewater will further neutralize the electrical load until it reaches zero zeta potential; as a result, the colloidal particle charge neutralizes, and the electrostatic repulsion decreases or is almost eliminated [28]. Generally, when a chemical coagulant is added to water, a hydrolysis process occurs, producing cationic species which react colloidally. The polymer bridging mechanism takes place when a polymer or polyelectrolyte coagulant with a long chain destabilizes the colloidal particles by making a bridge that forms a connection between them. The polymer coagulant adsorbs multiple particles to the polymer molecule surface [29]. Thus, strong clusters of macro flocs are produced and tied together by bridges. The flocs formed by polymer bridging are flaky with irregular void spaces. The sweep flocculation coagulant traps the colloidal particles and forces them to sink to the bottom. A net-like structure is formed by the hydrolysis process that makes up precipitation of amorphous metal hydroxide. The double-layer compression includes a coagulant that helps the colloidal particles to reduce the repulsion force and assemble. This mechanism works by means of the presence of a high concentration of electrolyte ions around the colloidal; thus, an opposite charge enters the diffused double layer which surrounds the colloids; as a result, the density is increased [30].

The strongest flocs are those formed through polymer bridging, followed by those formed through charge neutralization and sweep flocculation. The flocs formed through charge neutralization are compacted but not strong, because they depend on the physical rather than chemical bonds. Analysis such as initial floc aggregation, the flocculation index, and the relative settling factor indicated that flocs produced by sweep flocculation have good settling behavior but have a slower formation rate. Flocs produced by double-layer compression are bigger due to the high aggregation rate, but their settling behavior is affected by the unnecessary friction force formed between flocs. Moreover, the coagulant's ionic charge significantly affects the strength of flocs. Divalent ions produce flocs stronger than monovalent ions and require less time to settle. Generally, the dominant coagulation mechanism for natural coagents is charge neutralization [10].

3. Factor Affecting Coagulation Process

Determination of optimum operating conditions is crucial, as an added coagulant is utilized thoroughly to remove the contaminants. Deferent optimal conditions can be achieved for different coagulants. A deep understanding of the reaction between pollutant and coagulant is needed to achieve high performance in addition to decreasing the cost and sludge volume. Many parameters affect the efficiency of the coagulation process for water and wastewater treatments, and these parameters are varied to control the optimal conditions for the highest efficiency. Coagulant dosage, pH, turbidity, mixing speed and time, and temperature are the main operating factors affecting coagulation speed [31]. These factors significantly impact the coagulation process, affecting the effectiveness and efficiency of coagulants in water and wastewater purification processes.

3.1. Coagulant Dosage

The optimal coagulant dosage is an important parameter that entirely controls coagulation reactions. The influence of coagulant dosage can be discussed for three different levels. The optimal coagulant dosage effectively aggregates the colloidal particles in water and wastewater. An underdosage inhabits the proper assembly of colloidal particles, whereas an overdosage pollutes the wastewater and causes an increase in organic load, turbidity, and higher slurry volume, which leads to an increase in the treatment cost [10].

3.2. pH

pH is an acidity/alkalinity measurement that varies between 1 and 14. The pH of water and wastewater is an essential environmental factor, as it affects chemical reactions during the treatment process [32,33]. The amphoteric coagulant molecules' charge highly influences the pH during the treatment process. In addition, alkalinity, which is defined as the capacity to neutralize acidity, controls the efficiency of the coagulation process. Most chemical-based coagulants, especially ferric-based coagulants, absorb a high percentage of alkalinity. Thus, adding a coagulant to wastewater with low alkalinity produces poor flocs. Additional alkaline agents such as caustic soda, slime, or soda ash should be added to the wastewater to overcome this problem. A pH value differing from the optimum pH produces a mixture of negative and positive charges of amino acids, which decreases the coagulant's cationic efficiency [29]. Moreover, pH determines the optimum coagulant dosage as it affects the protein molecule ionic charge. Therefore, the optimum pH's determination and adjustment must be performed before implementing the coagulation process.

3.3. Initial Turbidity

Initial turbidity is an essential factor that affects the coagulation process. The presence of a colloidal particle in water causes turbidity that affects the clarity of the water. Soil, abundant microorganisms, organic matter, decaying matter, colored compounds (pigment and dye), algae, and plankton induce turbidity in water, making it look murky, cloudy, and undesirable. Colloidal particles and turbidity are a challenge in water and wastewater treatment, as the increased rate of turbidity means more pollutant molecules are available, which means a higher number of collisions between the coagulant and pollutants may be produced [34]. More collisions result in sturdier and larger flocs, which settle faster.

On the other hand, a low initial turbidity decreases the collision chance between coagulants and pollutants. As a result, small flocs are formed, which settle slowly. Moreover, a low initial turbidity forms a flake-like structure that needs more time to sink.

3.4. Mixing Speed and Time

The mixing speed and time is an essential operation condition that affects the efficiency of the coagulation process. Rapid mixing is used during the coagulant's addition to evenly enhance the distribution of coagulant through the wastewater and destabilize the suspended particle, whereas gentle mixing is required to increase the collision between particles to form macro flocs [29]. These two speeds control the entire coagulation process as the efficiency of the coagulation process depends on the speed and time of mixing. Inadequate speed and time may inhabit the homogeneous agglomeration of the particles and increase the floc shear and tear.

4. Natural Coagulants

Recently, natural or green coagulants and their application for water and wastewater treatment have received attention, as they do not conserve alkalinity and maintain pH. In addition, natural coagulants do not add metals to the effluent, as chemical coagulants do; a lower sludge volume is produced, and thus, the cost of disposal is lower [10]. Natural coagulants are classified into plant-based coagulants and non-plant-based coagulants. Plant-based coagulants can be prepared from leaves, seeds, fruit wastes, the bark of trees, and other sources. Plant-based coagulants have been more widely investigated than non-plant-based coagulants due to their greater affordability [22]. A wide range of natural coagulants, such as moringa seeds, banana peel, jatropha curcas, cassava peel starch, watermelon, pawpaw, beans, nirmali seeds, and okra have been studied previously [35].

Natural coagulants in powder forms are usually added directly to wastewater. The preparation methods of natural coagulants depend on their source [36–38]. Figure 2 shows the preparation stages for natural powder coagulants from seeds. Oil extraction is an essential step for high oil-content seeds such as *Moringa oleifera*, which contain 30–40% oil, as when a coagulant made from high oil-content-based seeds is used without oil extraction, the organic matter in the treated wastewater will increase. Table 1 illustrates the main application forms of natural coagulants.

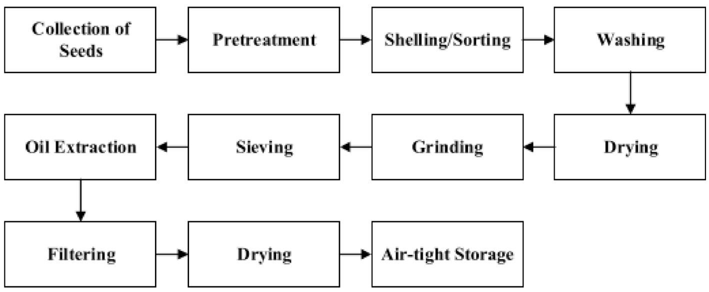

Figure 2. Flow chart of natural coagulant preparation from seeds, copied with permission from Ref. [10], Copyright, 2021, Elsevier.

4.1. Plant-Based Coagulant

Natural coagulants are used for water treatment; however, they are not used for industrial wastewater due to their higher costs than chemical coagulants. Generally, natural coagulants effectively treat water or wastewater with low turbidity ranging from 50 to 500 NTU (Nephelometric Turbidity Units). The primary sources of plant-based coagulants are *Moringa oleifera*, Nirmali seeds, cactus, and tannin. The extracted natural polymers from these seeds are biodegradable and eco-friendly [36]. Anionic polyelectrolytes are extracted from Nirmali seeds; this extract has hydroxyl (-OH) and carboxylic (-COOH) groups, increasing coagulation efficiency. The combination of galactan and polysaccharides extracted from Strychnospotatorum seeds may increase the turbidity removal efficiency up to 80%. The availability of the hydroxyl group (-OH) in the galactan and galactomannan enhances the adsorption process between the surface of colloidal and these polymers; thus, the polymers' bridging action may increase. The polyelectrolytes neutralize the negative colloidal particles and adsorb onto the surface particles. Natural coagulants possess several functional and charged groups such as -COOH, $-NH_2$, and -OH. Generally, the action of natural polymeric coagulants combines polymer bridging and charge neutralization.

Table 1. The main application forms of natural coagulants.

Natural Coagulant	Application Form	Reference
Moringa oleifera	Seed paste	[38]
	Press cake (solid)	[39]
	Powder	[40]
Chitosan	Powder	[41]
	Stock solution (0.1 M HCl)	[42]
	Solution (1% acetic acid)	[43]
	Stock solution (0.1 M HCl and distilled water)	[44]
Rice starch	Starch solution	[45]
Jatropha curcas	Press cake (solid)	[46]
Watermelon seeds	Oil-free powder	[47]
Banana pith	Powder	[48]
Ocimum basilicum	Mucilage	[49]

4.2. Animal Base

The source of animal-based coagulants is usually obtained from the exoskeleton of shellfish extracts, animal bone shell extracts, and chitosan. Chitosan is a polymer (cellulose-like biopolymer) with a high molecular weight produced from the deacetylation of chitin, extracted from the shells of crabs, lobsters, shrimps, diatoms, fungi, insects, freshwater and marine sponges, and mollusks. The applicability of using chitosan as a natural coagulant has been studied intensively for wastewater treatment in the agricultural industry, textile industry, food processing industry, paper mills, soap and detergent industry, and other industries [34]. The main advantages of using chitosan as a coagulant are that when added to acidic wastewater, it reacts and produces positive charges that destabilize colloidal particles' negative charge [37].

5. Pharmaceutical in Water and Wastewater

Pharmaceuticals are a set of developed chemicals used for human and veterinary medication. Recently, they have been classified as ecological contaminants that threaten both humans and environments [50]. Pharmaceuticals include antibiotics, analgesics, both legal and illicit, beta-blockers, steroids, etc., and they have been detected in wastewater treatment plants' effluents, sediments, sludge, natural waters, groundwater, and drinking water. The presence of pharmaceuticals in the soil may trigger the development of antibiotic-resistant genes [51].

Currently, pharmaceuticals and their biotransformative compounds are bioaccumulating and harmfully affecting the ecosystem. However, these chemicals have been discharged to the environment for a long time, their environmental effects have only been considered recently. Many pharmaceuticals (around 160) have been detected in water bodies in low concentrations. These chemicals are classified as pseudo-persistent pollutants which environmentally persistent and are continuously discharged into the environment at low concentrations. These pharmaceuticals' eco-toxicological impacts on aquatic and terrestrial life are unknown [52].

5.1. Pharmaceuticals' Consumption and Fate

The consumption of pharmaceutical compounds has increased dramatically due to many reasons, such as a decrease in production cost and chronic disease treatment demand. As a result, the presence of these compounds has increased. Currently, the environmental management of pharmaceuticals is challenging, as these substances are found in wastewater treatment plants' effluents in low concentrations (usually in ng/L). Sophisticated analytical apparatuses and complex methods are needed to quantify pharmaceuticals at this low concentration [53].

Pharmaceuticals are generally moved and transported by the demonstrated routes in Figure 3 [54]. After consumption, metabolism in the human body, and extraction, pharmaceuticals usually reach aquatic environments by being discharged in treated domestic wastewater effluents [55]. During this route, pharmaceuticals may go through chemical reactions and transformation, forming by-products, which are sometimes more harmful and persistent than their parent compounds. Most of these compounds are non-biodegradable in conventional treatment methods; as a result, they remain and are discharged through wastewater treatment plants' effluents into water bodies such as lakes, rivers, and estuaries [56]. In veterinary products, pharmaceuticals reach aquatic systems through subsequent outflow and manure and direct application in aquaculture [57]. Microorganisms may convert the metabolic compounds to their parental form in surface and groundwater [58]. The ecological concern related to pharmaceuticals in water resources is not directly related to their quantity but to their availability and persistence, which directly affects aquatic life through their toxicity and their potential effect on endocrine function [54,59].

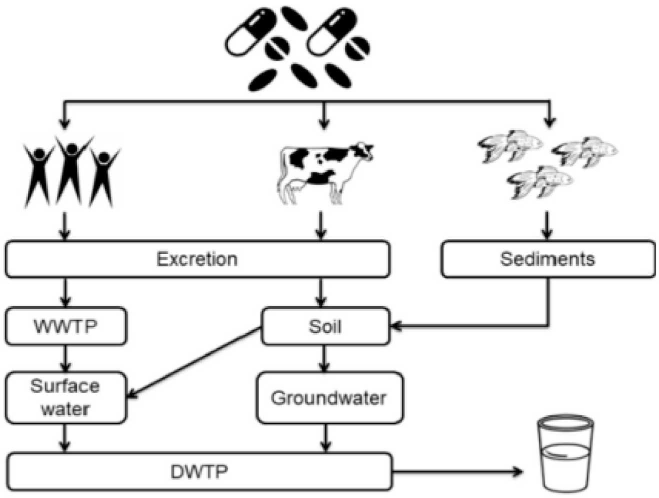

Figure 3. Pharmaceuticals' fates and environmental pathways, copied with permission from Ref. [54], Copyright, 2019, Elsevier.

5.2. Technologies for Pharmaceutical Wastewater Treatment

Pharmaceutical removal from water and wastewater is challenging due to their low concentration and resistance to degradation. Many technologies have been investigated for pharmaceutical removal from water and wastewater [60]. In this section, the pharmaceutical removal methods are discussed.

Activated sludge systems have been used for domestic and industrial wastewater treatments for a long time. Recently, the efficiency of this conventional treatment method for pharmaceuticals removal was investigated. Ren et al. [61] studied the removal of 21 parimutuels by an activated sludge treatment system. The result show that 14 compounds were biodegradable, whereas seven were non-biodegradable. Thus, activated sludge treatment methods are not efficient in completely removing pharmaceuticals from wastewater, as it is not designed for this type of pollutant. Electrocoagulation is more efficient and effective than chemical coagulation. In electrocoagulation, anodes are used to treat contaminants, and the formed coagulants are used for their degradation. Many studies investigated the use of electrocoagulation treatment methods to remove pharmaceuticals such as dexamethasone, doxycycline hyclate, hydrolyzed peptone, caffeine, sulfamethazine, and cephalexin from wastewater. The results show a high removal efficiency (generally above 90%), indicating that these systems efficiently remove pharmaceuticals [62]. The main advantages of using electrocoagulation treatment are its easy chemical maintenance and high efficiency for colloidal particle removal. However, electricity and sacrificial electrodes are the main drawbacks of using this method, as they need to be replaced [63].

Advanced oxidation processes are effective in removing pharmaceuticals that conventional biological methods cannot remove. Among these methods, the Fenton reaction represents hydroxyl radical formation by a reaction between hydrogen peroxide (H_2O_2) and Fe (II). The hydroxyl radical is considered among the strongest oxidants that can oxidize a wide range of organic matters with low selectivity [64]. Therefore, Fenton-based reactions are commonly used for degradation emergency contaminants such as pharmaceuticals. pH control is essential for the Fenton reaction; thus, this treatment technology is usually performed at an acidic pH (3–5). The Fenton reaction method is found to be an effective method for a wide range of pharmaceuticals removal such as hydroxylamine, cyclohexanone, pyridine, toluene [65]. Many reports revealed that membrane bioreactor technologies can remove more micropollutants than conventional activated sludge systems due to their high MLSS (Mixed Liquor Suspended Solids) concentration and high sludge retention time, which allow the growth of low growth bacteria [66]. These bacteria can degrade complex organic compounds. The removal of acetaminophen, carbamazepine, mefenamic acid, ibuprofen, diazepam, naproxen, and ketoprofen by a membrane bioreactor was studied. Overall, more than 85% removal efficiency was obtained [67]. The major drawback of membrane bioreactors is the fouling of membranes that need frequent cleaning and sometimes replacement [68].

Photocatalysis is a reaction in which the presence of a catalyst accelerates the photoreaction [69–71]. The main advantage of photocatalysis reactions is the need for temperature or pressure or chemical agents such as hydrogen peroxide. However, this method is costly. Titanium oxide is the most studied catalyst for photocatalysis reactions due to its biological and chemical stability, inertness, and low cost compared to highly photoactive semiconductor materials. Titanium oxide can be used many times without losing its photocatalyst activity [72,73]. Nevertheless, the separation of titanium oxide from the reaction matrix is complicated. In addition, the transformation of organic matter is incomplete, and by-products, sometimes with a higher toxicity than parent compounds, are produced. Figure 4 shows the problems of using titanium oxides as a catalyst in photocatalysis reactions for pharmaceutical removal [74]. Ozonation has been used as an advanced treatment in many wastewater treatment plants worldwide to enhance contaminant removal. Ozone is a colorless, unstable gas used as a disinfectant for organic and inorganic pollutants. Two mechanisms are used to degrade organic matter by ozonation; (1) an indirect attack by hydroxyl radicals produced by ozone decomposition, and (2) a direct electrophilic attack by ozone [75]. The main drawbacks of using ozone are the high operational cost; the by-products may be toxic; and that ozone is less soluble in water [68].

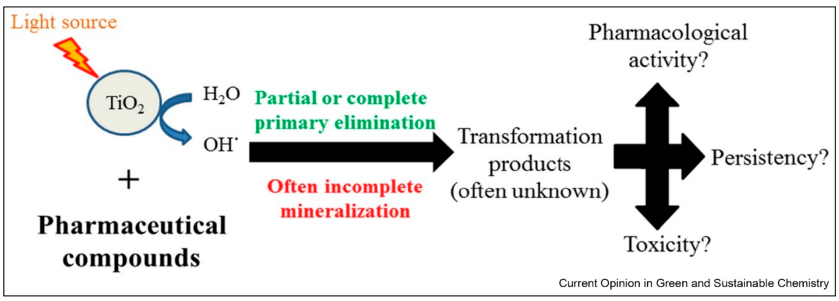

Figure 4. TiO_2-related problems, copied with permission from Ref. [62], Copyright, 2021, Elsevier.

6. Application of Natural Coagulants for Pharmaceutical Removal

Recently, green water and wastewater treatment technologies have gained more attention. Among these technologies, natural coagulants are a promising method for wastewater treatment [76]. In this section, the recent advancements made in using natural-based coagulants are presented.

In a recent study, Nonfodji et al. [77] prepared a natural coagulant from *Moringa oleifera* seeds, and they studied its performance for hospital wastewater treatment. The results indicate that the removal efficacy of turbidity and COD was 64 and 38%, respectively. In a subsequent study, Thirugnanasambandham and Karri [78] compared the COD, turbidity, and color removal by two types of coagulants; a natural coagulant (Azadirachta indica A. Juss) and a chemical coagulant (aluminum sulfate). Remarkably, the results indicate that natural-based coagulants may not only be effective for COD, turbidity, and color removal, but may also be economically competitive, as the operating costs were USD 0.56/m^3 and USD 1.73/m^3 for natural coagulants and the chemical ones.

In another study, Maharani et al. [79] investigated the removal of COD and BOD from pharmaceutical waste using moringa seed coagulant and tapioca starch coagulant. The results point to high BOD (Biochemical Oxygen Demand) and COD removal for both natural coagulants. For moringa, the BOD and COD removals were 90 and 71%, respectively, whereas for tapioca, they were 95 and 94% for BOD and COD, respectively. These results indicate that natural coagulants might be a promising treatment technology for pharmaceutical waste treatment. Oliva et al. [80] studied the use of rice husk ash functionalized by *Moringa oleifera* protein for amoxicillin removal from water solutions. They also investigated the effect of operating parameters such as coagulant dosage, initial amoxicillin concentration, and contact time. The results indicate that the used biomaterials are feasible for pharmaceutical removal from water. Olivera [81] examined the potential of using biomaterial extracted from *Moringa oleifera* for the extraction of diclofenac and oxytetracycline from wastewater. The results show the high potential for pharmaceutical removal from wastewater using biomaterial.

The removal percentages were 88% for diclofenac and 50% for oxytetracycline. Santos et al. [82] examined tetracycline removal from river water by using *Moringa oleifera* seeds. The results show 50% tetracycline removal efficiency at 0.5 g/L *Moringa oleifera* dosage. Iloamaeke and Chizaram [83] examined the removal of pharmaceuticals by Phoenix dactylifera seeds-based coagulants. The results show that a maximum removal efficiency of 99.86% was achieved at a 100 mg/L coagulant dosage, a 50 min settling time, and a pH of 2.

Sibartie and Ismail [84] studied the performance of H. Sabdariffa and J. Curcas as a neutral coagulant for pharmaceutical wastewater treatment. The results demonstrate that at a coagulant dosage of 190 mg/L and pH 4, the maximum removal efficiency was achieved for turbidity (5.8%) and COD (30%) by H. Sabdariffa, while J. Curcas works best at pH 3 and a coagulant dosage of 200 mg/L to remove 51% of turbidity and 32% of COD. Table 2 presents the application of natural coagulants to remove different types of pharmaceuticals.

Table 2. Application of natural coagulant for the removal of different types of pharmaceuticals.

Coagulants	Properties	Contaminants	Conditions	Main Results	Reference
Moringa oleifera seeds	Plant-based	COD (hospital wastewater)	Initial COD 238 mg/L; pH 6, 8; Coagulant dosage 0–4000 mg/L; Rapid mixing: 200 rpm for 3 min; Gentle mixing: 45 rpm for 30 min; Settling time 60 min.	*Moringa oleifera* seed polymers are promising bio-coagulants for hospital wastewater treatments.	[77]
Azadirachta indica A. Juss.	Plant-based	COD (urban sewage)	Initial COD 3030 mg/L; pH 4.5;Coagulant dosage 2000–6000 g/L; Rapid mixing: 100 rpm for 1 min; Gentle mixing: 40 rpm for 30 min; Settling time 60 min.	Natural coagulants effectively reduced COD, turbidity, and color at optimum conditions compared to chemical coagulants	[78]
Moringa seed coagulant, tapioca starch coagulants	Plant-based	COD (Pharmaceutical waste)	pH 6–8; Coagulant dosage 3780 mg/L; Rapid mixing: 100 rpm for 10 min; Gentle mixing: 60 rpm for 15 min;	The high removal efficiency observed with the use of tapioca flour coagulant is due to an amide group that contains a high positive charge	[79]
Rice husk ash functionalized by *Moringa* oleifera protein	Plant-based	amoxicillin	Dosage 500, 1000, 1500 mg/L; Contact time 30, 60, 90 min; Mixing speed 150 rpm; Initial amoxicillin concentration (100, 200, 300) mg/L	Rice husk ash functionalized by *Moringa oleifera* protein can be an effective treatment method for an antibiotic from water	[80]
Moringa oleifera adsorpant	Plant-based	Diclofenac and Oxytetracycline	pH 3–10; Dosage 2000 mg/L; Initial diclofenac and oxytetracycline concentration 0.2–1 mg/L; Stirring speed 150 rpm.	The removal efficiency is highly pH-dependent; diclofenac removal efficiency was 4.8% at pH 8 and 87.3% at pH 2, while the removal efficiency of oxytetracycline at pH 3 and 10 was 31 and 50%, respectively	[81]
Moringa oleifera seed	Plant-based	Tetracycline antibiotic	Tetracycline initial concentration 5 mg/L; Coagulant dosage 250–2500 mg/L; pH 5–8; Rapid mixing: 120 rpm for 1 min; Gentle mixing: 30 rpm for 15 min; Settling time 30 min	*Moringa oleifera* seed is a natural, simple, and environmentally friendly technology for antibiotic removal from contaminated water	[82]
Phoenix dactylifera	Plant-based	Pharmaceutical effluent	pH 4–10; Coagulant dosage 200–400 mg/L; Rapid mixing: 100 rpm for 2 min; Gentle mixing: 40 rpm for 20 min; Settling time 50 min	SEM analysis indicated that phoenix dactylifera adsorbed pharmaceutical particles on the surface; thus, phoenix dactylifera can be an effective green coagulant for emergency pollutant removal	[83]
Hibiscus Sabdariffa and Jatropha Curcas	Plant-based	Pharmaceutical Wastewater	Contaminant initial concentration 660 mg/L; pH 2–12; Coagulant dosage 40–200 mg/L; Rapid mixing: 100 rpm for 10 min; Gentle mixing: 40 rpm for 25 min; Settling time 50 min	Compared to chemical coagulants (Alum), natural coagulants such as J. Curcas have better performance in terms of pharmaceutical wastewater treatments	[84]

7. The Transition from Chemical to Natural Coagulant: Comparative Evaluation on Performance

The transition from chemical coagulation to natural coagulation can be an important step towards increasing green water treatment technology, reducing health risks and environmental pollution [23]. Natural coagulants can be obtained from plant or animal sources. Natural coagulants were discovered years ago, before chemical coagulant; over the years, the application of natural coagulants decreased due to the development of chemical coagulants. Recently, the rise of green water treatment technology, besides the environmental problems related to chemical coagulants, has motivated the consideration of natural coagulants again. This section presents a comparative discussion of natural and chemical coagulants.

Many studies evaluated the performance of natural coagulants for removing pollutants from water and wastewater; they concluded that natural coagulants can be competitive in terms of removal efficiency [26]. Table 3 presents the comparison performance of natural and chemical coagulants. The combination of chemical and natural coagulants may increase the performance of the coagulation process. In a study, the combination of alum and banana peels removed 94% of turbidity, whereas the use of alum and banana peels alone resulted in turbidity removal efficiency of 73.1 and 65.6%, respectively [85].

The advantages of using natural-based coagulants over chemical ones are: (1) natural coagulants may produce less sludge than chemical coagulant; thus, the environmental sustainability increases, while the sludge handling cost decreases; (2) the natural coagulant dosage is less than that of chemical coagulants; thus, the cost and sludge production is lower; (3) the toxicity of natural coagulants is lower than that of chemical coagulants [86]; and (4) the use of natural coagulants does not require skilled workers, as they have a low health impact and do not represent such as potential environmental hazard [23].

However, natural coagulants have some disadvantages that hinder their widespread use: (1) rapid mixing during the coagulation process induces cell rupture; thus, the organic matter load may increase and react with disinfectants in the following treatment process, resulting in disinfectant by-products [87,88]; (2) the vast majority of natural coagulants are extracted from plants, so the supply of these coagulants may be affected by seasonal production [89]; (3) natural coagulants are bio-based materials; thus, this material can decompose during long-term storage [9]; and (4) some natural coagulants are used as medicines; the high consumption of these materials in water treatment could affect their supply to the medicine sector [10].

Table 3. Comparison performance of natural and chemical coagulants.

Type of Wastewater	Chemical Coagulant	Removal Performance	Natural Coagulant	Removal Performance	Reference
Arsenic-contaminated surface water	Ferric chloride	Maximum arsenic removal of 69.3% at 40 mg/L coagulant dosage	Cellulose and chitosan	Maximum arsenic removal of 84.62% at a 1 mg/L cellulose dosage and 75.87% at a 25 mg/L chitosan dosage.	[90].
Turbidity in Surface water	Alum	Turbidity removal of 78.72% at a dosage of 100 mg/L	Sago and chitin	Turbidity removal of 69.15% at a sago dosage of 300 mg/L, and 67.73% at a chitin dosage of 300 mg/L	[91]
Paper mill industry	Alum	Turbidity removal of 97.1%, COD removal of 92.7%	*Moringa oleifera* seed	Turbidity removal of 96%, COD removal of 97.3%	[92]
Paint industry	Ferric chloride	Color removal of 89.4%, COD removal of 83.4%	Cactus	Color removal of 88.4%, COD removal of 78.2%	[93]
Concreate plant	Ferric chloride and Alum	Turbidity removal of 99.9%	*Moringa oleifera* seed	Turbidity removal of 99.9%	[94]
Confectionary	PAM	TSS removal of 93.5% COD removal of 95.9%	Cactus	TSS removal of 92.2% COD removal of 95.6%	[95]
Paper and mill	Alum	Color removal of 80% TOC removal of 40%	Chitosan	Color removal of 90% TOC removal of 70%	[96]
Dam water	Alum	Turbidity removal of 98.5%, color removal of 98.5%	Watermelon seed	Turbidity removal of 89.3%, color removal of 93.9%	[97]

8. Recommendation and Future Prospective

All the mentioned disadvantages of implementing natural coagulants for water and wastewater create challenges for future research. The current extraction methods of coagulants from plants and animals are complex; thus, a new reliable and straightforward extraction method should be developed for the easily accessible use of natural coagulants. Some studies reported a higher removal efficiency of chemical coagulants than natural coagulants. However, optimizing the natural coagulant extraction methods can increase the performance of these green coagulants; thus, intensive research is needed in this domain. The utilization of sources for natural coagulant production is a great challenge, as the water and wastewater industries consume many of these coagulants. More research needs to search for new sources, such as inedible plants or/and new medicine plants for natural coagulant production. Further investigations are required to determine the optimum conditions for a green coagulation-flocculation process for various wastewater types. More studies should be conducted to investigate the efficiency of natural coagulants for micropollutants' removal from water and wastewater.

9. Conclusions

The removal of pharmaceuticals from water and wastewater is challenging due to their low concentration and their resistance to biodegradation. Several studies reported the feasibility of using natural-based coagulants for water and wastewater treatments. The main mechanisms that natural coagulants use for pharmaceutical removal from water and wastewater are charge neutralization and polymer bridging. Plant-based natural coagulants are more affordable than animal-based ones. Although the application of natural coagulants for emergency pollutants, especially pharmaceuticals, is limited in the literature, the available data demonstrate a promising future for these bio-coagulants in this domain. A natural coagulant has advantages over a chemical coagulant as a low dosage is required, less sludge is produced, and low/no toxicity is presented. For the complete transition from chemical coagulants to natural coagulants, further research is required in areas such as developing reliable extraction methods, searching for new natural sources, determining the optimal conditions for pharmaceutical removal, and evaluating the effect of environmental parameters on the process' performance.

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