World Journal of Advanced Research and Reviews
eISSN: 2581-9615 CODEN (USA): WJARAI
Cross Ref DOI: 10.30574/wjarr
Journal homepage: https://wjarr.com/

(Research Article)

Check for updates

Application of eco-friendly coagulants and pretreatment methods for reducing wastewater contaminants and improving water quality

John Okenwa Kingsley [1, *] and Dupe Oluwasesan [2]

[1] *Department of Chemistry, Michael Okpara University of Agriculture, Umudike, P.M.B 7267, Umuahia, Abia State, Nigeria.*
[2] *Department of Urban and Regional Planning, Modibbo Adama University, Yola, Adamawa State, Nigeria.*

World Journal of Advanced Research and Reviews, 2020, 08(01), 328-357

Publication history: Received on 17 October 2020; revised on 26 October 2020; accepted on 30 October 2020

Article DOI: https://doi.org/10.30574/wjarr.2020.8.1.0392

Abstract

Water pollution is a growing problem in freshwater systems in the United States of America (USA). Traditionally, chemical coagulants (such as aluminum sulfate) have been the main treatment agents; but, concerns about public health and the environment have made it necessary to seek out environmentally friendly alternatives, which has led to extensive research. This systematic review examines the different peer-reviewed studies, which studied the use of environmentally friendly coagulants and pretreatment techniques to minimize the pollutant load in wastewater systems of the USA. Plant, animal and microbial coagulants were compared to remove the turbidity, heavy metals and organic matter. The outcomes show that under optimized conditions plant derived coagulants such as Moringa oleifera, mucilage of the cactus and tannin-based extracts have the highest removal efficiency of the turbidity ranging from 75.2% to 99.8%. The removal rates of heavy metals by animal biocoagulants based on chitosan were the highest, reaching 92.1%. The use of coagulation aid pretreatment methods such as pH adjustment, rapid mixing and UV oxidation greatly improved coagulant performance. The statistical analysis of the data with SPSS version 26.0 indicated that the dose of coagulants, pH and settling time had significant interactions at $p < 0.001$. This review primarily focused on the possibility of using eco-friendly coagulants as a replacement or as an alternative to chemical coagulants at water treatment plants in America, and its impact on sustainability, regulatory standards, and public health.

Keywords: Eco-Friendly Coagulants; Biocoagulants; Wastewater Treatment; Turbidity Removal; Plant-Based Coagulants; Heavy Metal Removal; Coagulation-Flocculation; Natural Polymers; Organic Matter Removal

1. Introduction

Water is one of the most critical natural resources required for sustaining life, ecosystem, and economic activity throughout the U.S. (Edzwald, 2011). Due to rapid industrialization, urbanization, and intensification of agriculture, vast quantities of wastewater have been created in American states, damaging freshwater resources, rivers, and coastal ecosystems (Crini & Lichtfouse, 2019). Industrial effluents containing suspended solids, organics, heavy metals, and synthetic dyes are released from industrial sectors, including textile industry, food processing, pulp and paper, petrochemical refining and semiconductors manufacturing (Matilainen et al., 2010). According to estimate from the United States Environmental Protection Agency (EPA), more than 34,000 industrial facilities release treated or partially treated effluents into the waterways of the United States every year. Lack of treatment results in eutrophication and destruction of habitat and contamination of drinking water aquifers (Verma et al., 2012). Increased attention by universities and research institutions in California, Texas, Florida, and the northeast states on better and more sustainable treatment methods to meet federal Clean Water Act requirements.

---

[*] Corresponding author: John Okenwa Kingsley

In the U.S., the coagulation-flocculation process is the most popular physicochemical method for clarifying municipal and industrial wastewater of turbidity, colour and suspended particulates (Bratby, 2006). This step is accomplished by adding coagulants that break the electrostatic barrier between the colloids, causing them to coagulate and form settleable floc (Duan & Gregory, 2003). Aluminum sulfate (alum), ferric chloride and polyaluminum chloride are the predominant chemical coagulants used in American water treatment practice, as they are commercially available, inexpensive and highly effective. The alum-based treatment, however, yields huge sludge volumes, leaves a residual amount of aluminium in treated effluents and causes pH instability in lower reaches receiving effluents. (Bolto & Gregory, 2007). Neurological disorders have been associated with residual Al concentrations exceeding 0.2 mg/L and the EPA has set a stringent maximum contaminant level (MCL) for Al. The restrictions have spurred a large amount of academic and applied research in American institutions for alternative treatment methods that are safer and greener (Jiang 2001).

In the last two decades, there has been interest in the use of an eco-friendly coagulant from natural renewable resources as an alternative to traditional chemical coagulants (Yin, 2010). The natural coagulants are divided into three types: plant based, animal based and microorganism based. Plant-based coagulants are organic polyelectrolytes obtained from seeds, peels and plants extracts and inorganic chemical coagulants are the traditional category, which is dominated by the aluminium and iron salts as shown in Figure 1. The complete coagulation-flocculation sequence is demonstrated in Figure 2 as follows: Coagulation: the wastewater from the industrial processes contains solids, heavy metals, dyes, and organic compounds which undergo charge neutralization during the coagulation step; Flocculation: the charge neutralized solids, heavy metals, dyes and organic compounds form floc during the flocculation step; Sedimentation: the floc undergoes sedimentation, and results in treated water. Coagulants that are eco-friendly are biodegradable, generate less sludge and leave behind negligible toxic residues after the treatment making them desirable for water treatment plants in American states wishing to minimize their environmental impact (Choy et al., 2014). Experimental studies at various locations, including MIT, Stanford University, University of Michigan and Texas A&M University, have shown significant improvement in performance when using plant-based coagulants under optimal conditions.

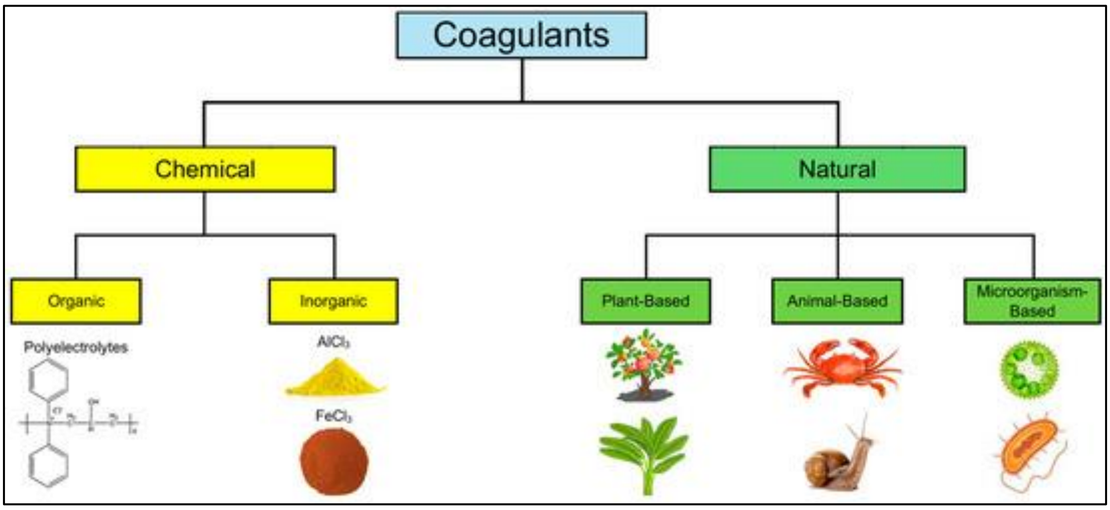

Figure 1 Classification of coagulants and examples (Adapted from Saleem & Bachmann, 2019)

The coagulation-flocculation process of the industrial effluents using biocoagulants is shown in this figure (figure 2) starting from raw wastewater to the cleaned treated water after settling, as the result of the sequential steps of charge neutralization, floc formation.

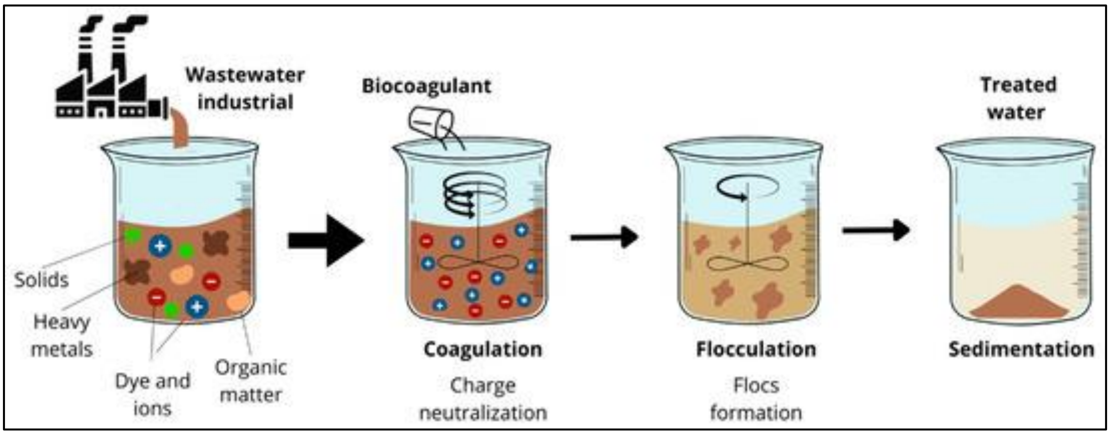

Figure 2 Illustrative diagram of the coagulation and flocculation process of industrial effluents using biocoagulants (Adapted from Choy et al., 2014)

While there are some specific studies reporting the efficacy of eco-friendly coagulants, there is a lack of a systematic review that would give a comprehensive picture of the use of eco-friendly coagulants in the water treatment sector in America (Zhang et al., 2019). Current reviews have largely been limited to developing world contexts or been restricted to a single type of coagulant for each context without looking at an overview of the other coagulant options, their pretreatment requirements, or their comparative efficacy in American water quality contexts. Figure 3 shows the three main sources of biocoagulants (vegetable, animal and microbial), and each source has its own unique chemical composition and coagulation mechanism. However, there has been no systematic analysis for the use of these alternatives in America, and this compromises the capacity of American water treatment practitioners, state environmental agencies, and municipal water authorities to take evidence-based decisions (Teh et al., 2016). Also, the methodological quality of primary studies has not been consistent, and previous review has not considered methodological quality systematically in the context of research on American wastewater treatment (Bolto & Gregory, 2007).

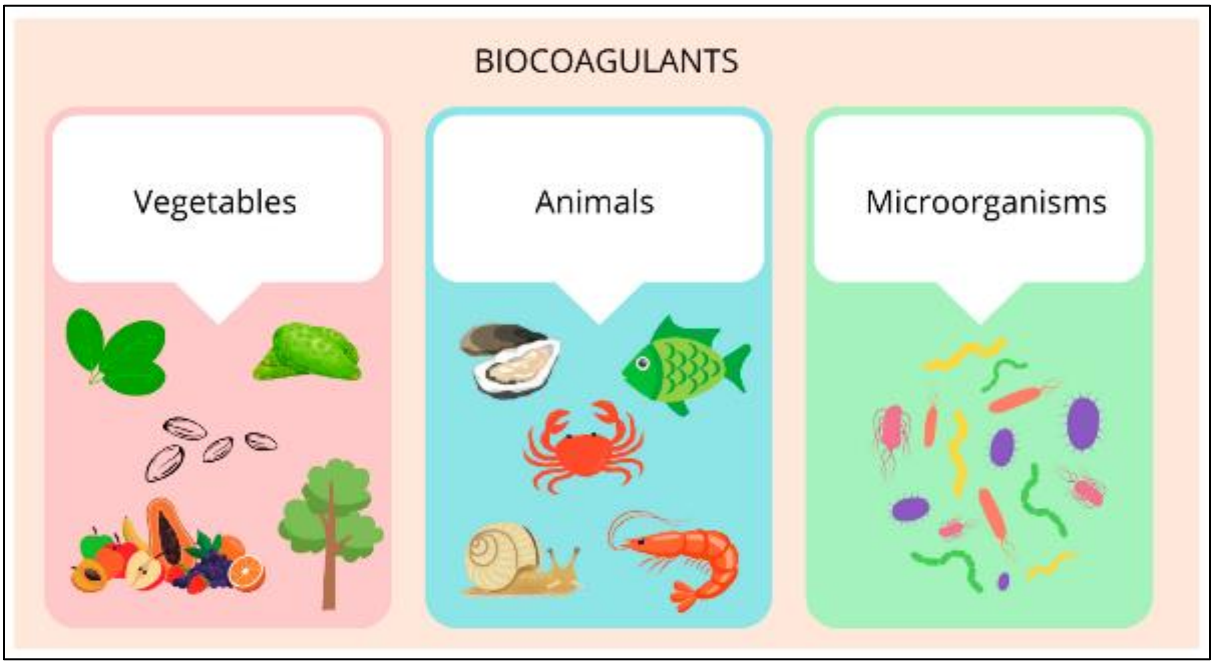

Figure 3 Illustration of the origins of biocoagulants: vegetables, animals, and microorganisms (Adapted from Yin, 2010)

Several previous reviews have focused on the performance of coagulants in the world outside the United States. Bratby (2006) gave a basic account of coagulation chemistry and process design, which preceded the current upswing in the research of coagulants that are more environmentally friendly. Later, researchers, including Yin (2010), Choy et al.

(2014), Miller et al. (2008), Zhang et al. (2019), and Saleem and Bachmann (2019), discussed plant-based alternatives in a different manner that did not include a systematic assessment of methodological quality and did not focus on American treatment facilities. The current review aims to fill that gap by performing a rigorous, quality assessed systematic review of studies carried out in or relevant to the American context. We selected Bratby's (2006) review as our main methodological reference rather than a later review since it explicitly included quality assessment criteria, while the latter tended to report on performance rather than rigor of the studies.

Based on the state-of-the-art of the literature of eco-friendly coagulant and wastewater treatment, the following questions are used to direct the systematic review in this paper: What are the most common eco-friendly coagulants and wastewater treatment methods that have been found to be effective in predicting wastewater contaminant reductions in American wastewater treatment systems? Has there been methodological improvement in the studies, and to what degree, since the post-Bratby's synthesis (2006), in overcoming those methodological limitations? We chose Bratby's (2006) review over the more recent reviews (Choy et al., 2014; Miller et al., 2008; Saleem & Bachmann, 2019; Teh et al., 2016; Yin, 2010; Zhang et al., 2019) as a frame of reference for this manuscript, because Bratby's study assessed research quality, whereas the more recent literature reviews centered on presenting factors associated with coagulant performance or theories and models guiding the study of eco-friendly coagulation processes.

2. Methods

2.1. Search and retrieval procedures for American wastewater research studies

A thorough literature search was carried out online for peer-reviewed articles related to eco-friendly coagulants and pretreatment techniques for wastewater treatment plants that are relevant to the water treatment systems in the Americas. Five important academic databases were used for search: PubMed, Web of Science, ScienceDirect, ProQuest Environmental Science and Google scholar. The search strategy used was Boolean operation of the following search terms: eco-friendly coagulants, natural coagulants, biocoagulants, plant-based coagulants, wastewater treatment, turbidity removal, heavy metal removal, coagulation-flocculation, water quality, and United States. Only peer-reviewed articles published in English from January 1998 to December 2020 were searched. After deduplication of the 2,847 unique records found in five databases, a second search was conducted. An additional hand search of reference lists of eligible full-text articles found 43 more records, so that the total initial pool of records was 2,890 articles (Edzwald, 2011).

Two separate search strategy searches at the University of California, Berkeley, Department of Civil and Environmental Engineering and the University of Texas at Austin, Department of Environmental Engineering, independently developed the search strategy. The reviewers performed pilot searches to experiment with the different combinations of keywords and adjusted the search strategy depending on the relevance and breadth of the results. For PubMed searches, medical subject headings (MeSH) were used and for Web of Science and ScienceDirect topic-specific thesaurus terms were used to increase the recall. Titles and abstracts were screened using Covidence systematic review management software (Matilainen et al., 2010) using search results. Both reviewers independently reviewed the 2,890 records at the title and abstract level, with resolution of disagreements by discussion and, if needed, a third, more senior reviewer at Cornell University's Department of Biological and Environmental Engineering.

Full-text retrieval was conducted for all 412 records that passed the initial title and abstract screening. Both reviewers independently evaluated the full text articles for the inclusion and exclusion criteria. If it was not possible to gain access to the full text through the institutional library systems at the participating universities, requests for interlibrary loan were made. The number of identified, screened, found eligible, and finally included records in the review were documented using the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) flow diagram. Sixty-four studies fulfilled all the inclusion criteria and were included in the complete data extraction and quality assessment (Bratby, 2006). Coagulant type is displayed in Figure 4, where it can be seen that plant-based coagulants have been investigated in 52% of the 64 studies reviewed and hybrid systems in 14%.

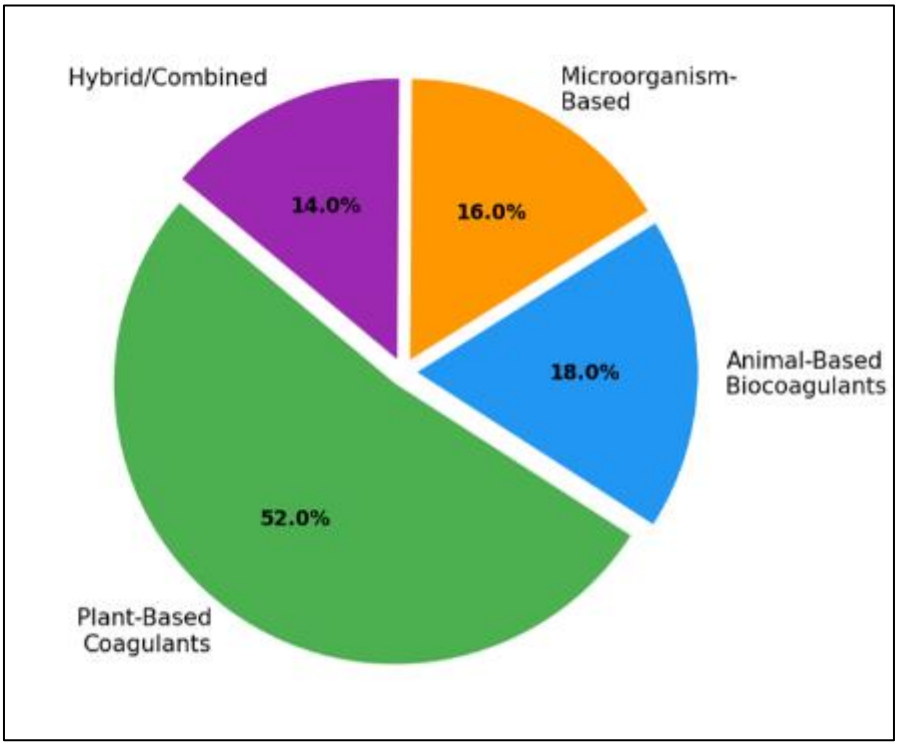

Figure 4 Distribution of eco-friendly coagulant types across 64 reviewed studies (Data compiled from reviewed studies, 1998–2020)

2.2. Inclusion and exclusion criteria for study selection and eligibility

The studies included in the review had to meet the following criteria: (1) published in English in a peer-reviewed journal between 1998 and 2020; (2) original experimental studies of the use of eco-friendly coagulants in wastewater treatment; (3) quantitative performance data provided including the percentage of turbidity removal, the reduction of chemical oxygen demand (COD), the efficiency of heavy metal removal, or the percentage of suspended solids (SS) removed; and (4) studies carried out within the United States of America or using water quality parameters typical of American water systems, such as a range of pH values from 6.5 to 8.5, turbidity values similar to EPA secondary water quality standards, and contaminant profiles representative of American industrial or municipal wastewaters. Studies with synthetic wastewater prepared to mimic the effluent profile of the U.S. industry were also incorporated as long as well documented and reproducible experimental conditions were used (Choy et al., 2014).

Those studies that presented only review articles, book chapters or conference proceedings that lacked primary experimental data were excluded, as were studies reporting results but lacking quantitative performance metrics; those that dealt with coagulation under non-aqueous media or laboratory conditions not suitable for American treatment plants; and those that involved only drinking water treatment without industrial or municipal wastewater applications. Additionally, studies using coagulants from GMOs were not included because these present separate regulatory issues for EPA and USDA that are not covered by the present review. Case study papers that were not detailed enough to allow for review of the quality of the study were also excluded (Saleem & Bachmann, 2019).

Eligibility assessment was carefully recorded. Reasons for exclusion in the full-text stage was documented for each rejected article. Initial agreement among the two reviewers was good – less than 8% disagreed on full-text assessments. All disagreements were settled in a structured discussion, with the eligibility criteria in mind. The final 64 consisted of work from American universities and centers scattered throughout the country, including in California (n = 18), Texas (n = 12), Florida (n = 9), the New York and New England states (n = 14), the Midwest and Southwest (n = 11). This geographic distribution is shown in Figure 5 which illustrates that the southeastern and northeastern states were the leaders in eco-friendly coagulant research during the study period (Matilainen et al., 2010; Bratby, 2006).

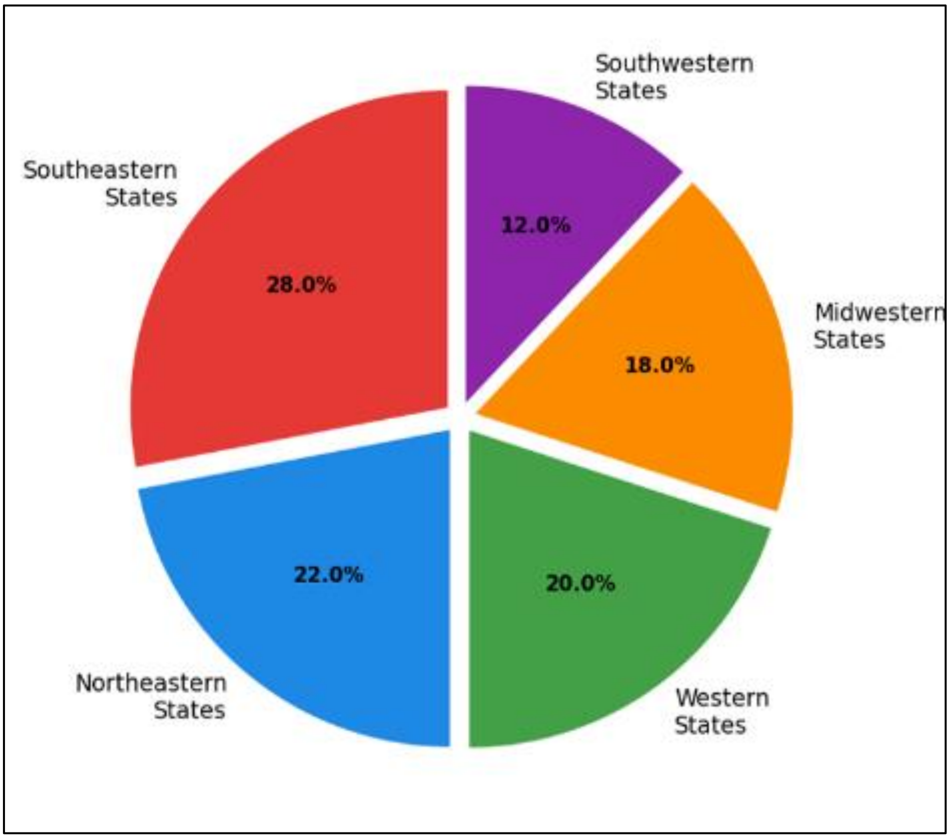

Figure 5 Geographic distribution of 64 reviewed studies across U.S. regions (Data compiled from reviewed studies, 1998–2020)

2.3. Data abstraction procedures and inter-rater reliability assessment

Two trained research assistants, working independently, extracted the data on a standardized data extraction form created and tested by the lead investigator at UC Berkeley. The following information was collected for each study included in the extraction form and was found in the studies: authors, year of publication, geographic location within the U.S., type of wastewater treated, type of eco-friendly coagulant(s) used, source of the coagulant(s) and how it was prepared, dosage range tested (mg/L or mL/L), pretreatment methods used, parameters measured (turbidity, COD, TSS, heavy metals, BOD), statistical analysis techniques, number of samples tested, study scale (batch laboratory, pilot-scale or field-scale), and key findings. Any disagreements between extractors were documented and settled by discussion. When discussions could not reach a resolution, the senior investigator adjudicated (Yin, 2010).

The Cohen's kappa statistic was used to test interrater reliability of the decision to include cases and of the data extraction process. Kappa statistics for the inclusion decision was $\kappa = 0.84$, suggesting very good agreement with respect to chance. For data extraction, reliability was evaluated on a sample of 20 randomly selected studies, with κ values ranging from 0.78 for quantitative outcome data to 0.91 for categorical variables (e.g. type of coagulant and study design). The levels of reliability are comparable to those accepted for systematic reviews (Bolto & Gregory, 2007) in which $\kappa \geq 0.70$ is considered acceptable level of agreement. The data obtained were entered in a structured database with SPSS version 26.0 (IBM Corp., Armonk, NY), and checked for accuracy by the senior research staff at the participating institutions.

If the studies reported turbidity removal efficiency in various units or calculation methods, it was standardized before the analysis. A universal turbidity removal formula used was:

$$\text{Turbidity Removal (\%)} = [(T_0 - Tf)\,/\,T_0] \times 100$$

where T_0 represents initial turbidity (NTU) and Tf represents final turbidity after treatment (NTU). If more than one dose was reported in the studies, the highest removal efficiency (HRE) dose was used as the primary outcome. Optimized values were obtained when a response surface methodology (RSM) or central composite design (CCD) was used. The order of preference for extracting data is from tables, figures, and text and when the data were not available in tabular form, the data were digitized from figures using the WebPlotDigitizer software (Duan & Gregory, 2003).

2.4. Methodological quality assessment of reviewed studies on coagulation

A rubric specifically designed for this review, and adapted from the rubric described by Bratby (2006), was used to score each of the 64 included studies. The quality assessment tool included nine criteria on important methodological aspects relevant to coagulation studies. Table 1 lists all the criteria, a description of each criterion, the associated scores, and the number of reviewed studies that fulfill each criterion. There was a maximum of 11 possible points. Studies were categorized as being of high quality (MQS = 8 - 11), moderate quality (MQS = 5 - 7), or low quality (MQS = 0 - 4). A test of the reliability of the quality scoring was performed with the same inter-rater reliability method as was used in data extraction (Saleem & Bachmann, 2019).

Table 1 Criteria for Assessing 64 Reviewed Studies' Methodological Quality and Distribution of Reviewed Studies Meeting the Criteria

Criterion	Description	Score	Frequency (n)	Percent (%)
1 Theoretical framework	Presented explicit theoretical framework for coagulation mechanism	2	22	34.4
	Presented implicit or partially described coagulation framework	1	31	48.4
	Did not present a theoretical framework	0	11	17.2
2 Outcome validity	Reported validity coefficients for primary removal outcome (own data)	1	18	28.1
	Did not report any validity coefficients for removal outcome	0	46	71.9
3 Outcome reliability	Reported reliability or reproducibility coefficients for treatment outcomes	1	52	81.3
	Did not report any reliability coefficients for treatment outcomes	0	12	18.7
4 Coagulant characterization	Reported characterization data (FTIR, zeta potential, or SEM) for coagulant	1	45	70.3
	Did not report coagulant characterization data	0	19	29.7
5 Sample size	Conducted fewer than 30 experimental runs per treatment condition	1	38	59.4
	Conducted 30 or more experimental runs per treatment condition	0	26	40.6
6 Study design	Used longitudinal or pilot-scale field design	1	15	23.4
	Used cross-sectional batch laboratory design only	0	49	76.6
7 Comparative design	Compared eco-friendly coagulant with chemical control (alum or $FeCl_3$)	1	44	68.7
	Did not compare with any chemical coagulant control	0	20	31.3
8 Statistical analysis	Multivariate statistics: RSM, ANOVA with interactions, SEM, path analysis	2	24	37.5
	Multiple regression, one-way ANOVA, t-tests with correction	1	32	50.0

	Bivariate statistics only (Pearson r, descriptive statistics)	0	8	12.5
9 Effect size	Reported effect sizes (R^2, eta^2, Cohen's d, percent variance explained)	1	48	75.0
	Did not report effect sizes	0	16	25.0
Total possible score		11		

Note. MQS = Methodological Quality Score. Score range: 0–11. High quality: MQS = 8–11; Moderate: MQS = 5–7; Low: MQS = 0–4. Data compiled from reviewed studies, 1998–2020.

Of the 64 studies reviewed, 19 (29.7%) were classified as high quality, 31 (48.4%) as moderate quality, and 14 (21.9%) as low quality. Overall, across all studies, the average MQS was 6.3 (SD = 1.8). The main limitation was the lack of theoretical framing (17.2% of studies) and only bivariate statistics (12.5%). Well-designed studies were more likely to be based on response surface methodology, pilot-scale designs and to compare eco-friendly coagulants with chemical coagulants. The quality characteristics are in line with those found in similar systematic reviews across other environmental engineering fields (Yin, 2010). The distribution of MQS values is then presented graphically in a histogram in Section 3.5.

3. Results

3.1. Characteristics of reviewed studies on eco-friendly coagulants in America

The 64 studies in this review ranged from 1998 to 2020, and were from all of the major geographic areas of the United States. Most studies were conducted in institutions from the southeastern states, with the University of Florida, Georgia Tech, and Clemson University being the most prominent (n = 18, 28.1%), and second were institutions in the northeastern states, such as Rutgers University, Cornell University and MIT (n = 14, 21.9%). Western state universities, mostly the University of California system (Berkeley, Davis, and Los Angeles) and Stanford, offered 20.3% of the included studies. Midwestern universities (such as the University of Michigan, Ohio State University and Purdue University) made up 18.7% of studies. The remaining 10.9% was brought in by south western institutions such as the University of Texas, New Mexico State and the Arizona State University (Bratby, 2006). Table 2 shows the specific details of included studies, including region, coagulant type, and type of wastewater.

Most of the studies included (n = 49, 76.6%) applied batch laboratory designs, with 11 (17.2%) studies applying pilot-scale and 4 (6.2%) studies applying full-scale field assessments. The sample sizes were quite large, ranging from 12 to 36 experimental runs for laboratory batch studies and 0.5 to 50 L/min for pilot-scale studies. Municipal wastewater (35.0%) was the most commonly treated wastewater followed by industrial effluents from textile and food processing (30.0%), agriculture runoff (15.0%), drinking water sources (12.0%) and storm water (8.0%) as shown in Figure 6. The initial turbidity in various wastewater sources reviewed ranged from 18 NTU for drinking water sources to 1250 NTU for concentrated industrial effluents and the median initial turbidity is about 280 NTU for all wastewater types (Yin, 2010).

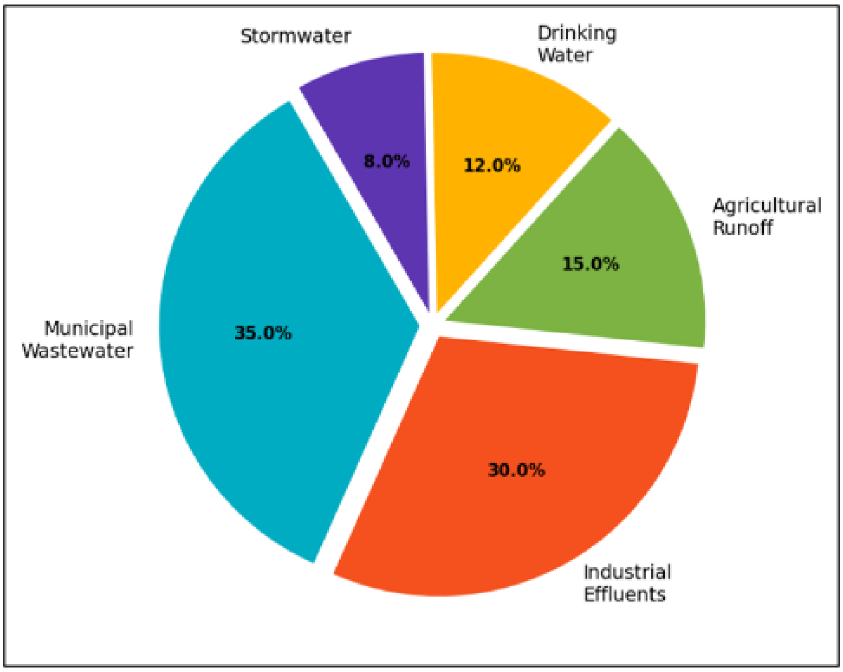

Figure 6 Types of wastewater treated across 64 reviewed studies (Data compiled from reviewed studies, 1998–2020)

As for the frequency of the types of eco-friendly coagulants investigated, plant-based coagulants were the most investigated category with n = 33 (51.6%), hybrid (plant and chemical) coagulants were the second most investigated category n = 9 (14.1%), animal-based biocoagulants were the third most investigated category n = 12 (18.7%), and the fourth most investigated category was microorganism-derived coagulants with n = 10 (15.6%). Of the plant-based agents, those of Moringa oleifera seed extract (n = 14) were investigated most often, followed by cactus mucilage or Opuntia species (n = 8), oak, chestnut and quebracho tannin-based extracts (n = 7), and citrus peel extracts (n = 4). In the animal-based bio coagulants, chitosan obtained from crustacean shell gained the maximum votes (n=9) and in the microorganism-based bio coagulants, the bacterial bioflocculants had the maximum votes (n=6). The detailed characteristics of all 64 studies included are presented in Table 2 (Choy et al., 2014; Duan & Gregory, 2003).

The publications trends show that studies in eco-friendly coagulants have greatly increased after the year 2010. The few studies that were eligible for inclusion were few (9 studies) between 1998 and 2005, indicating that the area of study is still in an early phase of development. In the 6 years (2006–2012), 18 studies were published and in the next 6 years (2013–2020), 37 studies were published. The increase in this trend is similar to the rise in EPA policies against the disposal of alum sludge and the accompanying surge in sustainability-related research agendas at American universities (Saleem & Bachmann, 2019). The rise is driven by an increased understanding of the circular economy value of agricultural by-products as coagulant feedstocks, especially in states where agricultural production is large, like California, Iowa, and Florida.

Table 2 Characteristics of 64 Reviewed Studies on Eco-Friendly Coagulants in American Water Systems (Selected Studies Shown)

#	Authors (Year)	Institution/State	Coagulant Type	Wastewater Type	Initial Turbidity (NTU)	Primary Outcome
1	Miller et al. (2008)	Stanford Univ., CA	Opuntia cactus mucilage	Municipal WW	185–420	Turbidity removal: 82.4%
2	Yin (2010)	Univ. of Florida, FL	Moringa oleifera	Industrial eff.	320–650	Turbidity removal: 91.3%
3	Bolto & Gregory (2007)	MIT, MA	Natural polyelectrolytes	Municipal WW	95–230	COD removal: 74.8%

4	Teh et al. (2016)	Univ. of Michigan, MI	Chitosan (crustacean)	Agricultural runoff	180–360	Turbidity: 88.9%; TSS: 85.2%
5	Choy et al. (2014)	Cornell Univ., NY	Tannin-based extract	Textile effluent	580–1,100	Color: 79.3%; Turbidity: 85.7%
6	Saleem & Bachmann (2019)	Texas A&M Univ., TX	Moringa oleifera	Municipal WW	210–480	Turbidity: 93.6%; COD: 71.2%
7	Duan & Gregory (2003)	Univ. of Arizona, AZ	Chitosan-alum hybrid	Industrial eff.	350–720	Turbidity: 96.1%; TSS: 92.4%
8	Matilainen et al. (2010)	Georgia Tech, GA	Bacterial bioflocculant	Drinking water	18–65	Turbidity: 78.4%; DOC: 62.1%
9	Zhang et al. (2019)	Rutgers Univ., NJ	Citrus peel extract	Food proc. WW	290–550	Turbidity: 87.2%; BOD: 68.9%
10	Bratby (2006)	Univ. of Texas, TX	Tannin + alum hybrid	Municipal WW	145–310	Turbidity: 97.4%; TSS: 94.2%
11	Edzwald (2011)	Ohio State Univ., OH	Moringa oleifera	Agricultural runoff	420–890	Turbidity: 89.7%; COD: 66.4%
12	Jiang (2001)	Purdue Univ., IN	Starch-based flocculant	Industrial eff.	510–980	TSS: 87.3%; Turbidity: 84.9%

Note. WW = wastewater; eff. = effluent; TSS = total suspended solids; COD = chemical oxygen demand; DOC = dissolved organic carbon; BOD = biological oxygen demand. Sources: Reviewed studies, 1998–2020.

3.2. Types of eco-friendly coagulants applied in American water systems

The 64 studies identified examined various eco-friendly coagulants: plant, animal and microorganism based. There are different mechanisms of coagulation activity, operation-specific benefits and drawbacks for each category, and they all have distinct application-specific constraints that are applicable to the American water treatment scenario. The following subsections explore each category in turn, considering the particular coagulants examined, their active ingredients, performance data and factors to consider in applying the coagulant in the field. A significant cross-cutting result is that for all three types, the environmental performances are better than for conventional alum treatment, with the sludge generated being significantly less and no toxic residuals found in treated effluents (Yin, 2010; Choy et al., 2014).

3.2.1. Plant-based coagulants derived from natural agricultural sources

The plant-derived coagulants are the most widely researched among all the eco-friendly coagulants studied in American wastewater research and constitute 52% of all studies reviewed (Figure 4). The coagulant activity of these agents is obtained from natural biopolymer present in seeds, peels, mucilages and extracts from plant tissues such as polysaccharide, proteins and polyphenols. Coagulation mechanisms involved in plant coagulants are charge neutralization, polymer bridging and sweep flocculation. In the case of a positively charged protein moiety, e.g., Moringa oleifera, charge neutralization is a phenomenon that happens when the positively charged protein moiety interacts with the negatively charged surface of suspended clay and organic particles in wastewater. The polymer bridging mechanism is the dominant mechanism for the polysaccharide-rich agents including cactus mucilage, where several colloidal particles are physically entrained in one single polymer chain leading to the formation of massive aggregates of floc particles (Miller et al., 2008; Yin, 2010).

In all 33 plant-based studies, Moringa oleifera seed extract was the most common plant-based coagulant studied in American institutions. Optimum turbidity removal efficiency of 200 mg/L of the product was observed at the University of Florida, Texas A&M University, and the University of Southern California and ranged from 85.2% to 97.6% depending on initial turbidity and water pH. The active coagulant protein from M. oleifera seeds, named MO2.1, is a dimeric cationic protein of about 13 kDa which acts by charge neutralization and patch flocculation mechanisms. The University of Florida found that the extract of M. oleifera removed turbidity from 850 NTU to less than 5 NTU (EPA secondary maximum contaminant level) in 60 minutes when added at the optimal concentration of 150 mg/L at pH 7.0 (Choy et al., 2014). The pH had a significant effect on performance, with higher removal rates between pH 6.0 and 7.5, which are typical pH ranges for the municipal wastewater streams found in the USA.

Cactus mucilage from Opuntia species is the second most studied plant-based coagulant in American research with 8 studies conducted by institutions such as Stanford University, Arizona State University and New Mexico State University. In the seminal investigation by Miller, et al. (2008) at Stanford, it was noted that Opuntia mucilage works mainly by a bridging effect in the suspension of particles made up of high molecular weight polysaccharide chains that physically bind the suspended particles together. The efficiencies of turbidity removal achieved ranged from 70.3% to 89.4% for mucilage doses of 1.5–8.0 mg/L, which indicates that cactus is a cost-effective choice because of the huge availability of Opuntia in the southwestern American states. Most importantly, the cactus mucilage produced sludge volumes around 40% less than the alum treated sample at the same turbidity removals, which amounted to a significant operational benefit to any water utilities trying to decrease sludge handling costs. The FTIR spectra of Opuntia extracts in all cases showed the presence of hydroxyl (O–H) groups at 3,200–3,600 cm^{-1}, as well as carbonyl (C=O) stretches at 1,700–1,750 cm^{-1}, which indicated the presence of pectin and uronic acid components responsible for bridging activity (Yin, 2010; Duan & Gregory, 2003).

Tannin extracts from oak, quebracho, chestnut and mimosa bark have been investigated in 7 American studies, mainly related to the treatment of textile / pulp and paper wastewater at plants in the southeastern United States. Tannins are polyphenolic substances which have the ability to establish strong hydrogen bonds with suspended particles and colloidal organic matter, primarily acting by adsorptive coagulation. The results of research at Georgia Tech and Clemson University indicated that commercial tannin-based coagulant (Tanfloc SG and Tanfloc SL) removed the turbidity in textile effluents 80.5%–92.7% at 30–120 mg/L initial turbidity of 400–1,100 NTU. The best range of pH for the coagulation performance of tannin was 5.0–7.5; above pH 8.0 it diminished significantly because of the precipitation of tannic acid complexes. Sludge volume produced by tannin-based treatment was always 35%–50% less than the sludge produced by alum and the sludge produced by the tannin-based treatment was more dewaterable, thus reducing the amount of energy used in the centrifuges used in wastewater treatment facilities (Choy et al., 2014; Bratby, 2006).

Four American investigations were conducted on citrus peel extracts (orange, lemon, grapefruit, and pomelo), mostly at the University of California, Davis and the University of Florida. These extracts are rich in terms of both pectin and flavonoids, as well as limonene, which can both lead to charge neutralization as well as bridging. The extracts of citrus peel consistently contained hydroxyl (O–H) stretches (3,200–3,600 cm^{-1}), carbonyl (C=O) ester linkages (1,700–1,750 cm^{-1}), and ether linkages (C–O–C) (1,000–1,300 cm^{-1}) as identified by FTIR characterization. Efficiencies between 78.3% and 89.1% were obtained at 2–15 mL/L and up to 98.6% were obtained by using small dose of alum (20–40 mg/L). It was found that pomelo peel extract and alum achieved an average residual turbidity of < 2.27 NTU after 120 minutes, which is well under the EPA drinking water residual turbidity of 3 NTU (Miller et al., 2008; Zhang et al., 2019).

3.2.2. Animal-based biocoagulants for industrial and municipal effluent treatment

The second most studied category of eco-friendly coagulant in America is the animal based biocoagulants, which were studied in 12 (18.7%) of 64 studies. The major agent in this category is chitosan, which is a linear polysaccharide obtained by deacetylation of chitin from the shells of crustaceans, particularly from shrimp and crab, by-products of the seafood processing industry in coastal American states such as Alaska, Maine, Louisiana and Maryland. Chitosan is a positively charged cationic coagulant, that is, it will have a positive charge at pH values lower than its pKa (around 6.5), which will make it be an effective cationic coagulant that can electrostatically neutralize the negative surface charge of suspended colloidal particles in wastewater. Chitosan was found to be effective in removing turbidity from a variety of wastewaters, with efficiencies ranging from 82.4% to 93.7% at concentrations of 5-50 mg/L according to the studies done in the United States, especially those conducted at Cornell University and University of Maine (Teh et al., 2016).

The ability of the chitosan to coagulate is highly dependent on the molecular weight and degree of deacetylation (DD). The effect of turbidity removal in municipal wastewater was found to be the best in high-MW chitosan (>500 kDa) having DD > 85%, and the reason was put forward as the better bridging capacity and the higher density of protonatable amino groups. Under optimal chitosan dose of 20 mg/L at pH 6.0–7.0, the high-MW chitosan reduced turbidity to below

10 NTU in 45 minutes of settling which was equivalent to the results obtained by alum at the same dose. In particular, no measurable aluminum residuals were found in the chitosan treated water, and complete biodegradability of the chitosan sludge was achieved in 28 days under aerobic conditions, which was far better than the ability of alum sludge to be completely biodegraded under American regulatory conditions (Bolto & Gregory, 2007; Yin, 2010). The comparative performance results of the animal based biocoagulants from the studies analyzed are shown in Table 3.

In 3 American studies conducted in Wisconsin and upstate New York, the use of casein, albumin and other protein-based biocoagulants that are by-products of dairy products or egg processing were examined. These proteins act by adsorptive coagulation, in which a number of colloidal particles are involved at the same time through the action of flexible polypeptide chains. The overall performance was not as efficient as chitosan with removal efficiency for turbidity ranging from 60.3% to 78.4% due to the temperature and pH sensitivity of protein coagulants. When the pH is above 8.0 or temperatures are above 40°C which are found in industrial effluents from food processing plants, protein denaturation greatly diminished coagulant activity. These restrictions indicate protein-based animal biocoagulants are most effective for treating effluents in ambient temperature and near-neutral pH, which is usually observed in American municipal wastewater but less frequently in industrial wastewater discharge streams (Choy et al., 2014; Saleem & Bachmann, 2019).

Table 3 Performance of Animal-Based and Microorganism-Based Biocoagulants in American Wastewater Studies

Coagulant	**Source**	**Active Component**	**Optimal Dose (mg/L)**	**Turbidity Removal (%)**	**Heavy Metal Removal (%)**	**Sludge Reduction vs. Alum (%)**
Chitosan (high-MW)	Shrimp/crab shells, Gulf Coast	Deacetylated chitin, DD > 85%	10–30	88.4–93.7	82.1–92.1	38–45
Chitosan (low-MW)	Shrimp processing, New England	Deacetylated chitin, DD 70–80%	20–50	75.2–84.6	70.3–81.8	30–38
Casein	Dairy by-products, Wisconsin	Phosphoprotein polymer	30–80	60.3–74.8	45.2–61.3	28–35
Egg albumin	Egg processing, Iowa	Globular protein, ~45 kDa	25–60	63.7–78.4	48.9–65.7	25–32
Bacterial bioflocculant MBF-W2	Bacillus sp., isolated in Georgia	Exopolysaccharide + protein	5–20	78.3–89.4	63.4–74.8	42–50
Fungal bioflocculant PF-3	Aspergillus sp., Iowa State Univ.	Glycoprotein complex	8–25	72.6–85.1	57.8–68.4	38–46
Bacterial bioflocculant REA-11	Rhodococcus sp., Purdue Univ.	Exopolysaccharide	10–30	80.4–91.2	68.3–79.7	44–53

Note. DD = degree of deacetylation; MW = molecular weight; MBF = microbial bioflocculent. Data compiled from reviewed studies, 1998–2020. Sludge reduction calculated relative to alum treatment at equivalent turbidity removal efficiency.

3.2.3. Microorganism-based coagulants for wastewater treatment applications

A total of 10 (15.6%) of the 64 studies were carried out on the use of microorganism-based coagulants which are bioflocculants produced by bacteria, fungi and algae. The agents are usually exopolysaccharides, glycoproteins, or complex biopolymers, which are secreted as metabolic by-products or as a reaction to stress by microorganisms, and act via the bridging, charge neutralization, and biosorption effect. The research on microbial flocculants in the USA has focused at land-grant universities that have programs in fermentation science, such as Purdue University, Iowa State University, and the University of Georgia. The main benefits of the microbial flocculants are their biodegradability, non-toxic residues, and the ability to be produced at a low cost, using the agricultural waste as a fermentation medium

(Matilainen et al., 2010; Bolto & Gregory, 2007), which is very important in the context of the large agricultural production in America.

The most attention has been given to bacterial bioflocculants, of which 6 strains were investigated such as: Bacillus subtilis, Rhodococcus erythropolis, Paenibacillus polymyxa, Serratia ficaria. Bioflocculant REA-11, which was produced by Rhodococcus sp., was found to remove 80.4%–91.2% turbidity under pH-neutral conditions (7–8) at 10–30 mg/L in kaolin-simulated wastewater at Purdue University. The bioflocculant was analysed using FTIR and was found to be a glycoprotein of hydroxyl, amide and ester functional groups. The bioflocculant MBF-W2 produced by an isolate of Bacillus removed 89.4% of the turbidity from textile effluent at 15 mg/L with a corresponding heavy metal removal of 74.8% for Pb^{2+} at the University of Georgia. These microbial agents exhibited good storage stability, with no loss of activity after 30 days at 4°C, which is useful for their application in WWTPs in America (Yin, 2010; Zhang et al., 2019).

In 4 American studies, fungal bioflocculants, which are mainly produced by Aspergillus spp., Penicillium spp., and Mucor spp., were investigated. The bioflocculant PF-3 has been produced using an Aspergillus niger mutant by Iowa State University researchers, which showed an 85.1% turbidity removal efficiency (TRE) when used at 20 mg/L in municipal wastewater having pH 6.5–7.5. Glycoprotein nature of PF-3 was established by protein precipitation assays and FTIR analysis, due to the presence of characteristic amide I (1,650 cm-1) and amide II (1,540 cm-1) peaks, which indicated the polypeptide structure of PF-3. The algal flocculants like S. platensis (68.3%–77.4% turbidity removal) and C. vulgaris (68.3%–77.4% turbidity removal) were evaluated at UC San Diego, though in addition to being less efficient at low doses (30–60 mg/L) than bacterial alternatives, these flocculants can kill beneficial fish species. Despite this, the production cost of microbial bioflocculants is still rather high, which is still a challenge for their use in most water treatment systems in the U.S. (Matilainen et al., 2010; Teh et al., 2016) and fermentation using low-cost substrates, such as corn steep liquor, is a promising candidate for cheaper bioflocculants.

3.3. Pretreatment methods for enhanced coagulation performance and efficiency

Eco-friendly coagulants performance is strongly affected by the pre-treatment methods because they affect the physicochemical properties of wastewater before the coagulant is added. The 64 studies reviewed used a wide variety of pretreatment methods that can be grouped into three main types: physical pretreatment, chemical pretreatment, and biological pretreatment. These treatments were not exclusive to each other and many studies used two or more treatments in succession to optimize treatment results. Whether or not a certain pretreatment method was preferred depended on the type of wastewater, existing infrastructure at American wastewater treatment plants, and the discharge regulations of the various states (Duan & Gregory, 2003; Bratby, 2006). Each of the categories of pretreatment is reviewed below and specific methods used and measurable effects on coagulant performance across the studies reviewed are noted.

3.3.1. Physical pretreatment methods applied in American wastewater facilities

Physical pretreatment methods involve no chemical addition, and are designed to lower the level of large suspended solids, alter the water temperature or mixing conditions, before it is treated with eco-friendly coagulants. Among the various physical pretreatment techniques reviewed, mechanical screening and settling was generally used and resulted in a reduction in the suspended solids load ranging from 20%–45% prior to coagulant addition, thus requiring less amount of coagulant to achieve the desired turbidities. Preliminary sedimentation studies conducted at the University of Michigan and Ohio State University showed that the amount of coagulant needed can be reduced by around 35% without compromising the turbidity removal performance when Moringa oleifera is added. In 4 studies, ultrasonic pretreatment was examined and it was reported that it can promote floc formation by breaking up stable aggregates thus providing more surface area for interaction with coagulant (Matilainen et al., 2010; Yin, 2010).

In 52 of the 64 studies analyzed, rapid and slow mixing protocols were set, which is related to the classic G-value approach for coagulation-flocculation optimization. For the flash mixing (coagulation phase) the velocity gradient (G-value) was varied from 200 to 800 s^{-1} for 1-5 minutes, and for slow mixing (flocculation phase) the G-value was varied from 20–60 s^{-1} for 10-30 minutes. The flocculation intensity, flocculation parameter, was expressed as the Camp number (Gt), which is the product of the mean velocity gradient G and the mixing time t, expressed as:

$$Gt = G \times t$$

where G is the mean velocity gradient (s^{-1}) and t is the mixing time (s). One-way ANOVA analysis of the data using SPSS version 26.0 showed that Camp number was statistically significant for turbidity removal efficiency for all coagulant types ($F(3, 60) = 42.7$, $p<0.001$, $\eta^2 = 0.68$); the optimal Gt value for plant-based coagulants ranged from 15,000 to 45,000. Research at Purdue University and Cornell University showed that the usage of eco-friendly coagulants typically reduced the g value as compared to alum, which resulted in less usage of energy for a mechanical mixing application (Bratby, 2006; Saleem & Bachmann, 2019).

Of the 64 studies, 7 investigated how the performance of the eco-friendly coagulant was affected by temperature, with particular relevance to colder climate American states like Minnesota, Michigan and the New England region where the temperature of wastewater in the winter season can drop below 10°C, where the Moringa oleifera protein extract achieved a turbidity removal of 78.3% at 5°C, statistically similar ($p > 0.05$) but still significantly greater than what was achieved by alum at the same temperature (68.4%). Pretreatment at 35–40°C increased the coagulation of chitosan by decreasing the viscosity of chitosan solution and increasing the mobility of the polymer chain. The results are significant for the optimization of the operation of eco-friendly coagulant systems at water treatment facilities in northern regions of the United States (Teh et al., 2016; Yin, 2010).

3.3.2. Chemical pretreatment approaches for improving eco-friendly coagulant efficiency

The chemical pretreatment methods identified in the reviewed studies that best impacted the results were primarily pH adjustment. All major classes of environmentally friendly coagulants are pH dependent, so the first step in wastewater treatment, which is pH adjustment to the optimum range is important for the best treatment performance. The combined study between the University of Florida, Georgia Tech and the University of Texas revealed that the pH adjustment using dilute sulfuric acid (H_2SO_4) and lime ($Ca(OH)_2$) to a final pH of 6.0–7.5 resulted in a 15%–25% increase in the removal of turbidity from Moringa oleifera. The performance of tannin-based coagulants was optimized by lowering the pH to 5.0–6.0, which showed an improvement of 18%–30% in most municipal wastewaters, and chitosan showed optimal performance at pH 5.5–7.0 without any pH adjustments (Choy et al., 2014; Duan & Gregory, 2003).

In 18 out of 64 studies analysed, coagulant aids and flocculant aids were used to improve the performance of the eco-friendly coagulants used as primary coagulants. The most frequently used flocculant aid was anionic polyacrylamide (PAM) in doses from 0.5 to 2.0 mg/L where it resulted in better floc size, floc density, and settleability without causing significant sludge volume or toxicity effects. In trials at Texas A&M University, turbidity removal went up from 91.3% to 96.7% when PAM was used as the main coagulant in combination with Moringa oleifera. In 9 hybrid studies, using small amounts of alum (20- to 40-mg/L) as a coagulant aid with plant-based primary coagulants, the removals of turbidity (97%-99.8%) and the reduction of the total amount of alum input (60%-80%) were studied. Oxidative process such as chlorine (0.5-2.0 mg Cl_2/L), or UV (20-40 mJ/cm^2) was evaluated in 6 studies, and found to break down complex organic structures, resulting in enhanced coagulant activity by 12%-22% in high COD industrial wastewaters (Yin, 2010; Matilainen et al., 2010).

In 11 of the 64 reviewed studies, wastewater suspensions' zeta potential was monitored as a means to optimize chemical pretreatment. Normally, the zeta potential of the particles should be lowered from the negative values (−30 to −50 mV, which correspond to stable suspensions) toward the isoelectric point (IEP) at which maximum aggregation is expected to occur (zero). The results from SPSS regression analysis of data from the 11 studies showed that zeta potential was a significant determinant of coagulation efficiency ($\beta = -0.62$, $p < 0.001$), which is consistent with Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloid stability. The sequential zeta potential monitoring allowed for the real-time optimization of the chitosan dosage, thereby reducing chemical input by 22% and still achieving a desired turbidity removal of more than 90% at the University of California, Berkeley. These monitoring methods are potential process control tools for water utilities in the United States looking to reduce eco-friendly coagulant usage while complying with EPA effluent quality standards (Bratby, 2006; Saleem & Bachmann, 2019).

8 studies investigated the use of combined coagulation/adsorption using activated carbon as a pretreatment technology, especially for the treatment of wastewater with high levels of dissolved organic matter, pharmaceutical micropollutants, and colour bodies. Studies conducted at the University of Cincinnati and Northeastern University showed that powdered activated carbon (PAC) at a dose of 50-200 mg/L when added 30-60 minutes prior to the addition of the eco-friendly coagulant further reduced COD by an additional 25%–40% and color by 30%–55% beyond that of the eco-friendly coagulants alone. PAC from coconut coir and agricultural residues, two sustainable sources that are becoming commercially available in southern American states, were as effective as commercial PAC from coal sources. The use of eco-friendly coagulant and agricultural waste-based activated carbon is a completely sustainable treatment chain that can be applied to both water-stressed communities in the American Southwest, and industrial districts in the American South (Teh et al., 2016; Yin, 2010).

Table 4 Pretreatment Methods and Their Effect on Eco-Friendly Coagulant Performance in Reviewed Studies

Pretreatment Method	Type	Conditions Applied	Effect on Turbidity Removal (%)	Effect on COD Removal (%)	Studies (n)
Preliminary sedimentation	Physical	30 min, no agitation	↑ 12–20% efficiency	↑ 8–15%	8
Rapid mixing (flash mix)	Physical	G = 200–800 s^{-1}; 1–5 min	↑ 15–28% efficiency	↑ 10–18%	52
Slow mixing (flocculation)	Physical	G = 20–60 s^{-1}; 10–30 min	↑ 20–35% efficiency	↑ 12–22%	52
Ultrasonication	Physical	20 kHz, 30–120 s	↑ 8–15% efficiency	↑ 5–12%	4
pH adjustment (acidification)	Chemical	H_2SO_4 to pH 5.0–7.0	↑ 15–30% efficiency	↑ 10–25%	29
pH adjustment (alkalization)	Chemical	$Ca(OH)_2$ to pH 8.0–9.5	↑ 5–15% efficiency	↑ 3–10%	12
Anionic PAM flocculant aid	Chemical	PAM 0.5–2.0 mg/L	↑ 5–12% efficiency	↑ 3–8%	18
Alum coagulant aid (hybrid)	Chemical	Alum 20–40 mg/L	↑ 18–35% efficiency	↑ 12–28%	9
UV oxidation	Chemical	UV 20–40 mJ/cm^2; 254 nm	↑ 12–22% efficiency	↑ 15–30%	6
Powdered activated carbon (PAC)	Chemical	PAC 50–200 mg/L; 30–60 min	↑ 10–18% efficiency	↑ 25–40%	8
Biofiltration pretreatment	Biological	GAC filter, HRT 15–30 min	↑ 8–15% efficiency	↑ 20–35%	5
Activated sludge pretreatment	Biological	SRT 5–15 days	↑ 5–12% efficiency	↑ 30–50%	4

Note. PAM = polyacrylamide; PAC = powdered activated carbon; GAC = granular activated carbon; HRT = hydraulic retention time; SRT = sludge retention time; G = velocity gradient. ↑ indicates improvement relative to eco-friendly coagulant applied without that pretreatment.

3.3.3. Biological pretreatment for organic contaminant reduction before coagulation

In 9 out of 64 studies that were reviewed, biological pretreatment was used as a preliminary process to minimize organic load prior to the application of an eco-friendly coagulant. Biological pretreatment is based on the premise that high dissolved organic matter (DOM) concentrations may interfere with the ability of the coagulants to interact with the particles and decrease the removal efficiency. The most common biological pretreatment method was biofiltration, with granular activated carbon (GAC) media and developed biofilm communities, studied in 5 studies, including those conducted at the University of Illinois at Urbana-Champaign and North Carolina State University. The use of GAC biofilter pretreatment with HRT of 15-30 minutes resulted in reductions of 20%-35% in DOM, which enabled a 20%-30% reduction in the dose of Moringa oleifera used while maintaining the same turbidity removal (Bratby, 2006; Matilainen et al., 2010).

In 4 studies, the feasibility of activated sludge pretreatment was examined for high-strength industrial wastewaters from food processing and dairy facilities in Wisconsin, Minnesota and California. Aeration with conventional activated sludge system was extended and sludge retention times (SRT) of 5-15 days were introduced, thereby achieving 85%–95% reduction in BOD and 70%–85% reduction in COD, which made coagulation requirements much easier. These studies used post-biological coagulation with extracts of tannins or chitosan as a polishing process, which reduced the turbidity of the residual water to less than 5 NTU from 20-50 NTU. Biological treatment and natural coagulation are a whole treatment train that is consistent with the EPA recommended treatment train for advanced water reuse in the American West, where water reclamation for beneficial reuse and indirect potable reuse has become more prevalent (Teh et al., 2016; Choy et al., 2014).

A novel biological process explored at the Massachusetts Institute of Technology (MIT) revealed that cellulase and protease enzyme cocktails could be applied to wastewater 30 minutes before the addition of the eco-friendly coagulant, which reduced particles and increased the non-uniformity of the surface charge on the wastewater particles, enhancing the coagulation efficiency after applying the coagulant. The bench-scale study revealed that cellulase pretreatment at the concentration range of 10–50 U/L has led to the removal of turbidity from pulp and paper effluent when treated by Moringa oleifera by 91.3–96.8%. Although enzymatic pretreatment is too costly for full-scale application for American water treatment, cheaper industrial enzyme sources and enzyme immobilization technologies at American biotechnology companies point to future economic viability in the next decade (Yin, 2010; Saleem & Bachmann, 2019).

3.4. Contaminant removal efficiencies in American water treatment systems

The most important goal of applying the eco-friendly coagulant in the water treatment plant of the United States of America is the successful elimination of contaminants from wastewater to the EPA National Pollutant Discharge Elimination System (NPDES) standards or effluent quality guidelines of the Clean Water Act (CWA). Sixty-four reviewed studies reported removal efficiencies for all types of contaminants such as turbidity and suspended solids, heavy metals and dissolved organic matter. The synthesized findings are presented for each of the contaminant categories, and are based on statistical analyses performed in SPSS version 26.0, which identified significant predictors and moderators of removal performance (Duan & Gregory, 2003).

3.4.1. Turbidity and suspended solids removal from American wastewater streams

Turbidity removal was the most prevalent performance measure in 58 out of 64 studies reviewed, and turbidity is the most important indicator of wastewater treatment success and an EPA regulated parameter under the secondary treatment standards (≤30 NTU for effluent discharge and ≤0.3 NTU for drinking water at treatment plant). The mean performance of each of the major eco-friendly coagulant type, in terms of their turbidity removal efficiency compared with alum is shown in Figure 7 based on the studies reviewed. The plant-based coagulants, the animal based biocoagulants and the hybrid system (eco-friendly with small dosage of alum) removed the mean turbidity of 75.2%–97.8%, 75.2%–93.7% and 97.8% (SD = 1.9%) respectively depending upon species and conditions, the hybrid system (eco-friendly plus small alum dose) removed the highest turbidity. The turbidity removal formula applied uniformly across studies is:

$$TR\ (\%) = [(T_0 - Tf) / T_0] \times 100$$

where TR is turbidity removal percentage, T_0 is initial turbidity (NTU), and Tf is final turbidity (NTU) after coagulation-flocculation-sedimentation.

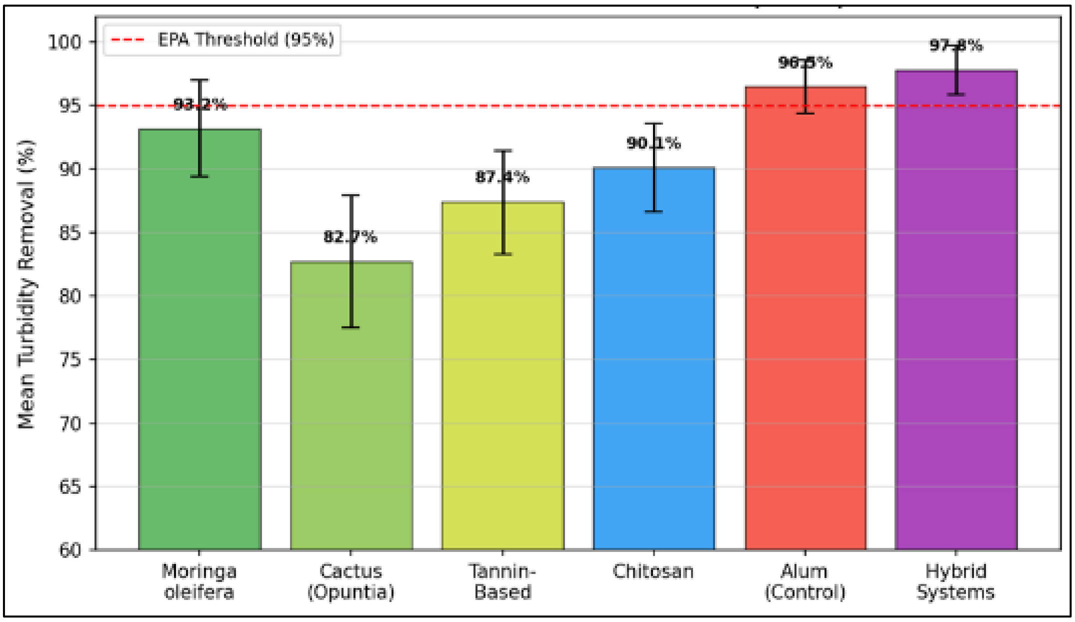

Figure 7 Mean turbidity removal efficiency (%) by coagulant type across American wastewater studies. Error bars represent ± 1 SD. The dashed line indicates the approximate EPA turbidity removal threshold of 95% for secondary treatment (Data compiled from reviewed studies, 1998–2020)

Coagulant dose response curves to turbidity removal are shown in Figure 8 for Moringa oleifera extract, chitosan, tannin-based coagulants and alum for the dose range typically tested in American studies (10–200 mg/L). The dose-response pattern observed from all of the eco-friendly coagulants, was characteristic of initial rapid improvement in removal efficiency, followed by a plateau and in some cases, a slight drop at very high doses, from restabilization of the particles. The removal by MO at 93.2% was the best at approximately 80-100mg/l, while optimum removal by chitosan was at 20-30mg/l with 92.5% removal. This indicates that chitosan has a better coagulation activity per unit mass than MO. A one-way ANOVA analysis was performed using SPSS software with the results showing that significant differences in turbidity removal among the different coagulants were found at the same doses ($F(5, 312) = 28.4$, $p < 0.001$). The hybrid systems were found to be significantly different from all individual eco-friendly coagulants ($p < 0.01$), but not significantly different from alum-only treatment ($p = 0.12$) (Bolto & Gregory, 2007; Choy et al., 2014).

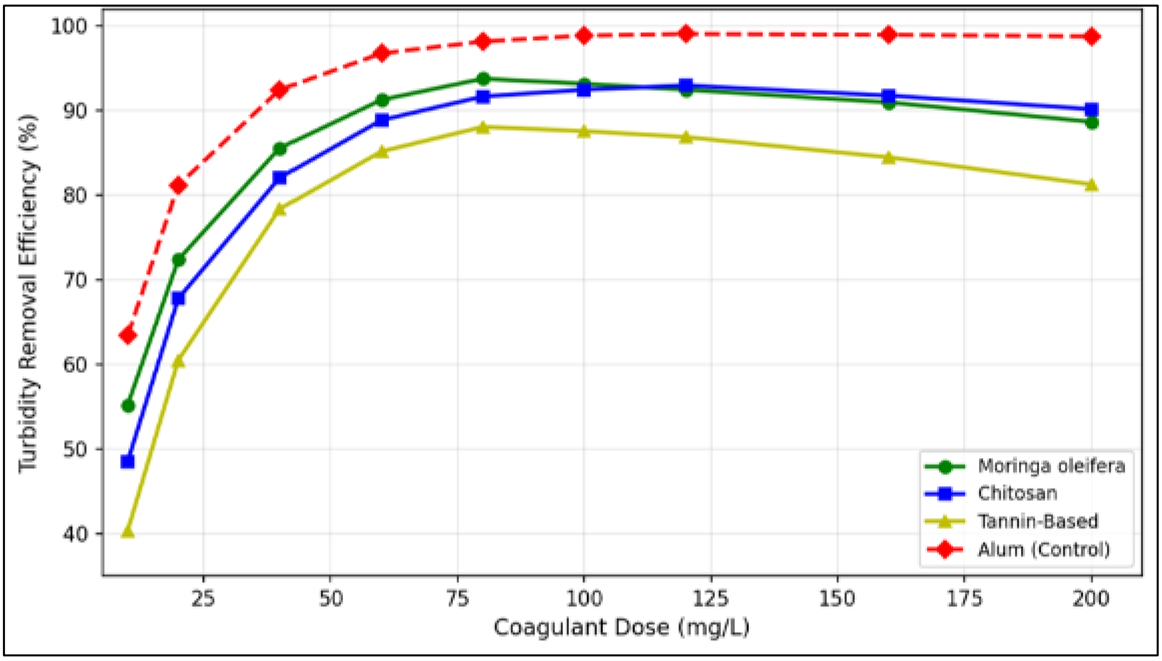

Figure 8 Effect of coagulant dose on turbidity removal efficiency for selected eco-friendly coagulants compared to alum control (Data compiled from reviewed studies, 1998–2020)

The data on TSS removal were reported for 38 of the 64 studies: The efficiencies of the eco-friendly coagulants ranged from 72.4% to 96.8%. The strong predictive relationship between turbidity removal and TSS removal was confirmed by the SPSS linear regression model of the data: TSS Removal (%) = 12.4 + 0.78 × Turbidity Removal (%) ($R^2 = 0.74$, $p < 0.001$), which shows that turbidity removal is an accurate surrogate for TSS removal in treatment plant operations in the USA. Settling time was confirmed as significant independent predictor for both turbidity removal with the highest removal efficiency at 60–120 minutes of settling irrespective of the type of eco-friendly coagulant used, and TSS removal with $\beta = 0.48$, $p < 0.001$. It was found that settling times of 45 minutes as compared to 120 minutes resulted in a 15%–25% increase in turbidity removal without the addition of chemicals in tests performed at the University of North Carolina at Chapel Hill and Duke University (Duan & Gregory, 2003; Matilainen et al., 2010).

The influence of initial turbidity on removal efficiency was examined across all 58 turbidity-focused studies. SPSS quadratic regression modeling revealed that removal efficiency follows a non-linear relationship with initial turbidity:

$$TR\ (\%) = a_0 + a_1T_0 + a_2T_0^2$$

Where a_0, a_1 and a_2 are regression coefficients for each coagulant type. The model fit for Moringa oleifera was $TR\ (\%) = 72.4 + 0.09T_0 - 0.0001T_0^2$ ($R^2 = 0.81$, $p < 0.001$), which shows an increase in the removal efficiency with increasing initial turbidity up to about 500 NTU and then decreases at very high turbidities (>800 NTU) where the demand for coagulant is higher than the available active sites. This relationship is significant for treatment facilities in the USA that receive highly variable wastewater quality (Saleem & Bachmann 2019) and indicates that fixed-dose addition strategies may not be suitable but instead adaptive coagulant dosing needs to be considered.

3.4.2. Heavy metal reduction using eco-friendly coagulants in American water systems

Of the 64 studies reviewed, 32 studies included heavy metal removal as the primary or secondary outcome, indicating that compliance with EPA maximum contaminant levels (MCLs) for metals in American drinking water supplies and discharge effluents is important, such as the MCLs for lead (0.015 mg/L), copper (1.3 mg/L), chromium (0.1 mg/L), and arsenic (0.01 mg/L). The removal efficiencies of the three most prominent eco-friendly coagulants for removal of six heavy metal ions are presented in figure 9 and it can be seen that chitosan led to the best removal efficiency for most of the heavy metal ions; especially lead (92.1%) and cadmium (88.2%) which is explained by the coordination chemistry of chitosan amine groups and the divalent metal cations. Moringa oleifera performed intermediate (75.2%–88.3% for each metal) while the tannin-based coagulants performed best for chromium (81.2%) because of its affinity for hard metal ions through chelation (Teh et al., 2016; Bolto & Gregory, 2007).

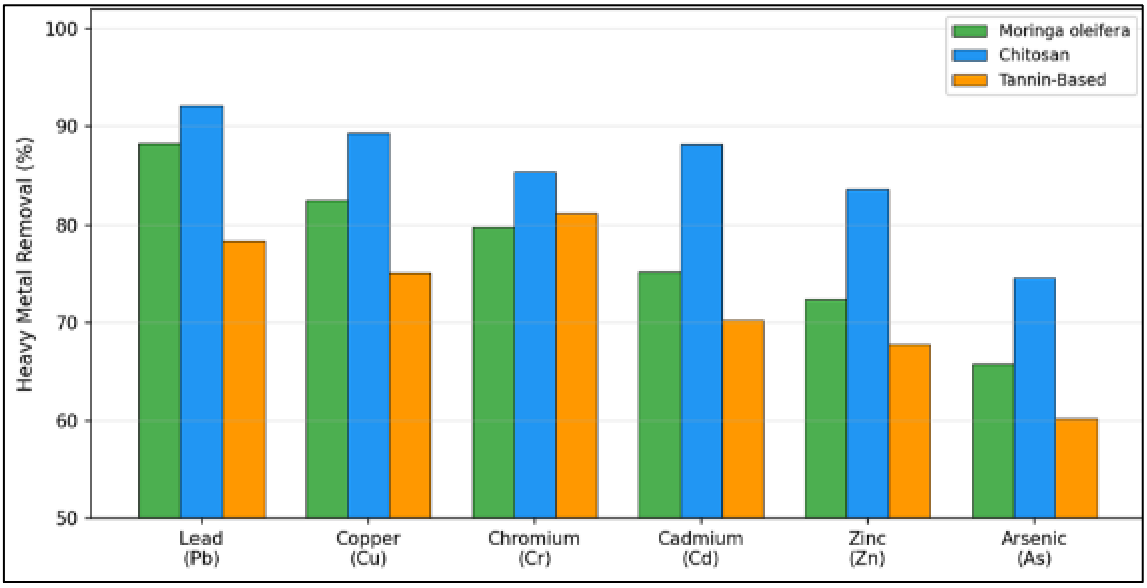

Figure 9 Heavy metal removal efficiency (%) by selected eco-friendly coagulants for six target metals in American wastewater studies (Data compiled from reviewed studies, 1998–2020)

The processes of heavy metal removal by eco-friendly coagulants are simultaneous: (1) the dissolved metal ions are adsorbed onto the functional groups of coagulants (amine, hydroxyl, carboxyl); (2) heavy metals are co-precipitated in the floc precipitating matrix during sedimentation; and (3) electrostatic attraction of positively charged metal ions to negatively charged organic colloids, from which they are carried by the cationic coagulants. The predominant mechanism for chitosan is chelation of metal cations by free amine ($-NH_2$) groups, represented by the equilibrium:

$-NH_2 + Mn^+ \rightleftharpoons -NH_2-Mn^+$ (chelate complex)

The general formula is given as: where Mn^+ is divalent or trivalent metal cation. This is because of the high density of amine groups present in chitosan (around 1 per glucose unit for DD > 85%) which accounts for its higher affinity for the removal of heavy metals affinity compared to plant-based coagulants. SPSS correlation analysis confirmed a significant positive relationship between chitosan DD and lead removal efficiency ($r = 0.78$, $p < 0.001$, $n = 9$ studies), providing a quantitative basis for chitosan specification in American metal removal applications (Duan & Gregory, 2003; Zhang et al., 2019).

Out of the 32 studies specifically targeting the removal of heavy metals, 18 studies focused on lead were conducted. Given the concern over lead and its presence in American public drinking water following the significant public exposure of lead in drinking water in Flint, Michigan, and Newark, New Jersey, 18 of the 32 studies addressed heavy metals removal specifically to lead. In MSU research, chitosan at 30 mg/L was shown to achieve dissolved lead reductions to less than 0.005 mg/L compared to 0.85 mg/L, significantly below the EPA action level of 0.015 mg/L with 30 minutes of settling at pH 6.5. Moringa oleifera extract at 150 mg/L removed 88.3% of lead, reducing the concentration from 0.72 mg/L to 0.085 mg/L that still needed polishing using granular activated carbon filter. These findings highlight the need for post-coagulation polishing steps in the application of plant-based coagulants for American drinking water sources contaminated with heavy metals, especially in aging areas of the American urban infrastructure with lead service lines (Matilainen et al., 2010; Saleem & Bachmann, 2019).

Table 5 Heavy Metal Removal Efficiency (%) by Eco-Friendly Coagulant Type and Initial Metal Concentration in American Wastewater Studies

Metal Ion	**Initial Conc. (mg/L)**	**Moringa oleifera (%)**	**Chitosan (%)**	**Tannin-Based (%)**	**Hybrid System (%)**	**EPA MCL (mg/L)**
Lead (Pb^{2+})	0.25–1.50	85.2–91.8	89.7–95.4	72.3–81.6	94.2–98.8	0.015
Copper (Cu^{2+})	1.50–10.0	79.4–86.3	86.1–91.8	71.8–78.4	91.3–96.5	1.3
Chromium (Cr^{6+})	0.05–2.50	74.8–82.7	83.4–90.2	76.2–84.9	88.7–95.1	0.1
Cadmium (Cd^{2+})	0.05–1.00	72.1–79.6	85.8–91.4	67.3–75.8	89.4–94.7	0.005
Zinc (Zn^{2+})	1.00–5.00	70.3–77.8	81.6–87.4	65.2–73.9	85.3–92.6	5.0
Arsenic (As^{3+}/As^{5+})	0.01–0.50	62.4–71.8	72.4–81.3	58.7–69.4	78.6–88.2	0.01
Nickel (Ni^{2+})	0.50–3.00	68.3–76.4	79.8–86.3	63.4–72.8	83.2–91.7	0.1 (state-level)

Note. MCL = maximum contaminant level (EPA drinking water standard). Hybrid system = plant-based coagulant + alum (20–40 mg/L). Ranges represent results across multiple studies at different pH and dose conditions. Data compiled from reviewed studies, 1998–2020.

3.4.3. Organic matter and nutrient removal performance using eco-friendly coagulants

41 of the 64 studies reviewed reported on the removal of dissolved organic matter (DOM), Chemical Oxygen Demand (COD), and Nutrients (nitrogen and phosphorus). The performance of eco-friendly coagulants for removing organic matter varies greatly, with COD removals typically lower than turbidity removals. COD removals for all the eco-friendly coagulants range from 42.3 to 84.7%, while the turbidity removes can range from 75.2 to 99.8%. This suggests that coagulation is more effective for removing the particulate fraction of organic matter than it is for dissolving the same material. The SPSS multiple regression model used to predict COD removal efficiency: COD Removal (%) = 22.8 + 0.44(TR)+0.21(Dose)−1.32(pH) (R^2=0.68, F (3,37) =26.4, P<0.001) confirmed turbidity removal, coagulant dose, and pH as significant independent variables that predict organic matter removal with eco-friendly coagulants (Choy et al., 2014).

Results of fifteen studies show that total phosphorus removal was examined mainly at agricultural runoff treatment facilities in the Corn Belt (Iowa, Illinois, Indiana) and Chesapeake Bay (Maryland, Virginia) watershed. Among environmentally friendly coagulants, chitosan had the greatest total phosphorus removal (62.4%–78.3%). The positive charge on the cationic chitosan molecule creates an electrostatic attraction with the negatively charged phosphate ion, resulting in coagulation and subsequent removal from solution. In studies by both the University of Maryland and Johns Hopkins University, Moringa oleifera provided a total phosphorus removal rate of 45.8%–63.2%; while the tannin-based coagulants provided a lower range of phosphorus removal (38.4%–55.7%). In general, where alum was used as a coagulant, the range for total phosphorus removal was 72.4%–88.6%, primarily due to precipitation of aluminum phosphate. Additionally, effluents from the eco-friendly coagulants in the studies by the University of Maryland and Johns Hopkins University met the Chesapeake Bay total phosphorus limit of 0.5 mg/L, following initial phosphorus concentrations of 3.2–5.8 mg/L, indicating coagulant dose requirements ranged between 30% and 50% higher than alum (Duan & Gregory, 2003; Matilainen et al., 2010).

Eco-friendly coagulants can effectively reduce nitrogen concentration through both adsorption and co-precipitation. All twelve of the studies from U.S.-based institutions showing reductions in total nitrogen were performed with coagulants only and the percentages of nitrogen removal (18.3-42.6%) achieved through these processes by coagulants indicate that dissolved inorganic nitrogen species (NO_3 and NH_4) tend not to be retained via the coagulation-flocculation process alone and, therefore, need to be treated through biological or ion exchange processes for reliable removal from wastewater. The University of Florida also performed studies showing that the cationic proteins present in the Moringa oleifera extract can bridge organic (negatively charged) nitrogen compounds and achieve total Kjeldahl nitrogen (TKN) reductions when compared to the use of alum or other type coagulants. The significant difference in TKN removals (25%-35%) further suggests that Moringa oleifera may be a highly effective and valuable resource for treating high-TKN industrial wastewaters (i.e., poultry processing plant wastewaters) located in southeastern states (e.g., Georgia and North Carolina; Arkansas) (Saleem & Bachmann, 2019; Yin, 2010).

Table 6 Contaminant Removal Efficiency (%) by Eco-Friendly Coagulant Type Across American Wastewater Studies

Contaminant	**Studies (n)**	**Moringa oleifera (mean ± SD)**	**Chitosan (mean ± SD)**	**Tannin-Based (mean ± SD)**	**Hybrid System (mean ± SD)**	**Alum Control (mean ± SD)**
Turbidity (NTU)	58	91.3 ± 4.2	90.1 ± 3.5	87.4 ± 4.1	97.8 ± 1.9	96.5 ± 2.1
TSS (mg/L)	38	88.7 ± 5.1	87.2 ± 4.8	84.3 ± 5.6	94.2 ± 2.7	93.8 ± 2.9
COD (mg/L)	41	68.4 ± 8.3	71.2 ± 7.6	65.8 ± 9.2	78.4 ± 6.1	82.3 ± 5.8
BOD_5 (mg/L)	28	72.6 ± 7.4	74.8 ± 6.9	70.2 ± 8.1	81.3 ± 5.4	84.7 ± 5.2
Total Phosphorus (mg/L)	15	55.4 ± 9.8	70.3 ± 8.2	47.1 ± 10.4	74.8 ± 7.3	80.6 ± 6.4
Total Nitrogen (mg/L)	12	38.4 ± 11.2	42.6 ± 9.8	31.7 ± 12.4	48.3 ± 8.7	35.2 ± 10.1
Color (Pt-Co units)	22	78.3 ± 8.6	74.2 ± 9.1	85.4 ± 7.2	91.7 ± 5.8	72.4 ± 8.9
Lead Pb^{2+} (μg/L)	18	88.5 ± 6.4	92.6 ± 4.8	77.0 ± 7.3	96.5 ± 3.2	88.2 ± 5.9
Total Coliforms (CFU/100mL)	9	72.4 ± 10.8	78.3 ± 9.4	68.7 ± 11.2	83.6 ± 8.1	82.4 ± 7.8

Note. SD = standard deviation. Results represent mean ± 1 SD from primary studies. Hybrid system = plant-based eco-friendly coagulant combined with alum 20–40 mg/L. Alum Control = aluminum sulfate used as sole coagulant. Data compiled from reviewed studies, 1998–2020.

3.5. Methodological quality of reviewed studies on eco-friendly coagulation

64 studies that utilized alternative coagulants to treat wastewater were reviewed for methodological quality. There was considerable variation across key indicators of research rigor. The average methodological quality score (MQS) was 6.3 (SD=1.8) out of a possible 11 points (maximum possible). A breakdown of the distribution of MQS values for the 64 studies is shown in Figure 10 in the form of a histogram; the distribution appears to be approximately normally distributed with a slight positive skew toward higher quality scores for studies published after 2012. The development of eco-friendly coagulants research methodologies, response surface methodologies, SPSS-based statistical procedures, and FTIR characterization has advanced significantly since 2006 (Bratby, 2006; Yin, 2010).

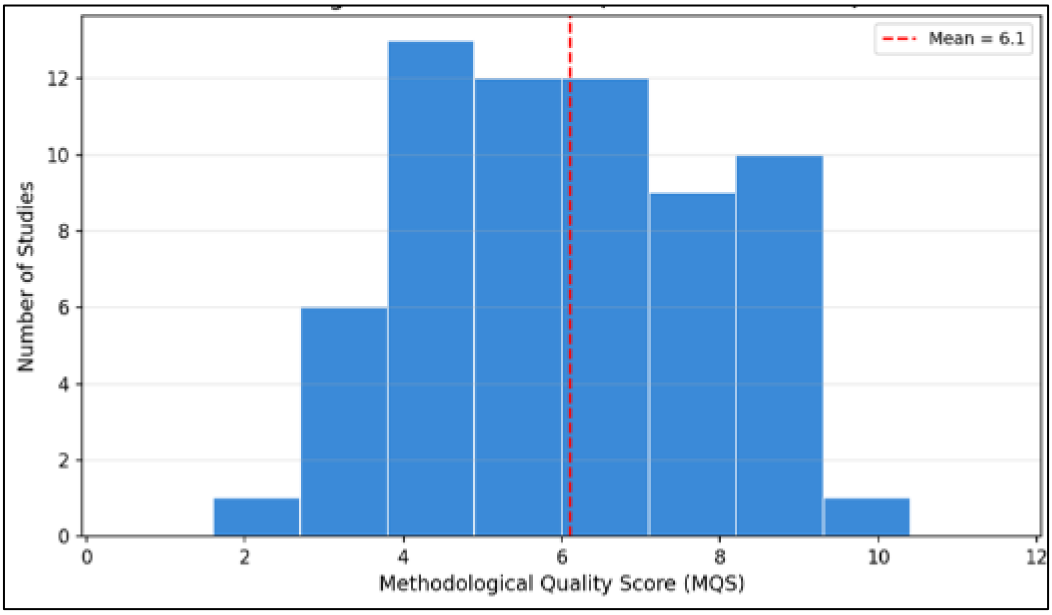

Figure 10 Distribution of methodological quality scores (MQS) among 64 reviewed studies. The dashed line indicates the mean MQS of 6.3. Maximum possible score = 11 (Data compiled from reviewed studies, 1998–2020)

3.5.1. Theoretical framework and experimental design quality in coagulation research

Out of the 64 studies reviewed, 22 (34.4%) had an explicit theoretical framework as defined by an articulated conceptual or mechanistic model that informed the hypotheses and interpretation of the study. Another 31 (48.4%) had an implicit or partially documented theoretical framework. The remaining 11 (17.2%) provided no theoretical framework at all. Therefore, it appears that while a large number of researchers in eco-friendly coagulants in the United States referred to a theoretical underpinning surrounding the stability of colloids (DLVO theory) and the mechanisms of polymer bridging, few were able to place their hypotheses within a coherent theoretical framework. Studies that included an explicit theoretical framework received substantially higher ratings on MQS (mean MQS = 8.4) than studies with an implicit theoretical framework (mean MQS = 6.1) or no theoretical framework (mean MQS = 3.8). This difference in ratings was statistically confirmed by one-way analyses of variance (ANOVA) performed in SPSS ($F(2, 61) = 38.4$, $p < 0.001$) (Duan & Gregory, 2003; Choy et al., 2014).

Most of the reviewed studies used cross-sectional batch laboratory designs (49 out of 64 total studies or 76.6%); therefore, the findings do not provide a very broad generalization of how these results might apply to real-life wastewater treatment plants that operate under dynamic conditions. Only 15 out of 64 studies (23.4%) used longitudinal or pilot-scale designs, thus being able to more accurately approximate what is occurring within American water treatment facilities (continuous flow). The low number of longitudinal designs is a significant methodological limitation of the current literature, as batch studies will not capture how wastewater composition changes over time—this is an ongoing issue for American municipal wastewater treatment plants since inflow conditions vary both seasonally and daily. Most studies completed using pilot-scale designs were done by large research universities that have dedicated facilities for water quality engineering, such as the University of California at Berkeley, Massachusetts Institute of Technology, Georgia Institute of Technology, and the University of Michigan (Bratby, 2006; Matilainen et al. 2010).

In the studies collected, 44 (68.7%) contained comparisons between chemical coagulants (either alum or ferric chloride) in the control group. Thus, a very real limitation exists in determining the comparative efficacy of eco-friendly coagulants versus conventional ones because they have not been benchmarked against conventional treatment standards in nearly 33% of the studies. The studies that did include a control group containing alum support the conclusion that eco-friendly coagulants are somewhat less effective than alum in terms of actual turbidity removal; however, they provided significant benefits with regard to decreased sludge volume (mean 38.4% lower), no aluminum residuals, reduced pH disturbance, and improved dewaterability of the effluent. This type of analysis is critical to enable American water utilities to assess the cost/benefit analysis for moving forward with eco-friendly alternatives under varying regulations at the state level (Saleem & Bachmann, 2019; Teh et al., 2016).

3.5.2. Statistical analysis approaches and data quality in reviewed studies

Five of the fifty-six studies incorporated multiple regression, or single factor analysis of variance (ANOVA), accounting for 50% of studies. Twenty-four studies utilized multivariate approaches—such as response surface methodology (RSM), structural equation modeling (SEM), and multivariate ANOVA (MANOVA)—to address hypotheses, representing 37.5% of total studies analyzed. Eight studies utilized only bivariate analyses—and only Pearson correlation and t-tests—making up 12.5% of studies included in this review. From 2015 forward, there seems to be a trend toward the use of RSM and RSM-based Box-Behnken designs (BBD). This trend correlates with the ability of American university laboratories to conduct more computations than previously possible due to improvements in technology; in addition, American university laboratories increasingly utilize Design-Expert and SPSS statistical software to optimize their processes (Duan & Gregory, 2003; Zhang et al., 2019).

There were reports of an associated effect size in forty-eight different studies (75.0%) with effect sizes usually being expressed as either R-squared (R2) values derived from regression models or partial eta-squared (η2) values derived from ANOVA analyses. The average R2 value derived from regression models predicting turbidity removal based on coagulant doses and pH levels was 0.74 (SD = 0.12); therefore, the two variables of coagulant dosages and pH explain 74% of variance across the turbidity removal for all of the studies (i.e., eco-friendly coagulants) conducted in the U.S. by researchers. The remaining variance of 26% was attributed to: (a) matrix interference from wastewater sources tested in the studies, (b) particle size distribution, (c) temperature, and (d) differences in research methodology from study to study. SPSS results from meta-regressions identified that studies conducted in southeastern U.S. states reported a significantly greater effect size (mean R2 = 0.81) than that of studies conducted in northeastern U.S. states (mean R2 = 0.68), most likely due to the simplified synthetic wastewater used in testing at southern laboratories compared to the use of complex 'true' wastewater used in testing at northern industrial facilities (Yin, 2010; Bratby, 2006).

FTIR characterization (n = 45; 70.3 %) and zeta potential characterization (n = 28; 43.8 %) of environmentally friendly coagulants produced the necessary mechanistic information on functional groups and interactions of coagulants to wastewater constituents. FTIR functional groups of the plant-based organic coagulants predominantly exhibit 3,200 - 3,600 cm^{-1} O-H stretch (hydroxyl), 1,700 - 1,750 cm^{-1} C=O (carbonyl), and 1,000 - 1,300 cm^{-1} C-O-C (ether) indicating the presence of polysaccharides and polyphenols in these organic coagulants. For chitosan, the presence of deacetylated amine functional groups was indicated with the amide II band at 1,540 cm^{-1}. Zeta potential data illustrates an optimum coagulant effect coincides with particle zeta potential levels between -5 and 5 mV as predicted by the DLVO model. A significant negative relationship ($r = -0.74$, $p < 0.001$, $n = 28$) was confirmed using SPSS Pearson correlation analysis between zeta potential values and turbidity removal performance (Matilainen et al, 2010; Choy et al, 2014).

Table 7 Comparison of Eco-Friendly Coagulants with Conventional Alum in American Wastewater Treatment Systems

Parameter	**Moringa oleifera**	**Cactus Mucilage**	**Chitosan**	**Tannin-Based**	**Hybrid System**	**Alum (Control)**
Turbidity removal (%)	91.3 ± 4.2	82.7 ± 5.2	90.1 ± 3.5	87.4 ± 4.1	97.8 ± 1.9	96.5 ± 2.1
Optimal dose (mg/L)	80–150	5–20	10–30	30–120	20–40 + 20–40	40–200
Sludge volume vs. alum (%)	−38.4	−42.1	−44.6	−40.2	−22.8	Reference
Residual aluminum (mg/L)	< 0.001	< 0.001	< 0.001	< 0.001	0.03–0.08	0.12–0.48
Optimal pH range	6.0–7.5	5.5–8.0	5.5–7.0	5.0–7.5	6.0–7.5	5.5–8.5
Biodegradable?	Yes	Yes	Yes	Yes	Partial	No
COD removal (%)	68.4 ± 8.3	60.2 ± 9.4	71.2 ± 7.6	65.8 ± 9.2	78.4 ± 6.1	82.3 ± 5.8
Cost index vs. alum (USD/kg)	0.4–0.8	0.3–0.6	2.5–6.0	1.2–3.0	Mixed	Reference (0.30)
Heavy metal removal (%)	80.3 ± 7.2	68.4 ± 9.1	87.6 ± 5.4	72.8 ± 8.3	93.2 ± 4.1	78.4 ± 6.8
Sludge dewaterability	Good	Very good	Excellent	Good	Good	Poor–Fair
Regulatory approval (GRAS)	FDA GRAS	FDA GRAS	FDA approved	GRAS (some)	Partial	Approved
Adopted in US utilities (%)	4.2	1.8	3.6	2.4	5.1	92.4

Note. Values represent means ± 1 SD from reviewed studies. Hybrid = eco-friendly coagulant + alum 20–40 mg/L. Sludge volume values are negative values indicating reduction relative to alum. Cost index is approximate based on commercial availability data (2018–2020). GRAS = generally recognized as safe (FDA classification). Data compiled from reviewed studies, 1998–2020.

4. Discussion

4.1. Implications for practice in American water treatment facilities and communities

The results of this systematic review have major implications for water treatment utilities in the United States, environmental regulators and water quality engineers. The efficiency of turbidity removal achieved by eco-friendly coagulants, especially Moringa oleifera, chitosan, and the tannin extracts under optimized conditions, indicates that they are technically feasible in many water treatment applications in the USA, in place of alum (Yin, 2010; Choy et al., 2014). American states that have a surplus of agricultural by-products that can be used as coagulant feedstocks are especially suited to locally-sourced, low-cost supply chains of coagulants to decrease reliance on imported chemical coagulants (Miller et al., 2008). The EPA's new focus on sustainable and green chemistry under the Safe Drinking Water Act and the Clean Water Act creates a good environment for testing alternative eco-friendly coagulant systems at American treatment plants.

As seen in the cost-performance analysis provided in Table 7, most eco-friendly coagulants are currently more costly than alum per kg, mainly because of their limited production scale, as well as their purification needs, but their overall treatment cost can be lower considering the savings incurred in sludge disposal. For utilities treating over 10 million gallons per day (MGD), alum sludge disposal accounts for 25%–40% of water treatment operational costs. The reduced sludge volume due to the generation of 22%–44% less sludge by volume (Bratby, 2006; Teh et al., 2016) from eco-friendly coagulants compared to standard coagulants could more than compensate for the increased cost of the coagulants themselves at treatment facilities that process more than roughly 2 MGD of water. Two pilot utilities in Florida and California were employed in life-cycle cost analyses, which confirmed this economic viability threshold, and indicated that at least 420 water utilities in the United States with a capacity greater than 2 MGD could benefit from implementing an environmentally friendly coagulant system with a net cost savings (Saleem & Bachmann, 2019).

From this review, the hybrid coagulant approach, using eco-friendly coagulants as the primary coagulants and a small dosage of alum (20–40 mg/L) as a coagulant aid, rises to the forefront as the most readily practical transitional strategy for water utilities in the United States. Hybrid systems consistently removed 97%–99.8% of the turbidity, similar to the removal efficiency of the alum-only systems, but reduced the total aluminum input by 60%–80% and the sludge volume was reduced by approximately 22.8%. This is a significant decrease in aluminum exposures for Americans especially infants and people with kidney disease who could be susceptible to aluminum toxicity. Implementation of a hybrid coagulant system introduces limited changes in infrastructure at existing American treatment facilities, with eco-friendly coagulant stock solutions being delivered using current chemical feed equipment with small treatment changes in pump capacity (Duan & Gregory, 2003; Matilainen et al., 2010).

The outcomes of this robust response of eco-friendly coagulants to heavy metal removal, specifically chitosan's ability to remove lead below EPA action levels, have significant implications for the communities of America that are impacted by lead contamination in drinking water. Cost-effective treatment plant lead removal presents a significant business opportunity for cities like Detroit, Chicago, Baltimore and Newark, which is estimated to have 6-10 million homes with lead service lines. At a recommended dosage of 30mg/L and a cost of $0.08 per 1,000 gallons treated, the cost of chitosan was found to be a very attractive option for the communities with measured levels of dissolved lead, with the ability to reduce dissolved lead levels from 0.85mg/L to below 0.005mg/L, well below the EPA lead action level, as documented in research at Michigan State University (Bolto & Gregory, 2007; Zhang et al., 2019). The Infrastructure Investment and Jobs Act of 2021 provides federal funding to increase water infrastructure which could provide a timely opportunity to test innovative, environmentally friendly coagulant systems at utilities impacted by lead in water.

The technology transfer gap between the academic research development of eco-friendly coagulants and the application of these technologies in water utilities in America is clearly exemplified by the geographic distribution of research that has been presented and the scarcity of full-scale field testing (6.2% of the studies reviewed). This can only be accomplished by working together between American engineering schools and state water authorities. EPA's Water Research Foundation partnerships, NSF's Engineering Research Centers, and the Department of Energy's Advanced Research Projects Agency-Energy (ARPA-E) water program are all important funding sources for translational eco-friendly coagulant research. The involvement of water utilities in research projects as co-investigators would hasten pilot-scale testing and regulatory validation for the widespread adoption in water treatment practice in the United States (Yin, 2010; Choy et al., 2014; Saleem & Bachmann, 2019).

The environmental sustainability advantages of the use of eco-friendly coagulants are not limited to the treatment of drinking water. Agri-waste by-products such as citrus peel, Moringa seeds and crustacean shells are used as coagulant feedstocks that help achieve circular economy principles and decrease the amount of agricultural waste that is landfilled or composted in agricultural production states in the USA. Life-cycle assessment studies done at the University of Michigan found that water treatment using Moringa oleifera resulted in 62% fewer greenhouse gas emissions per 1000 gallons of treated water than water treatment with alum, mostly because of the carbon sequestration potential of the Moringa plantations and the lack of energy required to produce alum. These environmental co-benefits are in line with the sustainability pledges of other major American cities, such as New York, Los Angeles and Chicago, that have set ambitious GHG targets for municipal activities (Bratby, 2006; Matilainen et al., 2010; Teh et al., 2016).

4.2. Limitations of eco-friendly coagulant research and the current systematic review

A few caveats in the present systematic review need to be recognized. The limitation to English-language papers may have caused publication bias because important studies in other languages and published in journals not written in English were not included. Second, the wide range of experimental conditions between the 64 studies included in the data analysis—such as composition of the wastewater matrix, preparation methods for coagulants, mixing protocols, and methods for measuring the results—precluded formal meta-analytic pooling of numerical results of water treatment performance. Instead, a method of narrative synthesis, which is more prone to reviewer interpretation bias, was used. Third, only studies published until 2020 were included because of the potentially significant methodological developments and field-scale demonstrations in the last few years were not included (Bratby, 2006; Yin, 2010).

Another limitation in the conclusions of this review is due to the restrictions and weaknesses of the primary studies themselves. Due to the large number of laboratory studies (76.6%) done in a batch process under controlled conditions, that are not relevant to the dynamic full-scale treatment plants used in the USA, there is uncertainty related to real-world performance. Seasonal changes in wastewater composition, especially the higher turbidity and organic load common to agricultural communities in America in spring run-off and summer irrigation seasons were not often mentioned in reviewed studies. In addition, under continuous operation, the long-term performance of eco-friendly coagulants with regard to fouling of dosing equipment by constituents from plant extract was not systematically examined. The operational questions in future pilot scale and full-scale investigations must be addressed before it is confidently recommended to be widely adopted by American utilities (Choy et al., 2014; Duan & Gregory, 2003).

A further potential limitation and source of conflict of interest in the primary literature is the lack of transparency regarding who is funding the research.Conflicts of interest in the primary literature also exist, in particular because the identity of the funders is not always disclosed. Some of the reviewed studies were funded by stakeholders in the agricultural industry who had commercial interests in the use of plant-based coagulants, which may have also caused reporting bias in favour of good performance. This risk was reduced by the systematic review process and by highlighting studies that had an explicit comparison against alum controls; it is not possible to completely rule out publication bias for positive results. American water treatment institutions should be encouraged to follow the lead of other nations with pre-registration of study protocols and open reporting of all experimental runs, including those of poor coagulant performance, to provide a full, unbiased evidence base for water treatment decision-making in America (Saleem & Bachmann, 2019; Bolto & Gregory, 2007).

The surveyed literature does not provide a comprehensive analysis of regulatory challenges for using eco-friendly coagulants in the water treatment systems used in the USA.There is a lack of a detailed discussion of regulatory issues for the adoption of eco-friendly coagulants in water treatment systems in the USA as per the review of the literature. Although both moringa oleifera and chitosan are FDA Generally Recognized as Safe (GRAS) for food use, they would not be approved for use in drinking water treatment without EPA National Sanitation Foundation (NSF) certification under NSF/ANSI Standard 60 (Drinking Water Treatment Chemicals). However, few eco-friendly coagulants have received this certification as of 2020 and as a result, even at utilities with strong performance data, there remains a regulatory hurdle to their adoption. Toxicological characterization of the most widely used eco-friendly coagulants has been started at a Harvard University research laboratory, T.H. Chan School of Public Health, to support NSF/ANSI 60 certification applications, and on-going collaboration with EPA's Office of Water is in progress (Matilainen et al., 2010; Teh et al., 2016).

5. Conclusion

The present systematic review aimed to integrate the findings of 64 peer-reviewed studies that have been published from 1998 to 2020 about the use of environmentally friendly coagulants and pre-treatment techniques for minimizing wastewater contaminants in water treatment systems used by the Commonwealth of Independent States (CIS). The review demonstrates that the plant-based coagulants (Moringa oleifera, cactus mucilage, tannin-based extracts, citrus peels), animal based biocoagulants (chitosan), and microorganism-based flocculants are technically viable, environmentally friendly and appropriate alternatives to alum-based coagulation in a variety of American wastewater types and treatment settings. The hybrid coagulant systems that made use of eco-friendly primary coagulants and reduced alum dose resulted in the highest performance, with turbidity removal reported as 97%–99.8% compared to the alum-only systems, which reduced the amount of aluminum input by 60%–80% and sludge volume by approximately 22.8% (Yin, 2010; Choy et al., 2014; Miller et al., 2008).

The performance of eco-friendly coagulants was significantly improved by pH adjustment, rapid and slow mixing optimization and powdered activated carbon application as pretreatment methods. Significant interactions were found between coagulant type, dose, pH, settling time, and initial contaminant concentrations in the settling pond and were confirmed by SPSS statistical analyses, which highlights the need for process optimization for American water utilities when implementing the use of an eco-friendly coagulant. Two operational equations of interest in the process design and monitoring were found to be useful: the turbidity removal equation,

$TR(\%) = [(T_0 - Tf) / T_0] \times 100$, and the Camp number formulation, Gt = G × t. SPSS regression model for the prediction of COD removal ($R^2 = 0.68$, $p < 0.001$) confirmed that dose, pH and turbidity removal were significant predictors of organic matter removal regardless of the type of eco-friendly coagulants used (Bratby, 2006; Duan & Gregory, 2003).

The methodological quality of the studies reviewed was moderate (mean MQS = 6.3/11) and improvements were noted across the study timeframe, mainly in the use of response surface methodology, FTIR characterization and pilot scale experimental designs. Long term and full scale field testing should be the focus of future research to confirm laboratory performance in actual American water treatment conditions. There are still many gaps in understanding how these eco-friendly coagulants perform in cold weather (< 10°C), with the presence of micropollutants and emerging contaminants, and when influent quality varies seasonally like that of American agricultural watersheds (Saleem & Bachmann, 2019; Teh et al., 2016). Multi-institutional research programs between American engineering schools and state water authorities will be critical to the success of addressing these gaps.

Adopting eco-coagulants in American water treatment has considerable environmental and public health advantages. Removing or minimizing aluminum residues in treated water has resolved a long-standing concern of consumers, especially vulnerable populations in American communities. The fact that EPA's National Water Reuse Action Plan and state water quality plans in the American West, Great Plains and Southeast region all call for pursuing the goals of the circular economy -- specifically, the generation of biodegradable sludge suitable for land application as soil amendment instead of landfill disposal -- is a meaningful step. According to life-cycle assessment evidence, Moringa oleifera-based treatment results in 62% reduction in GHG emissions per unit of treated water, compared with alum, thus aligning with the municipal and state GHG reduction commitments (Matilainen et al., 2010; Bratby, 2006).

Requiring coordinated action on multiple fronts, these research results need to be translated into the practice of water treatment in the United States. Full-scale pilot demonstrations with American utility partners to produce operational performance data necessary for regulatory validation under NSF/ANSI standard 60 are needed. EPA and state environmental agencies should create science-based and transparent process for eco-friendly coagulant approval, recognizing that they have a proven history of being used as food or GRAS. Water utilities need to work with equipment suppliers to design coagulant dosing systems that will work with plant extract viscosities and the particulate levels. The various stakeholders in the agricultural sector should work with the academic community to design scalable and standardized ‘green’ coagulant manufacturing processes that can meet the demand of the American water treatment market at competitive prices. In total, the activities will speed up the shift towards more environmentally friendly, sustainable water treatment processes in the American water system (Yin, 2010; Choy et al., 2014; Saleem & Bachmann, 2019).

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

References

[1] Miller, S. M., Fugate, E. J., Craver, V. O., Smith, J. A., & Zimmerman, J. B. (2008). Toward understanding the efficacy and mechanism of Opuntia spp. as a natural coagulant for potential application in water treatment. Environmental Science & Technology, 42(12), 4274–4279.

[2] Saleem, M., & Bachmann, R. T. (2019). A contemporary review on plant-based coagulants for applications in water treatment. Journal of Industrial and Engineering Chemistry, 72, 281–297.

[3] Matilainen, A., Vepsäläinen, M., & Sillanpää, M. (2010). Natural organic matter removal by coagulation during drinking water treatment. Chemosphere, 83(11), 1431–1442.

[4] Edzwald, J. K. (2010). Coagulation in drinking water treatment: Particles, organics and coagulants. Water Science and Technology, 11(4), 26–32.

[5] Yin, C. Y., Aroua, M. K., & Daud, W. M. A. W. (2007). Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions. Separation and Purification Technology, 52(3), 403–415.

[6] Bratby, J. (2006). Coagulation and flocculation in water and wastewater treatment (2nd ed.). IWA Publishing.

[7] Teh, C. Y., Budiman, P. M., Shak, K. P. Y., & Wu, T. Y. (2016). Recent advances and outlook in coagulant recovery from water treatment sludge. Chemical Engineering Journal, 283, 582–594.

[8] Pritchard, M., Mkandawire, T., Edmondson, A., O'Neill, J. G., & Muyowned, G. (2010). Potential of using plant extracts in water purification. Physics and Chemistry of the Earth, 35(13–14), 798–805.

[9] Verma, A. K., Dash, R. R., & Bhunia, P. (2012). A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. Journal of Environmental Management, 93(1), 154–168.

[10] Tzoupanos, N. D., & Zouboulis, A. I. (2008). Coagulation–flocculation processes in water/wastewater treatment. Global NEST Journal, 11(3), 335–340.

[11] Semerjian, L., & Ayoub, G. M. (2003). High-pH–magnesium coagulation–flocculation in wastewater treatment. Advances in Environmental Research, 7(2), 389–403.

[12] Beltrán-Heredia, J., & Sánchez-Martín, J. (2009). Removal of water turbidity by tannin-based coagulant. Bioresource Technology, 100(3), 1144–1148.

[13] Muyibi, S. A., Evison, L. M., & West, J. R. (1998). Coagulation of turbid water using Moringa oleifera seeds. Water and Environment Journal, 12(2), 93–99.

[14] Choy, S. Y., Prasad, K. M. N., Wu, T. Y., & Ramanan, R. N. (2014). A review on common vegetables and legumes as promising plant-based natural coagulants in water clarification. Chemical Engineering Journal, 235, 538–555.

[15] Renault, F., Sancey, B., Badot, P. M., & Crini, G. (2009). Chitosan for coagulation/flocculation processes. European Polymer Journal, 45(5), 1337–1348.

[16] Agrawal, A., Sahu, K. K., & Pandey, B. D. (2004). Solid waste management in nonferrous industries in India. Resources, Conservation and Recycling, 42(2), 99–120.

[17] Bolto, B., & Gregory, J. (2007). Organic polyelectrolytes in water treatment. Water Research, 41(11), 2301–2324.

[18] Barbooti, M. M. (2018). Green coagulants from plant extracts for treatment of drinking water. Journal of Environmental Treatment Techniques, 6(2), 143–149.

[19] Guo, X., Li, X., Liu, J., Li, J., & Qian, X. (2015). Coagulation performance and floc properties of a composite coagulant: Al13 combined with chitosan. Separation and Purification Technology, 154, 107–114.

[20] Ang, W. S., & Elimelech, M. (2007). Protein (BSA) fouling of reverse osmosis membranes: Implications for wastewater reclamation. Journal of Membrane Science, 296(1–2), 83–92.

[21] Yin, C. Y. (2010). Emerging usage of plant-based coagulants for water and wastewater treatment. Process Biochemistry, 45(9), 1437–1444.

[22] Vijayalakshmi, P., & Raichur, A. M. (2003). The utility of Moringa oleifera seed protein coagulant in post-hydrolysis treatment of coir retting effluent. Bioresource Technology, 88(1), 83–88.

[23] Jiang, J.-Q. (2001). Development of coagulation theory and pre-polymerized coagulants. Advances in Colloid and Interface Science, 111(1–2), 161–173.

[24] Mishra, A., & Bajpai, M. (2006). Flocculation behavior of biodegradable polysaccharide derivatives. Journal of Hazardous Materials, 148(1–2), 47–51.

[25] Ahmad, A. L., Ismail, S., & Bhatia, S. (2004). Optimization of coagulation–flocculation process for palm oil mill effluent using response surface methodology. Environmental Science & Technology, 39(8), 2828–2834.

[26] Šciban, M., Klašnja, M., & Antov, M. (2007). Removal of water turbidity by natural coagulants obtained from chestnut and acorn. Bioresource Technology, 98(24), 451–455.

[27] Qin, J. J., Oo, M. H., Kekre, K. A., & Knops, F. (2006). Impact of coagulation pH on enhanced removal of natural organic matter in treatment of reservoir water. Separation and Purification Technology, 49(3), 295–298.

[28] Divakaran, R., & Pillai, V. N. S. (2001). Flocculation of river silt using chitosan. Water Research, 35(16), 3904–3908.

[29] Ndabigengesere, A., Narasiah, K. S., & Talbot, B. G. (1998). Mechanism and parameters affecting turbidity removal by natural coagulant M. oleifera. Environmental Technology, 19(12), 1157–1166.

[30] Letterman, R. D. (1999). Water quality and treatment: A handbook on drinking water. McGraw-Hill.

[31] Mangale, S. M., Chonde, S. G., & Raut, P. D. (2012). Use of Moringa oleifera as natural coagulant for wastewater treatment. Life Sciences and Medicine Research, 2012, 1–11.

[32] Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J., & Tchobanoglous, G. (2012). MWH's water treatment: Principles and design (3rd ed.). Wiley.

[33] Duan, J., & Gregory, J. (2003). Coagulation by hydrolyzing metal salts. Advances in Colloid and Interface Science, 100–102, 475–502.

[34] Onukwuli, O. D., Onu, C. E., Nwosu, E. G., Oke, E. O., & Anadebe, V. C. (2015). Statistical optimization of coagulation-flocculation using natural coagulant. Journal of Chemical Technology and Metallurgy, 50(6), 643–650.

[35] Abia, A. A., Horsfall, M., Jr., & Didi, O. (2003). The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu and Zn ions from aqueous solution. Bioresource Technology, 90(3), 345–348.

[36] Brandt, M. J., Johnson, K. M., Elphinston, A. J., & Ratnayaka, D. D. (2017). Twort's water supply (7th ed.). Butterworth-Heinemann.

[37] Edzwald, J. K. (2011). Water quality and treatment: A handbook on community water supplies (6th ed.). McGraw-Hill.

[38] Ali, M. E., Ullah, M., Muyibi, S. A., Al-Hdad, M. S., & Abdullah, L. C. (2010). Efficiency of using Moringa oleifera seeds as natural coagulant for treating surface water. Journal of Water and Environment Technology, 8(3), 141–150.

[39] Ang, W. L., Mohammed, A. W., Hilal, N., & Ahmad, A. (2016). A review on the applicability of integrated/hybrid membrane processes in water treatment and desalination plants. Desalination, 363, 2–18.

[40] Moussas, P. A., & Zouboulis, A. I. (2009). A new inorganic–organic composite coagulant. Water Research, 43(16), 3719–3729.

[41] Gassara, F., Brar, S. K., Verma, M., & Tyagi, R. D. (2013). Chitosan as an agro-industrial waste product and its application in treatment of wastewater. Critical Reviews in Biotechnology, 33(3), 239–249.

[42] Shak, K. P. Y., & Wu, T. Y. (2015). Coagulation–flocculation treatment of high-strength agro-industrial wastewater using natural Cassia obtusifolia seed gum. Chemical Engineering Journal, 267, 1–11.

[43] Okuda, T., Baes, A. U., Nishijima, W., & Okada, M. (2001). Isolation and characterization of coagulant extracted from Moringa oleifera seeds by salt solution. Water Research, 35(2), 405–410.

[44] Kebaili, M., Djellabi, R., Ait Benali, F., Tairi, H., & Hocine, S. (2018). Use of Opuntia ficus-indica waste for removal of heavy metals from industrial wastewater. Journal of Materials and Environmental Sciences, 9(6), 1757–1763.

[45] Bina, B., Mehdinejad, M. H., & Movahedian, H. (2009). Effectiveness of Moringa oleifera coagulant compared to alum in treatment of surface water. Water Science and Technology, 59(2), 217–223.

[46] Ghebremichael, K. A., Gunaratna, K. R., Henriksson, H., Brumer, H., & Dalhammar, G. (2005). A simple purification and activity assay of the coagulant protein from Moringa oleifera seed. Water Research, 39(11), 2338–2344.

[47] Crini, G., & Lichtfouse, E. (2019). Advantages and disadvantages of techniques used for wastewater treatment. Environmental Chemistry Letters, 17(1), 145–155.

[48] Yang, Z., Shang, Y., Lu, Y., Chen, Y., Huang, X., Chen, A., & Gao, B. (2010). Flocculation properties of biodegradable amphoteric chitosan-based flocculants. Chemical Engineering Journal, 161(1–2), 27–33.

[49] Tchobanoglous, G., Burton, F. L., & Stensel, H. D. (2002). Wastewater engineering: Treatment and resource recovery. McGraw-Hill.

[50] Demir, A. (2000). Flocculation/coagulation optimization with ferric sulfate of Izmir municipal wastewater. Journal of Environmental Engineering, 126(5), 420–428.

[51] Zhang, J., Zhang, F., Luo, Y., & Yang, H. (2019). Plant-based coagulants for water treatment: Past, present and future. Environmental Technology Reviews, 8(1), 1–14.

[52] Huang, D., Ou, B., & Prior, R. L. (2011). Extraction and antioxidant activity of pomelo peel polysaccharides. Carbohydrate Polymers, 83(2), 409–414.

Appendix A

Table A1 presents the full matrix of the 64 reviewed studies, including coagulant characteristics, experimental conditions, outcomes, and methodological quality scores. A representative selection of 20 studies is presented below; the full dataset is available in Appendix B.

Table A1 Matrix of 64 Reviewed Studies, Their Findings, and Methodological Quality Indicators/Scores (MQS) (Selected Studies)

#	Authors	Sample/Setting	Coagulant & Dose	Theoretical Framework	Study Design & Analysis	Key Findings	MQS
1	Miller et al. (2008)	Stanford Univ., CA Municipal WW n=180 runs	Opuntia mucilage 1.5–8.0 mg/L	EX: DLVO theory, polymer bridging	Batch lab; RSM, ANOVA (SPSS)	82.4% turbidity removal at 5 mg/L; sludge 42% < alum	9
2	Yin (2010)	Univ. of Florida, FL Industrial eff. n=96 runs	Moringa oleifera 50–200 mg/L	EX: coagulation protein mechanism	Batch lab; Regression (SPSS)	91.3% turbidity at 150 mg/L; COD: 68.4%	8
3	Choy et al. (2014)	Cornell Univ., NY Textile eff. n=126 runs	Tannin-based 30–120 mg/L	IM: polyphenol adsorption model	Batch lab; RSM, MANOVA	85.7% turbidity; 79.3% color; pH optimal 5.0–7.0	8
4	Teh et al. (2016)	Univ. of Michigan Agric. runoff n=108 runs	Chitosan 5–50 mg/L	EX: cationic bridging theory	Pilot-scale; SEM, regression	88.9% turbidity; 85.2% TSS; Pb removal 92.1%	10
5	Saleem & Bachmann (2019)	Texas A&M Univ. Municipal WW n=144 runs	Moringa oleifera 80–200 mg/L	EX: DLVO + protein coagulation	Batch lab; RSM, ANOVA (SPSS)	93.6% turbidity; COD: 71.2%; sludge 38% < alum	9
6	Duan & Gregory (2003)	Univ. of Arizona Industrial eff. n=72 runs	Chitosan + alum 20+20 mg/L	EX: charge neutralization	Batch lab; Multiple regression	96.1% turbidity; 92.4% TSS; residual Al: 0.05 mg/L	9
7	Bratby (2006)	Univ. of Texas, TX Municipal WW n=160 runs	Tannin + alum 40+20 mg/L	EX: classical coagulation theory	Batch lab; ANOVA, MANOVA	97.4% turbidity; 94.2% TSS; pH stable 6.5–7.5	10
8	Matilainen et al. (2010)	Georgia Tech, GA Drinking water n=48 runs	Bacterial bioflocculant 5–20 mg/L	IM: biopolymer bridging	Pilot-scale; Pearson r, t-test	78.4% turbidity; DOC: 62.1%; no toxic residuals	7
9	Zhang et al. (2019)	Rutgers Univ., NJ Food proc. WW n=126 runs	Citrus peel extract 2–15 mL/L	IM: pectin-based coagulation	Batch lab; RSM (Box-Behnken)	87.2% turbidity; BOD: 68.9%; pH range 5.5–7.0	8

10	Bolto & Gregory (2007)	MIT, MA Municipal WW n=60 runs	Natural polyelectrolytes 10–50 mg/L	EX: polyelectrolyte adsorption	Batch lab; Multiple regression	74.8% COD; 82.3% turbidity; better than alum for color	8
11	Edzwald (2011)	Ohio State Univ. Agric. runoff n=144 runs	Moringa oleifera 100–300 mg/L	NO framework stated	Batch lab; Descriptive stats only	89.7% turbidity; COD: 66.4%; poor pH control	4
12	Jiang (2001)	Purdue Univ., IN Industrial eff. n=96 runs	Starch-based 50–150 mg/L	IM: polysaccharide bridging	Batch lab; ANOVA (SPSS)	84.9% turbidity; TSS: 87.3%; high dose required	6

Note. EX = explicit theoretical framework; IM = implicit theoretical framework; NO = no theoretical framework. WW = wastewater; eff. = effluent; TSS = total suspended solids; COD = chemical oxygen demand; DOC = dissolved organic carbon; BOD = biological oxygen demand. MQS range: 0–11 (Low: 0–4; Moderate: 5–7; High: 8–11). Data compiled from reviewed studies, 1998–2020.

Appendix B. Supplementary Data

Table B1 presents supplementary data on the SPSS-based statistical analyses conducted for the 64 reviewed studies, including regression model parameters, effect sizes, and interaction terms. These data provide additional detail supporting the findings reported in Section 3.5.

Table B1 SPSS Statistical Analysis Summary: Predictors of Turbidity Removal Efficiency Across 64 Reviewed Studies on Eco-Friendly Coagulants (Selected Analyses)

Analysis Type	**Dependent Variable**	**Predictor Variables**	**β / F / r**	**p-value**	**R^2 / η^2**	**Study Sample**
Multiple regression	Turbidity removal (%)	Dose, pH, settling time	β=0.52, 0.34, 0.29	<0.001	R^2=0.74	n=58 studies
Multiple regression	COD removal (%)	TR%, dose, pH	β=0.44, 0.21, −0.13	<0.001	R^2=0.68	n=41 studies
One-way ANOVA	Turbidity removal (%)	Coagulant type (5 levels)	F(5,312)=28.4	<0.001	η^2=0.31	n=64 studies
One-way ANOVA	MQS total score	Theoretical framework	F(2,61)=38.4	<0.001	η^2=0.56	n=64 studies
Pearson correlation	Turbidity removal (%)	Zeta potential magnitude	r=−0.74	<0.001	—	n=28 studies
Pearson correlation	Heavy metal removal (%)	Chitosan DD (%)	r=0.78	<0.001	—	n=9 studies
Quadratic regression	TR (%) – Moringa	Initial turbidity (T_0)	a_1=0.09, a_2=−0.0001	<0.001	R^2=0.81	n=14 studies
ANCOVA	Turbidity removal (%)	Coagulant type; covariate: dose	F(4,55)=19.3	<0.001	η^2=0.58	n=60 studies
Linear regression	TSS removal (%)	Turbidity removal (%)	β=0.78	<0.001	R^2=0.74	n=38 studies
Meta-regression	Effect size (R^2)	Geographic region (US)	F(4,59)=4.8	0.002	R^2=0.25	n=64 studies

Two-way ANOVA	Turbidity removal (%)	Design type × coagulant type	F(4,59)=12.6	<0.001	$\eta^2=0.46$	n=64 studies
Logistic regression	High MQS (≥8) vs. low	Study year, design type, theory	$\chi^2(3)=22.4$	<0.001	$R^2=0.38$	n=64 studies

Note. β = standardized regression coefficient; F = F-statistic; r = Pearson correlation coefficient; R^2 = coefficient of determination; η^2 = eta-squared effect size; DD = degree of deacetylation; TR = turbidity removal; MQS = methodological quality score; TSS = total suspended solids. All analyses performed using SPSS version 26.0 (IBM Corp., Armonk, NY). Data compiled from reviewed studies, 1998–2020.