Trend and current practices of coagulation-based hybrid systems for pulp and paper mill effluent treatment: mechanisms, optimization techniques and performance evaluation

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Abstract

This paper presents an overview of pulp and paper mills (PPM) production processes, the resulting release of wastewater effluent loaded with wide range of pollutants and associated environmental impacts. The review highlighted the different types of functional materials and their modified forms employed as coagulants for pulp and paper mills industries effluent (PPME) treatment that have been intensively studied as a promising strategy for PPM to achieve cleaner and sustainable treatments in accordance with sustainable development goals (SDGs) “6-Clean water and sanitation”, “9-Industry, innovation, and infrastructure”, and “12-Responsible consumption and production”. Standalone coagulation treatment processes are inherently ineffective towards meeting the increasingly stringent discharge requirements, coupled with their higher energy demand, and increased operational and maintenance costs. Owing to the recalcitrant nature of PPME contaminants, this review explored the effectiveness of the coagulation processes for decontamination of PPME. Furthermore, the review provides a state-of-the-art coagulation-based hybrid systems employed for enhanced PPME treatment. The process limitations, influencing factors and optimization techniques are highlighted. The review also highlights how sustained research in the subject area impacts on achieving cleaner production. The review also discusses coagulant classifications and the synergistic, antagonistic and shock load toxic effects of hybrid coagulants on toxicant biodegradation and their associated system efficiency. Moreover, it offers a guide for the development and application of sustainable hybrid-based coagulants for PPME treatment. The findings presented herein provide a vital theoretical foundation for sustainable

solutions to improve coagulation-based hybrid systems efficiency and their scale-up towards potential commercialization.

Keywords: Coagulation-flocculation; pulp and paper mill effluent; natural coagulants; hybrid coagulants; hybrid systems; sustainable development goals (SDGs)

1. Introduction

Pulp and paper mills (PPM) produces the third largest quantity of effluents after primary metals and chemicals industries (Toczyłowska-Mamińska, 2017). The technology type employed, scale of production, the raw materials requirements , the characteristics of the paper and pulp products produced, , variations in production rates and adopting in-plant treated wastewater reuse in the process collectively, impact on the quantity and characteristics of the final PPM effluent discharge (Kamali et al., 2015). Even though wood is the primary fibre source and the primary raw material used in the making of paper, non-wood agricultural products such as cossette, flax, hemp, hay, and reed as well as inorganic fibres are also raw materials used. Green liquor dregs, lime mud, ashes, slaker grits, grit bark, fibre, pigments, dirt, sugars, alcohols, turpentine, sizing agents, adhesives made of starch and synthetic materials, lignin compounds and dyes, NaOH, Na_2SO_4, bleach chemicals, thermal loads, toxic chemicals, mercaptans, and H_2S released from various stages in kraft pulp production are among the pollutants from the pulp (Abioye et al., 2023a). Consequently, alterations in gonad size, circulating sex steroid levels, increased vitellogenesis, induction of hepatic mixed-function oxygenases, masculinization, and immunological function have been seen at a few pulp mills (van den Heuvel et al., 2006b). The effluent from PPM endangered land and water ecosystems via production of more hazardous byproducts which threaten the living organism's life in these habitats as well as their biological diversity.

Treatment of PPME using coagulation is susceptible to leading to the formation of polymeric compounds. Through charge neutralization or adsorption, coagulants interact with colloidal components, causing coagulation and sedimentation (Birjandi et al., 2016b). Four different processes exist for how chemical coagulants might destabilize particulates: double-layer compression, charge neutralization, entanglement in a metal hydroxide precipitate, and inter-particle bridging. Flocculation has also been utilized through a liquid dispersion optical characterization device. The floc settling behavior is evaluated in terms of the kinetics of supernatant generation. The main goal of the approach is to track and examine changes in the sample's light transmission and backscattering in a cylindrical cell as a result of particle motions brought on by aggregation, creaming, and/or sedimentation (Adel et al., 2020). With the presence of numerous inorganic flocculants such as electrolyte salts, it is easier to turn off stability and commence flocculation using organic macromolecule flocculants. Furthermore, organic macromolecule flocculants have a beneficial effect on neutralizing and decreasing the surface charge of colloid, squeezing the double electrode layer of colloid, and enabling it simpler to destabilize, coagulate, and sediment through middle bridge activity. As per the flocculation theory, the longer the molecule chain, the greater the degree of interaction between particles in the suspension. The wider the flocculant's expansion space in the water, the further particles can be bridged. The more possibilities of colliding with particles, the longer and more stable the bridges and networks will be. The greater the adsorption (Birniwa et al., 2022b), the higher the cationic degree. Several factors have been reported to influence the coagulation process efficiency. Finding the ideal coagulant dose is crucial for preventing re-stabilization in the mechanism that is based on the neutralization of charges, particularly those located in the stern layer. The dominance of the sweep flocculation mechanism based on the production of gelatinous consistency during the process can be used to explain the improvement in removal efficiency that results from raising the coagulant dose until it reaches the optimum (Abdullahi et al., 2022). Thus, to ensure an efficient process optimization, through limited number of planned experiments, a mixture of novel techniques that offers sufficient information for designing experiments, building models, assessing the impacts of several variables, and accomplishing optimal treatment conditions for desired responses is necessary.

Despite significant progress in PPME treatment technologies and the identification of associated hazards, existing PPME treatment methods have limits, mainly in terms of efficacy. Currently, no single technology can eliminate all toxins due to their high energy and resource requirements, as well as their high maintenance and operating costs (Toczyłowska-Mamińska, 2017). However, additional treatment of the wastewater may be required to remove the hazardous and dangerous by-products created during the single coagulation treatment process. Although the treatability of bleaching wastewater was improved by ultrasonic irradiation, fenton-like oxidation, electrochemical treatment, and/or chemical precipitation treatment methods, none of them could produce treated effluents with a COD limit of less than 200 mg/L, indicating the need for a hybrid system that combines physico-chemical and biological processes to speed up the degradation of recalcitrant compounds in the samples before treatment. To choose and improve the efficacy of microbial activity for contamination removal when utilizing biological processes, genetic engineering innovation that can guarantee the technical and financial sustainability of the treatment technology is necessary (Mustafa et al., 2021). When choosing a particular hybrid system, it is important to take developing toxins, xenobiotic chemicals, their metabolites, and degradation pathways into account because these substances may have eco-toxic and bio-toxic effects on environmental health.

A hybrid treatment process is effective yet costly, and it necessitates adequate treatment plant design depending on the effluent's properties. As a result, before adopting the proposed hybrid treatment, the cost-benefit ratio of the various treatment options should be evaluated. Typical physical and chemical treatment processes coupled to coagulation include adsorption, primary settling, membrane processes, electrochemical coagulation, electro-activated peroxymonosulfate (PMS), acid pretreatment, chemical oxidation, advanced oxidation processes, microelectrolysis, dissolved air floatation, dielectric barrier discharge ionization technologies*,* thermochemical precipitation, and photocatalysis (Owodunni and Ismail, 2021). Whereas, the biological approaches include the biological activated sludge process, Upflow - Anaerobic Sludge Blanket Reactor (UASB), Aerobic stabilization basins (ASB), Fed batch reactor (FBR)/Sequencing batch reactor (SBR), Bio-electrochemical treatment system (BET) and Rotating biological contactors (Waqas et al., 2023b). Coagulation has the merits of being inexpensive and effective at controlling membrane fouling. Although the process produces a sludge that must be disposed of, coagulation seems to attain the maximum color removal at the lowest expense (Abdullahi et al., 2021). Raw wastewater does also foul membranes more than PPME processed with only coagulation. Furthermore, by eliminating colloidal and soluble substances narrower than membrane pores, it can enhance the quality of treated water (Waqas et al., 2023a). When compared to other expensive and energy-intensive methods like AOP paired with UV, the hybrid coagulation and adsorption technique is still the better option. The reduction of COD, BOD, and turbidity was also shown to be somewhat more effective with ultrafiltration than with adsorption on activated carbon.

Despite these efforts, state of the art reviews is yet to be reported on the use of coagulation-flocculation processes for PPME treatment. To give the reader the necessary information and context, this review started by presenting a general overview of PPM, their manufacturing methods, the resulting pollutants, potential sources within the mill, and their effects on the environment. The review further discussed the performance evaluation of several single coagulation processes that are extensively conducted, thereby highlighting their removal mechanisms, process optimization, performance evaluation and operational parameters. The reviewed research has been analyzed and discussed to provide in-depth information on the effectiveness of various materials and their modified forms, which have lately become attractive coagulants and potential solutions for PPME treatment to achieve a cleaner and more sustainable environment. This review paper also offers an up-to-date analysis of hybrid coagulation-based methods for the treatment of PPME. Weaknesses in the process, impacting process variables, and optimization strategies were noted. Future research projects and insights have also been suggested to address the information gaps, difficulties, and barriers for the implementation of coagulation and hybrid-based coagulation procedures in the treatment of PPME.

2.0 Methodology adopted for the review.

The search technique used in this study relies on various electronic databases to discover publications pertinent to the study's topic. Information was obtained from the core-collection databases accessible online at Web of Science (Lawal et al., 2023). Articles with the term’s "coagulation" or "flocculation" in the title, keywords, or abstract were retrieved. The term "pulp and paper mill effluent" was also used to identify articles that discussed paper mill wastewater. The next step was to link "coagulation" or "flocculation" with the terms "pulp and paper mill effluent" to identify any publications involving the effluents from PPME treated using coagulation and the search, which was restricted to publications published between 2005 and 2022, turned up 1184 articles. Subsequently, the research was then refined by limiting the findings to "search by document type". The number was then reduced to 985 by authors concentrating on "articles". This illustrates that the use of various hybrid techniques and materials for the treatment of PPME is starting to receive more attention from students and publications. After that, a final search was conducted to compile the most crucial papers for this review. Thus, the authors chose their papers by reading each article's title and abstract. There were 138 papers that were deemed suitable for the present review.

3.0 Pulp and paper mill (PPM)

The pulp and paper mill are globally considered a large user and producer of biomass-based energy due to the increase in paper demand in the sustainable, industrial, educational, and information-oriented society. The sector is completely reliant on natural resources, as it is a significant user of energy, water, and wood (Abn and Lim, 2009). The pulp and paper business are amongst the most vital ones worldwide, not only economically but also socially. It is ranked sixth in the industrial sector, behind cement, oil, leather, steel, and textiles. The pulp and paper industry ranks the fifth largest in the USA and leads the country’s economy as a major industry in Canada. In addition to North America, India, China Brazil, Sweden, Finland, Japan, Russia, and Indonesia emerging as new countries in the pulp and paper industry market, based on both abundant natural and human resources and recent economic development (Razali et al., 2011).

2.1 Pulp and paper production process

Globally, PPM production is increasing each year, and the process uses a lot of water. It ranks third in water use behind chemical industries. Its water usage is determined by industrial operations. Each ton of paper produced has an approximate water footprint of 30 cubic meters (Sandberg et al., 2018). To maintain their profitability and overcome the declining and competitive markets, pulp and paper mills are no longer limited to production of pulp and/or paper; rather, they do also adopt additional measures including waste heat delivery to district heating systems and production of the electricity, wood pellets, and dried bark as well as valuable chemicals such as ethanol and materials like carbon fiber, biofuels, etc. (Öztürk and Özcan, 2021). The industry heavily consumes forest and agro-based raw materials such as cellulosic derived from forest, fibers, wood, bamboo, bagasse, agricultural residues (wheat & paddy straw, vegetables, hemp, jute sticks, rice husk, kenaf, wheat, grasses, seaweed) (Kamali and Khodaparast, 2015). The industry also consumes wastepaper, energy, water and significant amounts of various commercial chemicals such as (organic/inorganic solvents, hypochlorite, caustic soda, Na_2S, coal, Na_2CO_3, sodium hydroxide, mineral acid, talcum powder, chlorine compounds, etc.) (Sharma et al., 2020b). PPM is established on pulp production and production of paper and/or paper products. The production process depicted in Fig. 1 typically involves six stages, namely, (i) raw materials handling, (ii) pulp manufacturing: biological, mechanical, organosolv, chemical, thermomechanical, recycled, and chemithermomechanical pulp are all used in the pulping process. Generally, the process begins with debarking. The resulting wood fragments are roasted at a high temperature and pressure. (iii) pulp washing and screening, (iv) bleaching; these involves two steps of oxygen delignification and final bleaching, (v) chemical recovery and (vi) paper making (Gupta and Gupta, 2019).

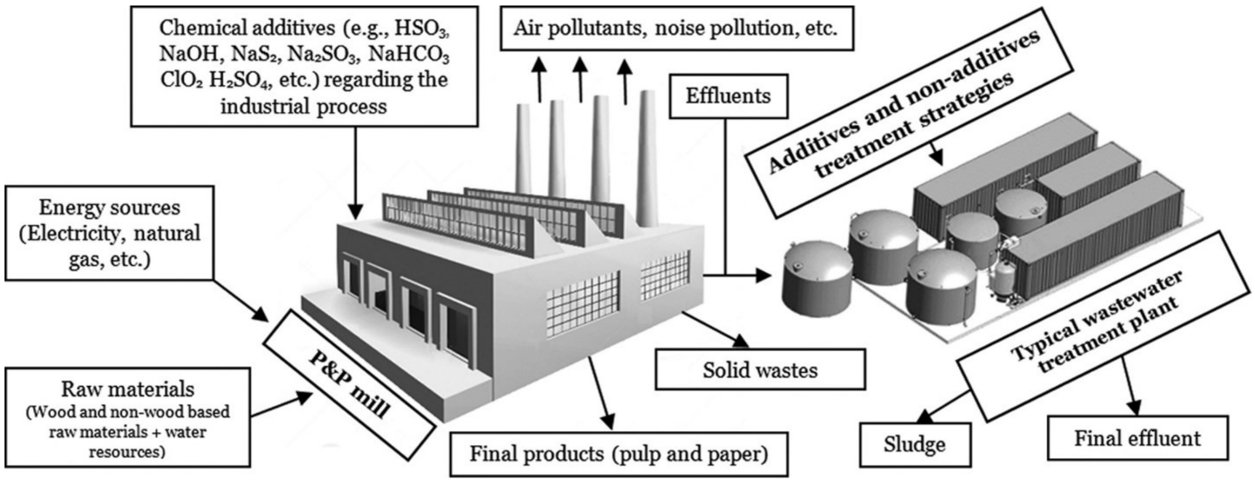


Fig. 1. Activity illustration of pulp and paper processing industry (Kamali et al., 2019)

2.2 Pollutants from the pulp and paper mill (PPM)

The pulp and paper mills are one of the most polluting industries discharging a variety of organic and inorganic pollutants such as ashes, green liquor dregs, slaker grits, lime mud and pulp mill sludge of wastewater treatment plants either in gaseous, liquid, or solid forms into the environment (Noor et al., 2023). The types and quantities of pollutants generated as shown in Fig. 2 are directly linked to the origins of wastepaper. This is only suitable for the enterprises which apply waste papers as feedstocks. From lightweight coated paper, higher amounts of organics and lower amounts of inorganics are released into the resultant effluents compared with newsprint paper. While with laser printing papers, the thermoplastic resins in the toner are often melted and subsequently attached to the paper using carbon black during the printing process (Kamali and Khodaparast, 2015). The main pollution sources in mills are raw material pulping, pulp bleaching, and paper making/coating. The annual trash production is possibly over one million metric tons. Green liquor dregs, lime mud and grits make up most solids in pulp mill waste.

The PPM generates 2.3% suspended solids, 41.8% bleached pulp waste, 5.25% dissolved organic matter (DOM), and 4.2% solid waste. These wastes contains heavy metals and other contaminants (Kumar et al., 2020). Adsorbable organic halides (AOX) and POPs are found in pulp paper sludge. They are plant phytosterols found in humic compounds and are classified as endocrine disruptors (EDCs). Degrading the ecology and harming living organisms is possible. These contaminants are teratogenic, mutagenic, and carcinogenic in humans and animals. Because the amount of garbage generated by this industry is expanding, it is considered a major source of pollution. Solid waste disposal options for the pulp and paper sector vary by country and existing restrictions. However, when the pollutants are improperly disposed of, they can have a significant impact on the environment, thereby, damaging the water, plant, soil and air (Simão et al., 2018).

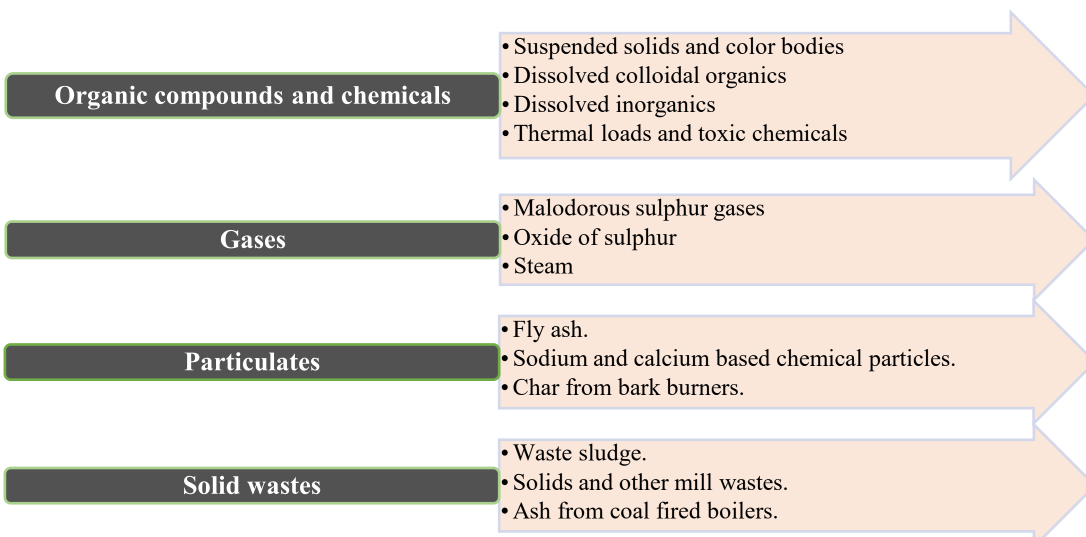


Fig. 2. Categories of key pollutants from PPM

PPM continue to face problems in terms of energy efficiency and compliance with rigorous environmental rules for the management of harmful pollutants, considering environmental responses and long-term regulatory requirements (Gupta and Gupta, 2019). Thus, multiple internal process improvements when combined with management measures, can reduce pollutants emitted during various stages of pulp and paper manufacturing. The European Commission (2001) describes the most effective approaches available for mills to use. Several studies have also been done to reduce pollutants throughout the pulp and paper production process. However, external processes like the secondary treatment, primary clarification, or tertiary treatment have remained the principal remediation methods utilized in pulp mills (Kamali and Khodaparast, 2015).

3.0 Pulp and paper mill effluent (PPME)

3.1 PPME generation and characteristics

The development of PPM is associated with large amount of fresh-water consumption accompanied with the generation and subsequent discharge of large quantity of wastewater (Abn and Lim, 2009). Pulp and paper industry is a very water-intensive industry (Subramonian et al., 2014). After the key metals and chemicals sectors, it is the third in terms of wastewater generation. PPME are separated into effluents from PPM and those from paper mills. Crushing, washing, concentrating, bleaching, digesting, and removing ink and fibre produces pulp wastewater, whereas paper wastewater is generated by processes including washers, beaters, paper manufacturing machines, screens, and adjusting & mixing tanks (Cabrera, 2017).

It has been reported that the final effluent discharged from the mill results from the mixture of wastewater coming out of the different manufacturing unit processes (wood preparation: fibrous raw material washing with alkali or filler, digester house, pulp washing, centric leaners, pulp bleaching, paper machine, chemical recovery) (see Fig. 1), steps and the methods employed therein. The quantity of wastewater generated from each single process is directly proportional to the amount of pulp produced in that process (Kamali and Khodaparast, 2015). Among the many stages of pulping, the chemical pulping stage produces wastewater with a high pollutant concentration that contains wood debris and soluble component (Chanworrawoot and Hunsom, 2012). Cellulose pulp manufacture generates a huge amount of effluent as a result of the raw materials being cooked. It is rich in dissolved carbohydrates, lignin, AOX, COD, inorganic chlorine compounds, and organo chlorine compounds. Due to the obvious usage of chlorine to brighten the pulp, the pulping bleaching operation produces effluent containing strong hazardous chemicals. It contribute 85% of the total color and 50% of the BOD (Amaral et al., 2014). The wastewater produced by a digester house is referred to as "black liquor" (Ashrafi et al., 2015).

PPME contains several particulate pollutants. The organic load in wastewater may be increased by certain raw materials used in paper manufacture (e.g. water, fibers, fillers, dyes, starch, retention aids, sizing agent, fluorescent whitening agents, and wet strength agent) (printing and information paper, sanitary tissue, wrapping paper, food packaging materials) (Kim, 2016). It is worth noting that wastewaters from PPM and distilleries can be recovered for valuable chemicals and energy because of the existence of a high organic/inorganic chemical load (Garg et al., 2010). According to literature, the wastewater also contain various toxic chemicals and recalcitrant compounds like resin acids, dibenzo-p-dioxin, dibenzofuran, adsorbable organohalogens, unsaturated fatty acids, extractives, waxes, sterols, suspended solids, phenolics, diterpene alcohols, terpenes, juvaniones, Sulphur compounds, dissolved chlorinated lignin, chlorinated hydrocarbons, carbohydrate, AOX, inorganic chlorine and organo chlorine compounds, suspended solids, BOD, COD, volatile organic compounds and total organic carbon. The effluent has a high COD, limited biodegradability, and roughly 700 organic and inorganic components (Kamali and Khodaparast, 2015).

Process types, wood materials, process technology, internal recirculation, and water volume all influence the properties of PPME. All the processes generate effluents with high BOD and COD concentrations. This indicates that the effluents include high levels of organic compounds (Abn and Lim, 2009). Medium pulp wastewater has a high chrominance concentration of COD and contains many toxic and harmful substances. Additionally, these wastewaters contain large levels of suspended particles and floating debris.

3.2 Impacts of PPME on the surrounding environment

PPME contains about 700 various pollutants. The effluent remains toxic and complex and causes substantial aquatic and soil contamination because of the increasing pollution concentration and the prevalence of color-contributing compounds. It also leads to thermal pollution, slime, and foam formation in the receiving environment (Gholami et al., 2020). The wastewater is rich in color (dark brown) and have a bad smell because of the presence of dissolved lignin and its degradation products, resin acids, phenols, hemicelluloses, and chlorinated compounds (Ariffin et al., 2012). The dark-brown coloration may increase water temperature and creates esthetical loss (Kankia et al., 2021b; Öztürk and Özcan, 2021). This reduces solar radiation penetration and the level of dissolved oxygen that negatively impacts on fish macrovertebrates, flora and fauna, phytoplankton, and produces toxicity. A study found that short-term exposure of PPME to aquatic and terrestrial ecosystems harmed the freshwater fish Rasbora daniconius. Behavioral changes revealed this (van den Heuvel et al., 2006a). Numerous studies have documented the negative effects of PPM on aquatic creatures. Respiratory & oxidative stress, genotoxicity, and liver damage are all reported in the investigations.

In a terrestrial setting, PPME irrigated soil revealed decreased moisture content, increased pH, and heavy metal accumulation. Affected nutrient dynamics The effluent from pulp mills has been shown to harm rice, mustard, and pea seed germination and growth. Degradation of water quality due to nutrient loading (nitrate and phosphorus) from pulp wastewater discharge. It is important to note that the rise in organic or inorganic chemicals poses a health concern to the pulp and paper recipient ecology as it promotes the formation of total coliform, *Klebsiella* sp., fecal coliform, E. coli, *Enterobacter* sp. etc. The high organic matter content can promote ponds, lakes, and other hydric bodies eutrophication (Simão et al., 2018). White water effluents from thermo-mechanical pulping comprise easily biodegradable components with a typically medium strength and concentrations ranging from 1000-6000 mg/L COD. These effluents are frequently responsible for corrosion problems in papermaking machines. The kraft process produces black liquors that comprise an aqueous solution of Na_2S and NaOH that is used to break up and remove lignin. They have been shown to have a detrimental effect on wastewater treatment systems and aquatic life (Kamali and Khodaparast, 2015). The PPME also has a detrimental impact on all aspects of the environment. These include: atmosphere, biodiversity, forest, water, air, land, agriculture, public health and economic wealth of a nation (Gupta and Gupta, 2019). It is a significant hazard to both wild and human life. It has the potential to have a detrimental effect on the receiving aquatic environment through the production of slime by microorganisms like Sphaerotilus sp. and the formation of scum, toxicity to exposed communities, thermal effects, color problems, and aesthetic issues in the event of insufficient treatment. Its presence increases the likelihood of toxicants bioaccumulating in the food chain.

As a result of the PPME's effects, effluent must be treated using adequate water treatment methods and technologies before being discharged into receiving water bodies and treated water must be reused to reduce water consumption throughout the pulp and paper manufacturing process.

3.3 PPME treatment

Wastewater from the pulp and paper sector contains fibre and can present distinct solid & liquid separation issues. As a result, it must be properly treated and recycled before to being discharged. Diverse treatment technologies have been applied to PPME to improve performance efficiency and meet severe regulatory standards. The correct treatment of PPME is based on the process's inherent characteristics. As a result of the unique blend of unit processes that take place in the manufacture of pulp and paper, there are no two paper mills that discharge the same effluents (Wong et al., 2006). The appropriate technology relies on the properties/characteristics and concentration of the substance to be removed, the effluent water purity criteria, sand, and economic variables. It has been proven that any treatment system/technology that meets the criteria does not produce secondary pollutants when used to treat wastewater.

3.4 PPME treatment processes

Effluent treatment processes from PPM can be grouped into three major categories as depicted in Fig. 3. The combination of physicochemical and biological processes tagged "hybrid process" has the possibility to maximize the benefits for every process individually. The efficiency of all these processes solely relies on their operational conditions and all have their respective advantages, weaknesses, and limitations.

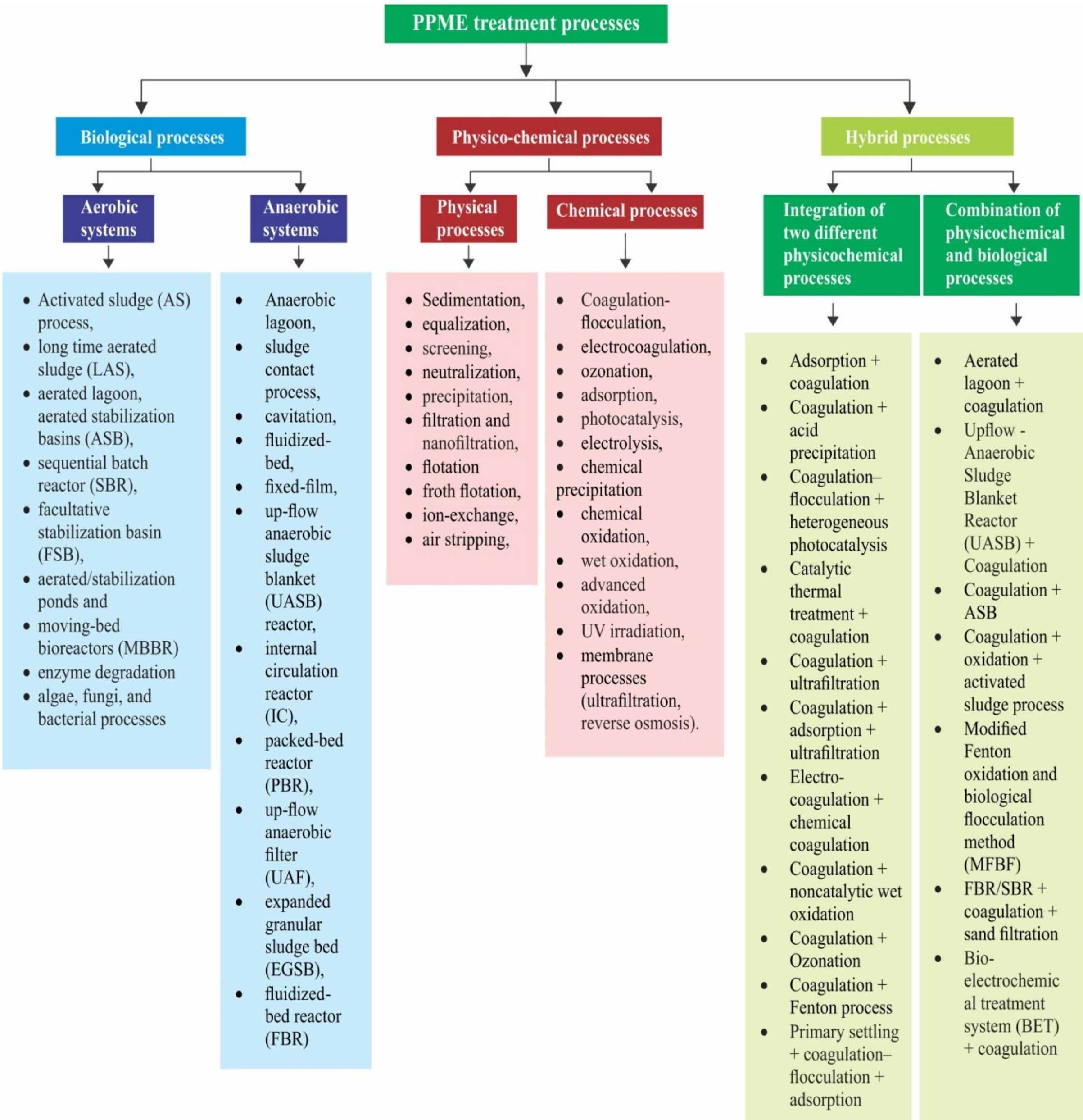


Fig. 3. Classification of PPME treatment processes

3.4.1 Physico-chemical processes

Physicochemical processes are typically used for PPME treatment at the pre-, post-, and advanced treatment stages (Gholami et al., 2020). The physicochemical processes can be sub-divided into physical and chemical processes.

(i) Physical processes

In PPM plants, the physical processes are utilized during primary clarification. The processes include sedimentation, equalization, screening, neutralization, precipitation, flotation and froth flotation, filtration. Sedimentation is the process by which the majority of suspended particles in wastewater are removed by the use of gravitational, centrifugal, and electromagnetic forces (Birniwa et al., 2021a). Froth flotation is a technique for selectively separating hydrophobic materials from a mixture of hydrophilic and hydrophobic components. This method is widely used in wastewater treatment (Jagaba et al., 2023).

(ii) Chemical processes

The chemical processes are mostly required and utilized during the tertiary treatment stage (Birniwa et al., 2022a). These include coagulation-flocculation, electrocoagulation, ozonation, adsorption, photocatalysis, electrolysis, chemical precipitation, chemical oxidation, wet oxidation, advanced oxidation processes, membrane processes, such as ultrafiltration, reverse osmosis. The primary merit of chemical treatment is that the majority of COD and TSS concentration are decreased during this procedure, and can result in cost savings prior to further treatment and the removal of color from effluent (Joanna et al., 2020).

There has been a surge in interest in electrochemical approaches, which are much more technical and cost-effective for large-scale use than other physicochemical treatment procedures. Electrocoagulation therapies might be viewed as prospective electrochemical treatment methods that are more effective in dealing with DOM at a high molecular weight than with low molecular weight chemicals. In PPME treatment under ideal working conditions, electrochemical treatment can improve biodegradability index from 0.11 to 0.46 while maintaining acceptable current efficiency and specific energy consumption (Chanworrawoot and Hunsom, 2012). Presence of powerful oxidants and coagulants, enhances the process performance of current wastewater treatments to improve the removal efficiency of humic chemicals, a precursor to trihalomethane (THM). The efficient method for THM control at treatment facilities currently according to the EPA, is "enhanced coagulation." Enhanced coagulation is a technique that enhances the filtering of wastewater contaminants to remove precursors. This technique is reported to be efficient by reducing process pH value to 4 or 5, increasing coagulant input rate, and use of ferric coagulants instead of alum to enhance removal (Abn and Lim, 2009).

Adsorbents are used to remove organic pollutants from wastewater via adsorption on carbon filters (Birniwa et al., 2021b). It may decolorize and remove refractory contaminants from PPME. Ion exchange resin and granular activated carbon adsorption methods demonstrated that they act on hydrophobic and high molecular weight fractions (Birniwa et al., 2023; Ciputra et al., 2010). However, it does not include the elimination of microbiological and other inorganic pollutants.

In general, advanced oxidation processes (AOPs) include the oxidation of complex substances by non-selective hydroxyl radicals produced by a sequence of complex events. Key references have examined the possibility of methods involving the application of various engineered nanoparticles for AOPs. This is mostly due to its economic viability and acceptable performance in the treatment of persistent contaminants found in PPME. However, further environmental and health hazards are a potential effects that needs to be studied (Kamali and Khodaparast, 2015).

Chemical precipitation allows the removal of both positive and negative ions (heavy metals, phosphates, sulphates etc.). It separates chemicals from dissolved components in wastewater by using a reagent to produce an insoluble compound with the substance to be separated (Abdullahi et al., 2020; Huuha et al., 2010). Using membranes increases microbial concentration and improves effluent quality. Minimal sludge generation, long sludge age, 100% removal of suspended particles, good effluent quality, high effectiveness in removing micropollutants, persistent organic contaminants and slow biodegradable contaminants are all advantages of MBR systems. This is due to membrane fouling by feed ingredients, which is the main issue with MBR systems. Solute molecules adsorb on the membrane surface, particles obstruct the pores, and suspended material deposits on the membrane surface forming a cake layer (Amaral et al., 2014). Resistance to filtration increases energy demand and cleaning frequency, which increases operational expenses. Diverse membrane methods have been used to remediate P&P mill waste. One of these technologies that can destroy pathogens is reverse osmosis (Li and Zhang, 2011).

3.4.2 Biological processes

Biological procedures are extremely good at treating newly created paper manufacturing effluents but are less effective for treating refractory paper manufacturing effluents (Mustafa et al., 2021). According to the research, PPME contains persistent organic compounds that are normally not biodegradable due to their BOD/COD ratios ranging between 0.02–0.07, which is far too low for efficient biodegradation (Birjandi et al., 2013). Samples having a biodegradability index < 0.3 are not suitable for biological degradation, as complete biodegradation requires an index of 0.40 (Birjandi et al., 2016a).

Biological wastewater treatment is low-cost, eco-friendly, and effective in reducing organic debris. To eliminate color and recalcitrant chemicals from PPME, standard biological techniques have failed (Kamali and Khodaparast, 2015). Thus, the typical PPME treatment methods could be adjusted to optimize the treatment of recycled paper effluents. If using biological treatment methods, pre-treatment is required to remove persistent elements that could be hazardous to microorganisms (Garg et al., 2010). The biological treatment processes are utilized during secondary treatment. They are designed to speed up natural decomposition processes and neutralize trash before it's released into the environment. It can be classified into two categories:

i. **Aerobic Systems (**Activated Sludge, Composting)

Organic matter + $O_2 \rightarrow CO_2$ + new cells ……………………………………………….……..… (1)

ii. **Anaerobic Systems (**UASB, Anaerobic Digester)

Organic matter $\rightarrow CH_4 + CO_2$ + new cells …………………………………………………... (2)

3.4.2.1 Aerobic process

Aerobic methods are preferred in most PPM due to their simplicity and low capital and operational expenses. They are normally run at low DO levels, and bacteria are exposed to times without DO An aerobic process contains many facultative bacteria (Gupta and Gupta, 2019; Kankia et al., 2021a). It also involves biofilm processes and biofiltration. Due to their wide pH range tolerance, metabolic diversity, and vast environmental adaptation in aerobic treatment, bacteria have demonstrated greater biodegradation potential (Usman et al., 2022).

Most PPM use aerobic biological wastewater treatment process. The use of organic molecules, on the other hand, results in a substantial carbon supply shortfall for anoxic denitrification. Activated sludge (AS) process, long time aerated sludge (LAS), aerated lagoon, aerated stabilization basins (ASB), sequential batch reactor (SBR), facultative stabilization basin (FSB), aerated/stabilization ponds and moving-bed bioreactors (MBBR) are the most widely employed aerobic techniques in the treatment of PPM. In PPM, AS and aerated lagoons are regularly employed aerobic technologies. In addition, activated sludge facilities create sludge with variable settlement qualities, are susceptible toxicity, shock loading, and have limited capacity to extract poorly biodegradable hazardous compounds (Muhammed et al., 2023).

SBR was recommended over AS for wastewater treatment because it produces less sludge, allows for wastewater treatment at a higher organic loading rate, and has better sludge settling qualities. The pulp industry's treatment technologies, which are often activated sludge or aerated ponds, can achieve an average decrease in BOD of 90 and 95%, but only between 40-60% in COD. The primary issue with these effluents is the presence of highly hazardous chemicals. Numerous these compounds possess significant resistance to chemical and biological degradation, owing to their hydrophobic properties, hence amplifying their toxicity via bioaccumulation (Amaral et al., 2014).

3.4.2.2 Anaerobic process

Anaerobic processes that include anaerobic lagoon, sludge contact process, cavitation, fluidized-bed, fixed-film, up-flow anaerobic sludge blanket (UASB) reactor, internal circulation reactor (IC), packed-bed reactor (PBR), up-flow anaerobic filter (UAF), expanded granular sludge bed (EGSB), and fluidized-bed reactor (FBR) have been utilized to treat PPME (Kamali and

Khodaparast, 2015). The economic and environmental merits of anaerobic processes over the aerobic processes are lower sludge production, lower chemical consumption, design simplicity and non-sophisticated equipment requirement, applicability in different scales, smaller space requirements due to smaller reactors usage, accommodating high organic loading rates, high rate of pathogen destruction with renewable energy production in the form of biogas (methane and CO_2), capability of retaining microbes with special functions, cost-effectiveness with regards low operating and capital cost and achieve maximum treatment efficiency while keeping hydraulic retention times to a minimum. According to a study, the pollutant removal efficiency of anaerobic processes was found to be harmed by high Sulphur concentration in chemical pulping effluent, especially at low pH levels (Salkinoja-Salonen et al., 1984). Additionally, anaerobic microbes have been shown to be more susceptible to hazardous chemicals than aerobic microorganisms (Gupta and Gupta, 2019).

The rigorous regulation of nitrogen discharge and the potential impact of PPME components during the biological treatment stage, calls for a growing requirement for enhanced research on their treatment and disposal. The coagulation-flocculation system and coagulation-based hybrid processes for pulp wastewater treatment will be the subject of this paper.

4.0 Coagulation-flocculation for PPME treatment

4.1.1 **Coagulation**

Coagulation is a process for combining colloidal and suspended particles and/or DOM into large aggregates. As a result, following sedimentation/flotation and filtering steps will be easier to remove them. Materials are added to wastewater to destabilize colloidal materials and drive microscopic particles to clump together into larger settleable flocs, which is a common wastewater treatment process (Kim, 2016). It is seen to be a potential solution for pollution load reduction, generation of huge water recovery, and the removal of suspended solids and organic substances (Wei et al., 2011). The size and shape of the floc, which is a porous, loosely associated aggregate made of several main particles, affects the pace upon which organic contaminants are removed. Floc structure is uneven and disordered, but it has fractal characteristics such as self-similarity and scale parallelism (Li et al., 2016).

Coagulation-flocculation as a pre-treatment or principal treatment technique is frequently used to eliminate suspended solids and natural organic matter from PPME for the first treated wastewater to contain less harmful solids. This can enhance the biodegradability of the effluent during the subsequent wet air oxidation process or biological treatment (Subramonian et al., 2014). Nevertheless, some studies have indicated that it is utilized in the tertiary treatment of PPME (Chaudhari et al., 2010). The study by authors (He et al., 2016) considers the coagulation process following biological treatment to be a techno-economically realistic for high-strength effluents. For boosting all-inclusive primary treatment efficiency, coagulation is habitually compatible with several other treatment procedures. It is a reliable technology for the treatment of high suspended particles wastewater, particularly those generated by colloidal matter, followed by sedimentation (Birjandi et al., 2016a). The process makes the wastewater easily filterable. Coagulation/flocculation have several advantages. It is a relatively simple technique that is effective and inexpensive. It is convenient to operate. It is highly efficient in water purification and wastewater treatment and has low capital cost.

4.1.2 Weakness of coagulation

The essential difficulty of coagulation has been defined as the selection of a coagulant and the calculation of its appropriate dose. Coagulant doses that are either low or too high can reduce coagulation capability. In the optimal coagulant dosage environment, excessive coagulant dose can result in partial discharge of coagulated sewage sludge due to produced sediment peptization. Chemical coagulants that have not been hydrolyzed are being displaced by coagulants that have been pre-hydrolyzed as they are thought to be somewhat more efficient in extracting eliminating chemicals that produce water color and turbidity (Joanna et al., 2020). However, their application in the coagulation process is associated with the following drawbacks: (i) lack of effectiveness at low temperatures, (ii) comparatively high procurement prices, (iii) negative health impacts, (iv) enormous sludge quantities, and (v) processed water with high pH., inappropriate chemical coagulation can result in significant aluminum residuals in treated water, as well as particle precipitation after treatment, creating turbidity, deposition, and pipe coating in the water distribution network. According to numerous studies, elevated concentrations of alum in the brain can induce Alzheimer's disease and several other neurodegenerative illnesses. As a result, alternate alternatives to chemical coagulants are required (El Gaayda et al., 2021). Tiny flocs or fragile flocs that split when exposed to physical forces may occur from too low a temperature during coagulation. As a result, flocculation is required to tackle these challenges and aid the quick sedimentation of flocs to achieve high effluent quality. Different materials like coagulant aids, could be used to improve sedimentation by increasing floc density. Coagulant aids include ionic, polymeric, or other compounds that can improve floc quality through a variety of ways. Therefore choosing the right one is critical for effective coagulation (Saraswathi and Saseetharan, 2012).

4.2 Flocculation

Flocculation is an effective and special economical separation process that typically employs a charged polymer (Kurniawan et al., 2022c). It is commonly utilized in paper mills for both the production of paper and the treatment of wastewater. It's a low-cost secondary treatment method for removing colloids, persistent organic matter, turbidity, dyes, suspended solids, chromaticity, fine particles, and heavy metals from wastewater (Zeng et al., 2012). It can be used to recover fibers from effluent as well (Mukherjee et al., 2014). Charged amide or carboxylic groups cause suspended particles to flocculate. Particles agglomerate during the flocculation process, resulting in larger flocs. They're tightly linked and much denser than individual particles. The sedimentation of the particle's aggregates is aided by increasing the total mass. Focused beam reflectance microscopy is widely used to assess flocculation activities, whereas laser diffraction spectroscopy is being used to study the evolution of floc features and flocculation kinetics (Maćczak et al., 2020).

According to the flocculant adsorption theory, composite flocculants have a superior coagulating influence than single-use flocculants, and "inorganic/organic" composite flocculants are superior to "inorganic/inorganic" and "organic/organic," because inorganic flocculants' main role to adsorb colloid is nicer than organic, but their chelating and bridging function is weaker compared to organic macromolecule flocculants (Ming et al., 2021). As a result, using both inorganic and organic flocculants together offers complimentary benefits and synergy to increase coagulation and settling performance. The composite flocculant could increase depositing velocity and adsorption rate by flocculating micro colloid into bigger flocs and improving the degree of polymerization and cohesive force of the flocs. It is recognized above all by exceptional quality and an affordable price (Zeng et al., 2012).

Flocculation is usually done with a charged oligomer or polymer (polyelectrolyte). Given the tiny size of molecules and high stability of the wastewater medium, chemicals that stimulate colloidal mixture instability and promote sub-millimeter particle agglomeration are needed, resulting in the development of flocs that can settle in seconds to hours (Grenda et al., 2020). Flocculants are chemicals that aid in flocculation. Flocculation performance is influenced by the characteristics of flocculant, its molecular weight, ionic nature, and wastewater type and suspension content. Flocculants with similar functional groups but varying molecular weights, chain topologies (linear or branching), and charge characteristics can have quite varied flocculation processes (neutralization or bridging) and effectiveness. As a result, using organic polymer structure-activity correlations to create high-performance flocculants and optimize the conditions in which they should be utilized in water treatment is beneficial (Razali et al., 2011). Molecular weight, charge type and density of the flocculant are important characteristics that determine the mechanism of flocculation and subsequent floc sedimentation. The available surface area, type, charge, and size of suspended particles, as well as the pH of the medium, all have an impact on the flocculation process' efficacy. Thus, a thorough understanding of flocs structure, flocculation kinetics, and associated mechanisms is critical in determining the best treatment circumstances, taking into account potential follow-up treatments (Guo et al., 2019).

Synthetic organic polymers, also known as polyelectrolytes, and natural polymer-based flocculants are the two main types of flocculants. Synthetic flocculants are the most extensively employed in wastewater treatment. Certain petroleum-based monomers found in synthetic flocculants, on the other hand, have the potential to be harmful to soil, and their non-biodegradability poses more severe problems in the natural environment (Zhu et al., 2015). These flocculants are expected to be biodegradable, renewable, highly reactive, non-toxic, with no secondary pollution to natural environment (Zeng et al., 2012). Polymeric flocculants have the benefit of producing compact, large, dense, and stronger flocs with excellent settling characteristics as compared to coagulated flocs. It can also help to lessen the volume of sludge. The performance of polymers is less affected by pH. It does not require residual or metal ions addition, and the alkalinity is maintained (Wong et al., 2006). Polyacrylamide (PAM) is a widely utilized polymeric flocculant since it is simple to synthesize with a variety of negative, positive, and neutral charge functionalities and may be employed to achieve superior settling capability at a cheap cost (Kim, 2016). The bioflocculant seems to be another type of flocculant. It's a type of macromolecular flocculant secreted by microorganisms that's biodegradable, non-toxic, and doesn't pollute the environment. They are widely useful in water and wastewater treatment, downstream processing, and food/chemicals processing (Gong et al., 2008). The traditional inorganic polymer flocculants have demerits of high dosage, sludge production, pH sensitivity, with low performance (Wu et al., 2010). In comparison to inorganic flocculants, organic flocculants offer a broader range of applications. Due to their great water solubility, low market price, high reactive activity for free radical polymerization, acrylamide-based polymers and derivatives are the most extensively used organic flocculants (Wang et al., 2019). Anionic polyacrylamide was added to ferric sulphate and PAC in a study. It increased the settling speed by a significant amount (Ahmad et al., 2008).

4.2.1 Flocculants/coagulant aids

Flocculants are divided into three categories: (i) mineral supplements such as PAC, synthetic organic polymers, and (iii) flocculants found in nature (Renault et al., 2009). Interestingly, recovered lignin from pulp wastewater can be used as a flocculating agent and fuel. Other flocculants include magnesium hydroxide, cationic polyacrylamide (c-PAM), calcium lactate, chitosan-g-PDMC, g-PAM-gPDMC, PVPg-PAM, locust bean gum, anionic polyacrylamide (APAM), and poly-diallyldimethyl ammonium chloride (polyDADMAC).

4.3 Theory and mechanism of coagulation/flocculation

The coagulation process is being used in wastewater treatment to clump small particles with each other to generate larger flocs that are easier to extract from the water after settling. Very small colloidal particles with an extraordinarily wide surface area and larger than atoms, are found in suspended particles greater than 1.0 μm in water. They are normally undetectable to the eyesight with sizes varying from 0.001 to 1.0 μm (Ghorbannezhad et al., 2016). The instability of colloids and suspended matter, as well as two key mechanisms of sweep flocculation & charge neutralization, can be used to separate organic molecules from wastewater in the presence of coagulants. The interactions amongst colloidal particles (contaminant) and the coagulant supplemented are explained by coagulation processes. The coagulant is vigorously stirred to dissolve and spread equally all over the water body while encouraging particle collisions. Improper mixing can cause partial coagulation; additionally, extensive mixing can disrupt coagulation, breaking interparticle bridging and causing instability. As soon as the coagulants successfully neutralize the charges, the suspended particles start to aggregate together, forming flocs (Owodunni and Ismail, 2021). The coagulation process is made up of four main processes for destabilizing colloidal particles in wastewater by applying a coagulant (Choudhary et al., 2015). As shown in Fig. 4, these processes are diagrammatically depicted.

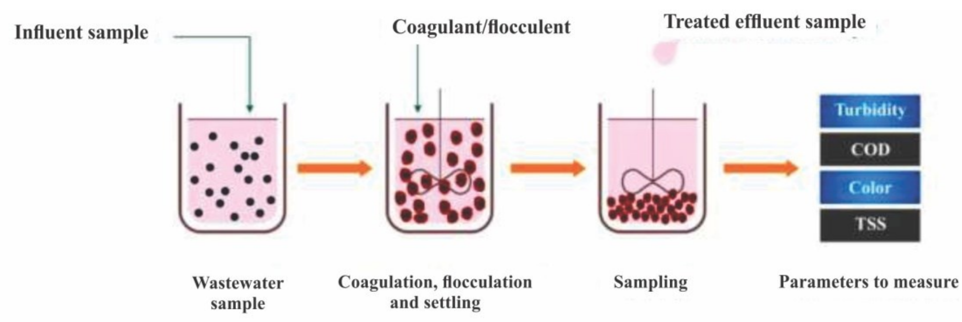


Fig. 4. Schematic process flow diagram for the coagulation-flocculation of PPME (Gholami et al., 2020)

The flocculation mechanism encourages flocs to cluster in the aqueous medium. After a complete quick mixing, an average mixing signalizes the start of the flocculation process, in which the particles' surface charge is lowered and their electrical attraction increases, resulting in flocculation. As both the particles clump together, they form an aggregate, their sizes grow larger, and the suspended particles become more visible. Larger flocs are generated as particles collide and interact as shown in Fig. 5, and they begin to settle at the bottom as readiness for the sedimentation process (Owodunni and Ismail, 2021).

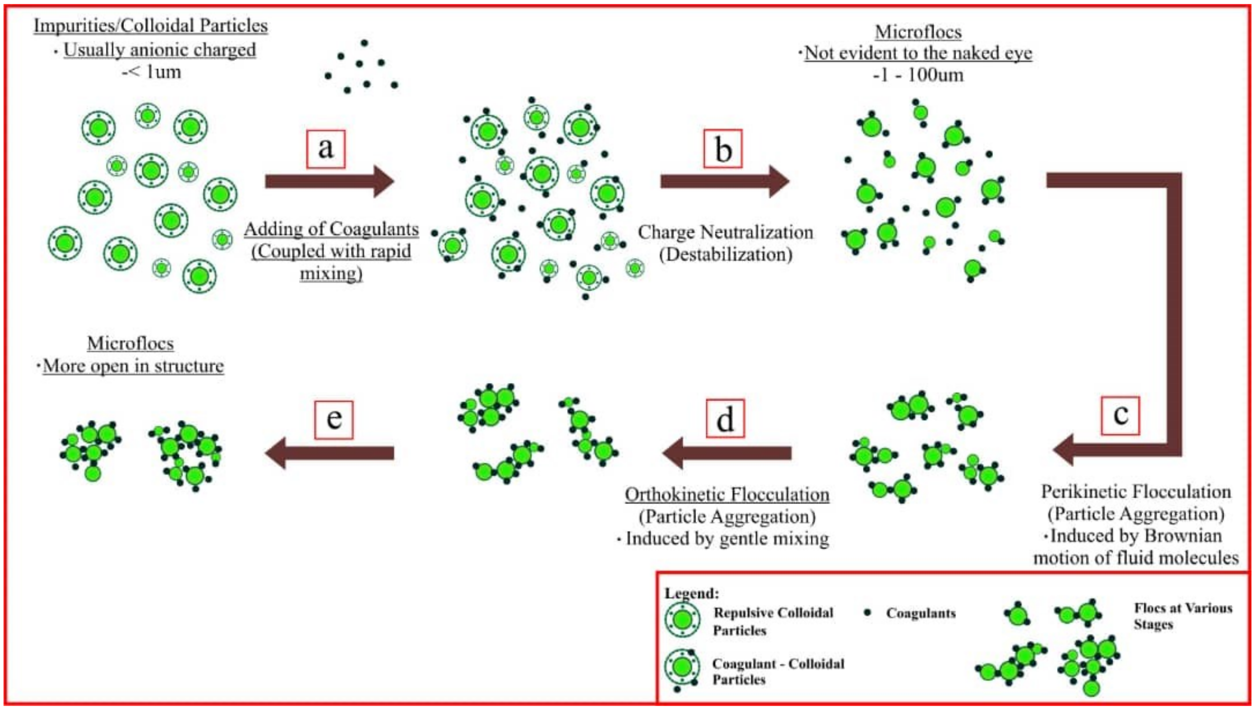


Fig. 5. Coagulation-flocculation mechanism of particles in wastewater (Choy et al., 2015)

(i) Sweep flocculation

The enmeshment of the contaminant mechanism occurs when the coagulant traps the suspended particles and causes them to settle at the bottom. The hydrolysis process that results in the precipitation of amorphous metal hydroxide produces a net-like structure. The hydrolysis of coagulants in wastewater leads to the generation of metal hydroxides. It has already been established that organic contaminant precipitate because of 'sweep flocculation,' which involves the entanglement and adsorption of suspended impurities in cationic metal hydroxides. The primary structure driving to sweep flocculation is the development of coagulant precipitates with the administration of substantial coagulant dosages. These particles may serve as nucleation sites, allowing precipitation to form more quickly. Sweep flocculation produces flocs that settle well but form at a slower rate. It also generates huge amounts of sludge due to high coagulant dosage utilization.

(ii) Double-layer compression

This process helps fine particles to resist the force of repulsion and pack together in wastewater. The presence of a high concentration of electrolyte ions all around colloidal causes an opposite charge to penetrate the diffused double layer that surrounds the colloids, resulting in higher density with a reduced volume (Alazaiza et al., 2022). This causes attractive van der Waals forces to overwhelm repulsive electrostatic reactions, leading to steeper electrostatic potential gradients. The particles approach each other and cluster as the net repulsive energy declines and reaches elimination. Because of the high aggregation rate, the resulting flocs are quite large. However, the efficiency of this coagulation mechanism is debatable, and it is normally avoided since the superfluous friction force created between flocs affects their settling behavior (Sulaiman et al., 2017).

(iii) Charge neutralization

The mechanism employs the attraction of oppositely charged electric ions to destabilize particles. The particle charges neutralize the electrical burden because of coagulant injection till the zeta potential hits zero. It is a sure sign of the appropriate coagulant dosage necessary for complete charge neutralizations when the net charge is approaching zero. Electrostatic repulsion would be reduced or eliminated because of this. The suspended colloids aggregate to form bigger flocs, resulting in flocculation (Alazaiza et al., 2022). Although they rely on physical interactions, the flocs created here have been compacted but not robust. Since particle instability can readily occur after the optimum dosage is surpassed, the efficiency of this mechanism is highly dependent on the coagulant dosage used. The pH range of 4-5.5 is the most suitable for charge neutralization (Nawaz et al., 2014).

(iv) Adsorption and bridging

The mechanism ensues when the coagulant produces a polyelectrolyte or polymer chain that can destabilize colloidal particles by forming bridges that can connect numerous particles to the coagulant. Because of the longer polymeric chains, bridging efficiency is boosted even more when greater molecular weight coagulants are utilized (Choy et al., 2015). As the colloidal particles are bound with each other through bridging, the polymer molecules adsorb to the surface of numerous particles, forming powerful clusters of macro flocs. Polymer bridging produces flaky flocs with uneven empty regions. Adsorption and bridging enmeshment cause particle organic and inorganic substances to form massive, amorphous flocs. Adsorption of dissolved organics onto the metal hydroxide coagulant surface as depicted in Fig. 5 is the most common method of precipitation (Garg et al., 2010). Through the basic coagulation mechanisms, pollutants and coagulant particles agglomerate and settle out in solution.

4.4 Jar test for efficient coagulation process

Coagulation process is mostly undertaken by administering small/accurate quantity of coagulants in a laboratory scale mechanically stirred jar test experimental set-up (see Fig. 6) during the treatment of PPME. On the basis of floc images on GRViewer, the fractal dimensions of the flocs, initial floc aggregation, flocculation index, and relative settling factor during coagulation were examined (Li et al., 2016). Although just a little amount of sample is needed for biochemical analyses of the coagulation assay, the water required for the analysis should be available in sufficient quantities for every experiment (Lawal et al., 2021). The coagulant extract is mixed in with the wastewater sample and homogenized right away. After completely mixing the solution, it is gently swirled to allow the rejected suspended particles to charge to the cationic stock solution. The fast mixing, which is normally done for a small period, occurs in second fractions, but the slow mixing, which takes much longer, accelerates the electrostatic flocculation, and allows larger flocs particles to condense the effluents. Slow mixing allows for adequate floc sedimentation, aggregation of heavy particles, and settling out to the underside of the container, resulting in sludge formation at the bottom and typically clean supernatant (Sulaiman et al., 2017).

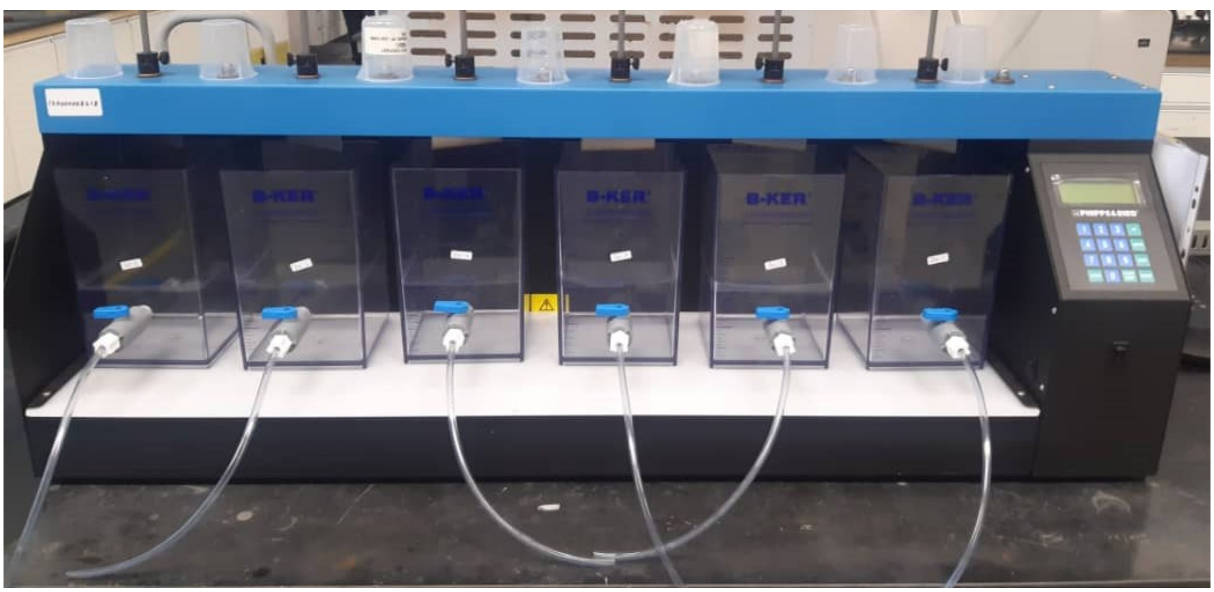


Fig. 6. Jar test apparatus

4.5 Factors that influence coagulation process efficiency

Coagulation-flocculation process efficiency depends on operating conditions involving several factors described in Fig. 7. These factors determine the process effectiveness, cost, and quality of the produced water (El Gaayda et al., 2021). The optimum condition for all factors to boost the efficiency of coagulation determined from the Jar-test results are used in practical application (Zheng et al., 2011). Contaminant removal is strongly influenced by the wastewater pH. The composition of the wastewater has an impact on the optimal pH range. This could change if certain substances or compounds are present. Lowering the pH leads lignin molecules to clump together, resulting in precipitation (Garg et al., 2010). Every coagulant has a pH range that is optimal for it. For very alkaline wastewater such as PPM, alum is often more efficient in the pH range of 4.5-7.0, while $FeSO_4$ is efficient in the pH range of 4-7. In chemical coagulation studies, using metal coagulants decreases the pH of the system.

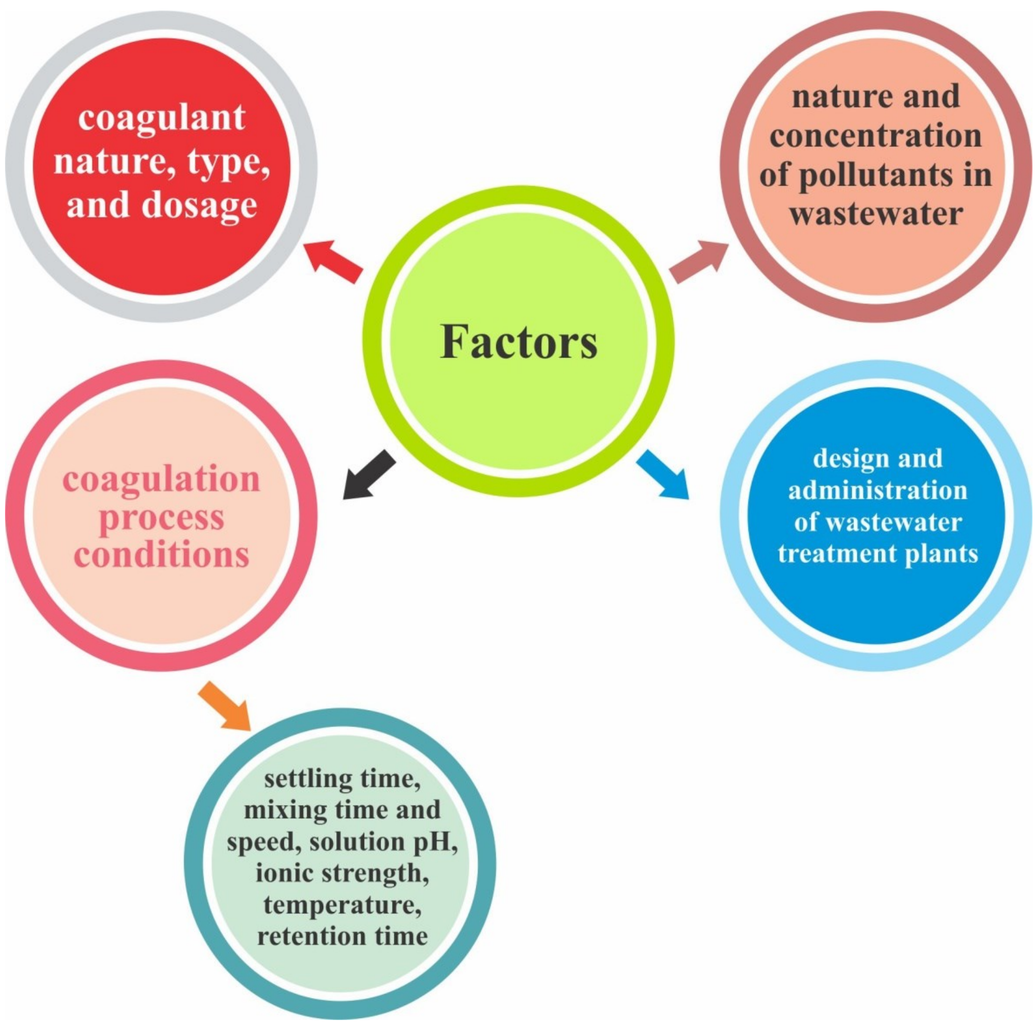


Fig. 7. Factors that influence coagulation-flocculation process efficiency

While eliminating toxins from wastewater, selection of the coagulant to be used is crucial. Coagulant dosing is also essential since the process necessitates caution and precision to attain the desired grade of treated water. The operator's knowledge and the manufacturer's authorized techniques are used to determine coagulant dosage on a continual basis. Given the lack of process improvements, low coagulant dosage frequently results in substandard treated water quality. As a result, determining the optimal range of coagulant dosage needed to accomplish maximum turbidity removal at the lowest treatment cost is critical. There are three distinct dose scenarios: underdosing, optimum dosing, and overdosing. Fig. 8 shows the impact of coagulant dosage on particle agglomeration efficiency via charge neutralization and bridging. Because of the stoichiometric connection, the mechanisms are negatively impacted. When the optimal coagulant dosage is surpassed, particle instability is likely. Due to total surface coverage of the coagulant, overloading of coagulants in a solution reduces the number of adsorption sites accessible for particle bridging. As the charge neutralization point is reached, the strength of the repulsive force between the particles weakens as the dosage of polymer coagulant is gradually raised. As a result, adding more coagulants won't make the coagulation process any better (Öztürk and Özcan, 2021). A very much lower than required coagulant dosage on the other hand, would result in incomplete and ineffective coagulation because most of the colloidal particles would remain in suspension (Choy et al., 2015). The coagulant dosage should be adequate for a good particle suspension, and the mixing speed must be high. The stability of the coagulant throughout storage is determined by other coagulant parameters like life span and quality (Alazaiza et al., 2022).

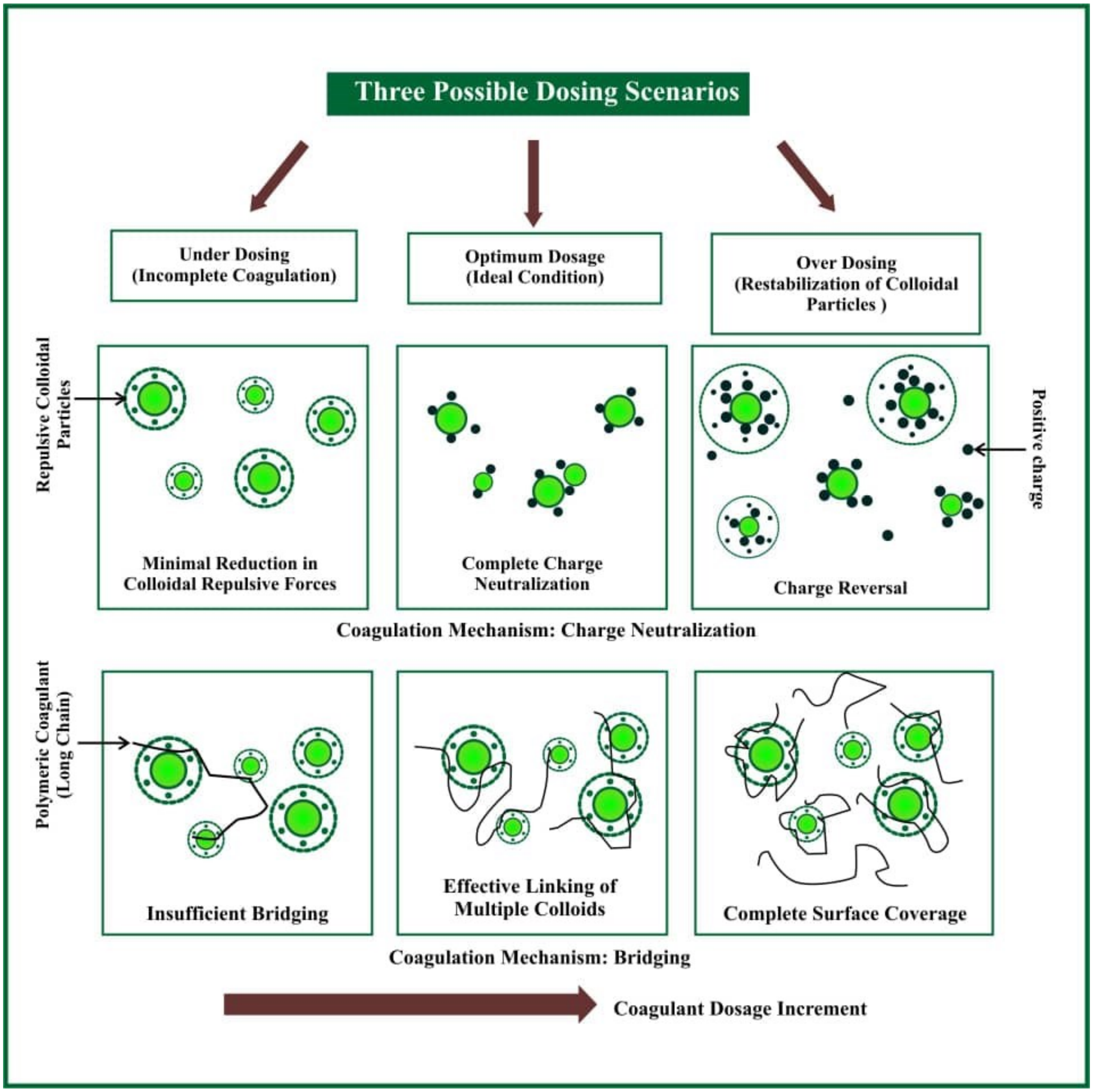


Fig. 8. Impacts of coagulant dosage on bridging and charge neutralization mechanisms (Choy et al., 2015).

Zeta potential (ZP) affects coagulation-flocculation process. It gives crucial insight into the effectiveness of the chemicals used and may shorten the time it takes to achieve stability prior to settling. The zeta potential analysis and electron microscope images of the flocs created could provide greater insight into the coagulant's main mechanism. The ability to anticipate the optimal coagulant dosage needed to induce efficient coagulation is greatly aided by the measurement of zeta potential. Because there is no electrostatic repulsion when the zeta potential is decreased to zero, optimal flocculation is attained (Ordaz-Díaz et al., 2017). The effluent from different paper factories differs significantly, owing to the variety of raw materials utilized and the technologies used in the industry. The coagulation process is affected by these changes in raw effluent quality (Boguniewicz-Zablocka et al., 2020).

4.6 Process optimization

Generally, in order to increase the effectiveness of coagulation process in unit operation, process parameters that influence the treatment process must be optimized. It has the potential to greatly improve process efficiency. It improves the effluent quality, lowers expenses, and makes the operations easier to carry out (Gholami et al., 2020; Yaro et al., 2023a). Due to the great complexity of the coagulation process and the range of available polyelectrolytes, process optimization has primarily relied on "trial - and - error" to discover the most cost-effective and optimal conditions during coagulation-flocculation (He et al., 2016). The use of the classical optimization strategy "one-factor-at-a-time approach (OFAT)" to explore the effect of variables on the response in traditional multifactor experiments seems to be no more suggested because it leaves all other factors constant at a certain set of conditions (Yaro et al., 2023b). It is also expensive, time-consuming, labor-intensive, and doesn't account for the effects of interactions among variables in multivariable systems. As a result, the process must be carried out consistently and statistically. Statistical experimental procedures, in contrast to traditional approaches, recommend simultaneous, systematic, and efficient variation of all components. They also show how to improve a process in the most efficient way possible. In recent times, Artificial Neural

Networks (ANNs), Response surface methodology (RSM) (Yaro et al., 2022; Zheng et al., 2011), and grey relational analysis (GRA)-based Taguchi (Saraswathi and Saseetharan, 2012) method are used in several industrial processes with output summarized in Table 1.

RSM is a widely used optimization technique in many industrial processes, including chemical engineering, wastewater treatment, biotechnology, food chemistry, and material science (Yaro et al., 2023c). The objective is to optimize experimental variables, model chemical, biological or physical processes and investigate the impact of operating factors (Ghorbannezhad et al., 2016). This provides information on direct, pairwise interaction, and curvilinear variable impacts on a certain response. It's also a cost-effective method for quantifying the individual and interaction effects of process parameters, even in the presence of complex interactions, as well as predicting the optimum response parameter values within the experimental range of investigation (Usman et al., 2021). The first step of RSM as depicted in Fig 9 requires the specific design selection. Among RSM's different design approaches, such as Box-Behnken Design (BBD), Doehlert Design (DD), Full Factorial Design, and Central Composite Design (CCD) which was perhaps the most popular. The following step is to apply proper assumptions to discover a true relationship between the collection of independent and dependent variables (Yaro et al., 2021). Whenever the linear model is inadequate to explain the shape of the response surface, a model is upgraded by applying higher order terms to the preliminary model.

As a result, a quadratic equation, as defined in Eq. 3, is used to describe the linear model (3)

$$f(x) = \beta_0 + \sum_{a=1}^{c} \beta_a x_a + \sum_{i=1}^{c} \sum_{b \geq i}^{c} \beta_{ab} x_a x_b + \varepsilon \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

RSM uses an experimental design to fit a model by least squares technique. Analysis of variances (ANOVA) is used to reflect significant quadratic models and graphically analyze the data to obtain the interaction between the process variables and the responses. The range and level of variables are presented in coded units. The interaction among the considered factors with the response are mostly shown in three dimensional plots. The coefficient of determination R^2 expresses the correctness and quality of the fit polynomial model, and the Fisher *F*-test in just the same application checks its statistical significance. The *P* value (probability) with a 95% confidence level is used to choose or reject model terms. The contour plots are created using the impacts of the factors being researched (Yaro et al., 2023d). The optimum region for maximum contaminant removal as well as maximum biodegradability index could be identified based on the primary characteristics in the contour plots.

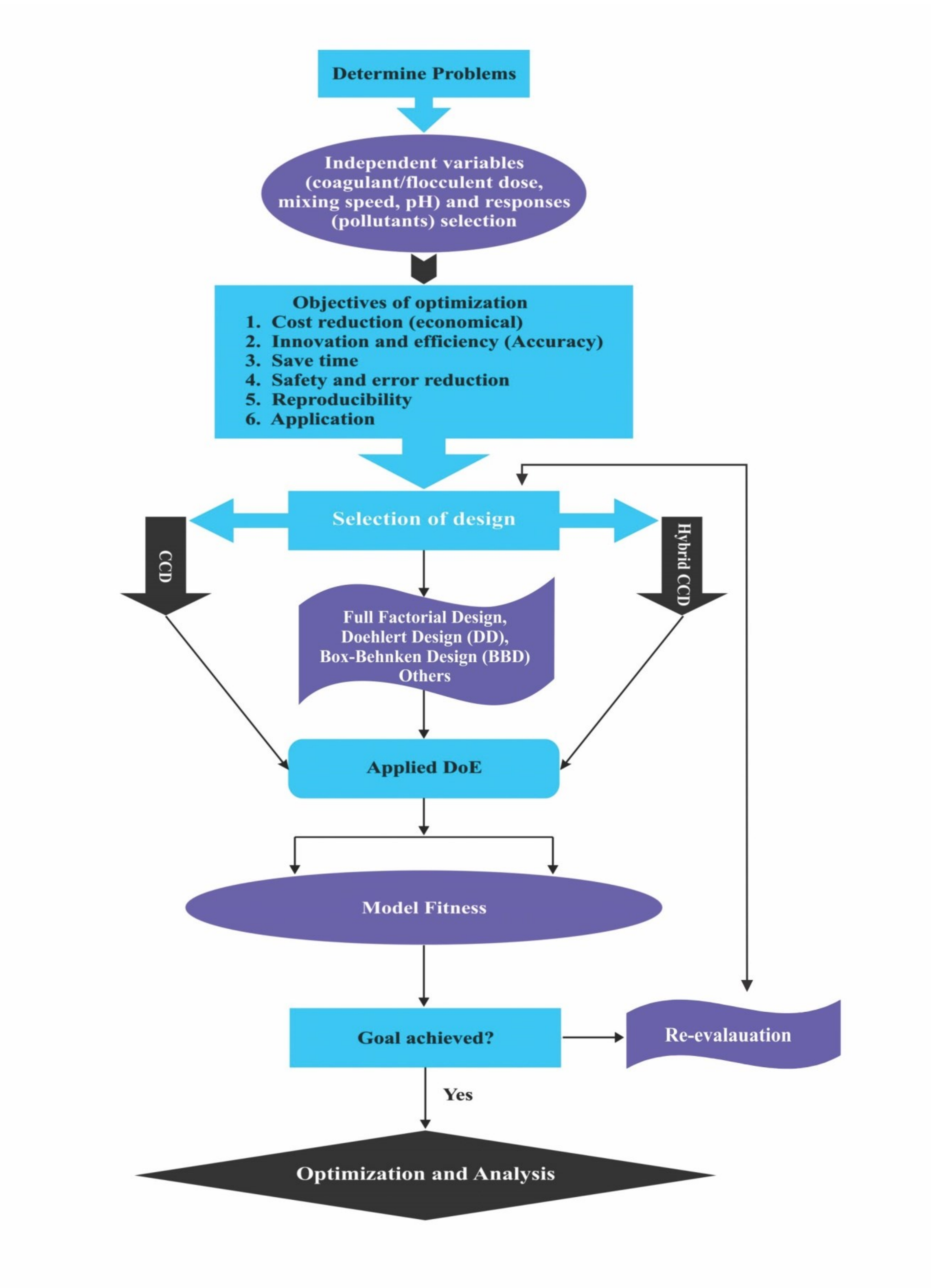


Fig. 9. Schematic model chart for process optimization by RSM (Pandey and Thakur, 2020)

In RSM, having a lot of experimental factors increases the number of coefficients in the quadratic model equation and the number of experimental trials exponentially. Uniform design (UD), which dictates the number of experimental trials simply by the level of factors instead of the number of factors, can be used to study additional factors with vastly fewer experimental trials to solve this problem. Whenever the underlying model in between responses and factors is unidentified or partially unidentified, UD is able to select experimental points uniformly in the experimental region and strongly representative in the experimental domain; it seeks to impose no strong assumptions on the model and can be used when the underlying model between the responses and factors is unknown or partially unknown; and it can cater for the highest number of levels for each factor across all experimental designs. As a result, coupling of UD and RSM might optimize a complex multivariate coagulation process with the fewest multilayer experiments possible (Wang et al., 2011a). The parameters of the response equations, as well as the associated study on variations, might be analyzed using Uniform Design Software.

Artificial Neural Networks (ANNs) is termed a biological neural network motivated statistical modelling approach because brain neurons can be trained to spot patterns and identify trends in non-specific and tedious non-linear data. It is an effective tool for describing and characterizing non-linear phenomena among coagulation's affecting components, as well as forecasting coagulation efficiency. It's a soft computing technique and good predictor that can make generalized observations from original data and derive proper inferences based on the population's latent component. The precision of their conclusions contributed to their widespread acceptance as forecasting models by researchers from various domains, and they were proven to be effective in solving nonlinear issues (Adeogun et al., 2021).

The most extensively used software tool, MATLAB 7.5 or 8.5, can be used to create a neural network model. The radial basis function (RBF) neural network is a popular feed-forward network in artificial neural networks. Fractal analysis has already been widely used in the field of environmental science. Many variables have been shown to be fractals with changing dimensions, which is valuable for separating scales of variation. As a result, fractal theory may have a potential application in numerous areas of coagulation, and its advances could be applied to flocs structure characterization. The fractal structure of flocs and their particle size are two important physical features that influence the effectiveness of unit processes in water/wastewater treatment plants. An upturned optical microscope can be used to examine the fractal structure of the flocs generated during the coagulation–flocculation process (Zheng et al., 2011).

The RBF model had a remarkable predicting power, implying that these factors were interconnected and had a significant impact on coagulation efficiency. Several studies employed a variety of non-linear functions to depict the relationship between various coagulation parameters. However, network could be better optimized than non-linear functions. As a result, the neural network should be utilized more frequently. The findings of the fractal dimensions revealed that the flocs structure had fractal properties with a high degree of self-similarity. With larger cutter sizes and higher COD removal effectiveness, the flocs got denser, and the fractal dimension of the produced flocs rose as well (Adeogun et al., 2021).

Taguchi approach based on grey relational analysis (GRA) to handle many performance variables necessitates research. GRA offers a wide range of applications in terms of determining ideal parameters for various treatment processes. GRA and analysis of variance (ANOVA) for the grey relational grade (GRG) were used to predict optimal combinations of coagulation–flocculation process parameters. The most significant parameter in GRG's ANOVA for several performance indicators was coagulant aid dosage. With the usage of GRA, performance features of coagulation– flocculation process parameters improved simultaneously. Equation (4) was used to compute the estimated GRG (γi) with optimal amounts of coagulation– flocculation process parameters:

$$\gamma = \gamma_m + \sum_{i=1}^{q} (\gamma_i - \gamma_m) \quad \text{------------------------------} \quad (4)$$

where γ_m = total mean GRG, γ_i = mean GRG at the optimal level, and q = number of machining parameters that have a substantial impact on a variety of performance aspects.

1 **Table 1.** Optimization, and removal efficiencies of PPME contaminants by coagulation-flocculation

Optimization of PPME treatment by coagulation-flocculation													
Influent characteristics	**Optimization techniques**	**Specific design method**	**Independent Variables**	**Responses**	**Coefficients of determination R^2**	**Coagulant**		**Flocculant material type and dose**	**Jar test operational conditions**	**Optimum condition (s)**	**Pollutant removal efficiency (%)**	**Findings**	**Ref.**
						Material type	**Dose**						
6.5 pH, 80.6 NTU, 156 COD; 41 BOD_5 (mg/L)	RSM	Box–Behnken	Coagulant dose, mixing speed, pH	Turbidity	0.657	Alum, Guar, Xanthan, Locust bean gums	1.5-5.0 mg/L	-	185 r/min flash mixing speed. 40 r/min slow mixing speed. 30 min settling	0.5 cm/min settling vel.	97.46 alum, 94.68 Guar 92.39 Xanthan and 92.46 Locust bean gum	With low inaccuracy of 3.62%, the produced model was an adequate prediction of SVI. At a desirability of 0.84, the anticipated SVI value was 5.63 mL/g.	**(Mukherjee et al., 2014)**

											turbidity		
7.2 pH, 841 TSS; 1453 COD (mg/L)	RSM	central composite design (CCD)	Coagulant dosage, Slow-mixing time	TSS, COD	0.9847	Cassia obtusifolia seed gum with alum	0.09 - 1.79 g/L	-	Flash-mixing at 150 rpm for 5 min. Slow mixing speed of 10 rpm and 3 min. time to settle.	0.17 g/L *C. obtusifolia* seed gum and 0.09 g/L alum dosages, at 3.4 min slow mixing	89.6 TSS, 55.4 COD	Alum and *C. obtusifolia* seed gum dosages might be lowered by up to 90.5 and 62.5%, respectively.	(Subramonian et al., 2015)
7.8 pH, 752 NTU, 825 TSS; 3257 COD (mg/L)	RSM	CCD	Coagulant and flocculent dose, pH	SVI, TSS, COD	0.979	Polyaluminum chloride (PAC)	1-5 g/L	Cationic polyacrylamide (c-PAM) 10–50 mg/L	1 min. of rapid mixing at 250 rpm. 30 min of slow mixing at 30 rpm	3690 mg/L PAC, 40.1 mg/L PAM, 5.41 pH, 89.1 mL/g SVI	35.3 COD, 77.5 TSS	The dose of PAC and c-PAM ensured that the netting mechanism worked well.	(Kim, 2016)

									30 min. of settling				
6.75-7.2 pH, 8000 PtCo, 1360 – 4200 FTU, 4553 BOD_5; 3740-5990 TSS; 6000-7000 COD (mg/L)	RSM	central composite rotatable design (CCRD)	Contact time, pH, alum:*Ocimum basilicum* ratio	SVI, TSS, BOD_5, COD	0.970	*Ocimum basilicum* (basil mucilage)	200-2000 ppm	-	5 min. of rapid mixing at 120 rpm, 5 min. of gradual mixing at 40 rpm. Settling time is 5-60 min. at pH 2-12.	alum:*Ocimum basilicum* ratio of 2.8, 8.3 pH, 49 min settling time, 129 ml/g SVI.	85 color, 82 TSS	Study discovered that the experimental values deviated from the forecasted data by 0.9% and 2.35% in TSS and color removal.	(Mosaddeghi et al., 2020)
5.5 pH, 3500 NTU, 1700 BOD_5; 4500 TSS; 4800 COD (mg/L)	RSM	CCD	Coagulant dose, pH, mixing time	COD, TSS, turbidity	0.998	Alum, PAC, and polelectrolyts (PE)	500-1500 mg/L	-	15 min. of slow mixing at 40 rpm, 30 min. of settling and 2	Alum, and PAC, and PE: 1500, 1500 and 20 mg/L, dosage, pH 7, 3, and	91.09 COD, 85.5 TSS, 93.38 turbidity	The linear squares model achieved the best accuracy that used PAC and PE. Coagulant dose had the largest effect on	(Ghorbannezhad et al., 2016)

									min. of rapid mixing at 200 rpm.	8.8 and mixing time of 137, 175, and 135 seconds.		the responses when alum and PAC were used. The longest mixing time had the most impact on the responses with PE coagulant. PE gave the highest contaminants removal.	
-	RSM	central composite face-centered design (CCFD)	coagulant dosage and pH,	TSS, SVI, Water recovery	0.9986	alum	800–1200 mg/L	Cationic polyacrylamide (1 mg/L)	2 min. @ 200 rpm rapid and 15 min. @ 40 rpm slow mixing. 30 min. settling for 30	1045 mg/L dose, 6.75 pH, 37.0 mL/g SVI, and >82% water recovery	99 TSS	Well within domain of the factors tested, the reduced quadratic models established for TSS elimination, SVI, and water recovery can be	(Ahmad et al., 2007)

									min. 6-8 pH			used for prediction.	
6.5 pH, 873 NTU, 940 BOD_5; 260 TSS; 3523 COD (mg/L)	RSM	CCD	COD, Coagulant, flocculent dose, pH	SVI, Turbidity, COD	0.987	alum and PACl; cationic polyacrylamide (C-PAM)	30-70 mg/L	Chemfloc 3876. chemfloc 1510 (1-15 mg/L)	2 min. of rapid mixing at 150 rpm, slow mix for 20 min. at 40 rpm and 30 min. settling time	30 mg/L alum, 9 mg/L Chemfloc and 10 mL/g SVI	96 COD, 95.82 turbidity	Dense and compressed flocs that settle more quickly were produced by c-PAM	(Birjandi et al., 2013)
6.99 pH, 1209 NTU, 1358 mg/L COD	RSM and uniform design (UD)	CCD	Coagulant dose, flocculant dose and pH	Turbidity and lignin removal. Water recovery	0.935	Aluminum chloride	350-2100 mg/L	Modified natural polymer,	2 min. of rapid mixing at 200 rpm, 10 min. of slow mixing at 40 rpm	8.35 pH, 871 mg/L coagulant dose, 22.3 mg/L flocculant dose	98.2 Turbidity	Confirmatory experiment demonstrated that the combination of UD and RSM is a strong and practical method for improving the	(Wang et al., 2011a)

									and 5 min. of settling			coagulation process	
6.4 pH, 230 NTU, 1.56 mS/cm specific conductance, 1210 TSS;1360 COD (mg/L)	Taguchi method	Grey relational analysis (GRA)	Coagulant dose, pH, Coagulant aid type and dose.	COD, TDS, Turbidity	0.9848	Bentonitic clay, Moringa oleifera, Vicia faba, and Pisum sativum	300-900 mg/L	$CaCO_3$, $FeCl_3$, $Al_2(SO_4)_3$ and ammonium sulfate (60-240 mg/L)	3 min. of rapid mixing at 100 rpm, 25 min. of slow mixing at 30 rpm and 30 min. of settling	coagulant dose, 500 mg/L, coagulant type, V. faba., coagulant aid dose, 120 mg/L; coagulant aid type, $Al_2(SO_4)_3$; pH, 9;	8.2 COD, 6.35 TDS, 26.1 turbidity	Coagulant type had no significant influence on Grey theory prediction design (GRG). Coagulant aid dose adds to fasten TDS, COD, and turbidity removal rates.	(Saraswathi and Saseetharan, 2012)
8.5-8.7 pH, 60-100 NTU, 300 -450 mg/L COD	Artificial neural network (ANN)	Radial basis function (RBF)	P/Al molar ratio, PPME initial pH, agitation	COD, Turbidity	-	polymeric phosphate-aluminu	0.36 g/L	-	-	1.2 P/Al molar ratio, PPME initial pH	73.5 COD, 99.5 turbidity	Findings demonstrated a potential ability for operational prediction by	(Zheng et al., 2011)

		neural network	speed and coagulant dosage			m chloride (PPAC)				of 9, 0.36 g/L coagulant dose, and 100 rpm speed		increasing COD removal effectiveness.	

Removal efficiencies of PPME by coagulation-flocculation

Influent initial characteristics	Coagulant				Coagulation mechanism	Flocculant material type and dose	Jar test operational conditions			Optimum conditions	Removal efficiency (%)	Ref.
	Category	Material	Form	Dose			Rapid mixing speed and time	Slow mixing speed and time	Settling time			
3133-3560 TSS; 3967-5840 (ppm), COD, 156-344 NTU, 1070-1970 PtCo. 6-7.3 pH	Organic + inorganic (hybrid)	Lentil extract + alum	Powder	5-40 Lentil extract; 470 alum (ppm)	Charge neutralization and polymer bridging	cPAM (3-15 ppm)	50 rpm for 5 min.	25 rpm for 5 min.	10 min.	470 ppm of alum, 45.8 ppm of lentil extract	50 COD, 70 Turbidity	(Ordaz-Díaz et al., 2017)

150 COD mg/L, 66 NTU, 7.5 pH	Inorganic made from waste materials	Poly-silicic-cation coagulants (PSiCs)	Solution	80 mg/L	Charge neutralization, adsorption, and capture	-	150 rpm for 2 min.	30 rpm for 10 min.	30 min.	pH 7–8.5	60 COD, 98 Turbidity	(Li et al., 2013)
1723 COD mg/L, 5449 PtCo., 8.1 pH	Inorganic	polyaluminium chloride (PAC)	Solution	0.5-4.5 g/L	Adsorption bridging and sweep coagulation	-	1 min.	5 min.	120 min.	pH 7.9, 1.5 g/L PAC dose, 90 min	97 color, 68 COD, 66 AOX, 87 cRFA	(Choudhary et al., 2015)
1027 COD; 4650 BOD_5; 5330 TSS; 195 Oil and grease (mg/L), 8003 NTU, 8190 PtCo., 7.3-8.3 pH	Inorganic + inorganic (Hybrid)	alum, ferric chloride and calcium carbonate	Powder	1-2 alum; 0.5-2 $FeCl_3{\cdot}6H_2O$; 0.5-1 $CaCO_3$ (g/L) dosages	Charge neutralization	PAM (40 mg/L)	100 rpm for 10 min.	50 rpm for max.	30 min.	500 mg/L $FeCl_3$ + 2000 mg/L alum	47 COD, 88 TSS, 80 Turbidity,	(Alavi and Ansari, 2021)

											98 Color	
1358 COD mg/L, 1209 NTU, 6.99 pH	Organic + inorganic (hybrid)	Chitosan-g-PDMC	Powder	0-30 mg/L	Charge neutralization and adsorption	PAM	-	-	30 min.	17.8 mg/L dose, and pH 7.1	79 COD, 95.2 Turbidity, 72.8 Lignin	(Wang et al., 2009)
7000 COD; 1400 BOD; 560 TSS (mg/L), 10.45 pH	Inorganic	$AlCl_3$, PAC and $CuSO_4{\cdot}5H_20$	Solution	5 g/L $AlCl_3$, 8 g/L PAC, 5 g/L $CuSO_4{\cdot}5H_20$ dosage	Floc formation, complexation, and adsorption	-	40 rpm for 5 min.	20 rpm for 15 min.	6 h	$AlCl_3$: 4.0 pH, PAC: 5.0 pH, $CuSO_4{\cdot}5H_20$ 6.0 pH	$AlCl_3$: 72 COD, 84 Color PAC: 83 COD, 92 Color $CuSO_4{\cdot}5H_20$	(Chaudhari et al., 2010)

											76 COD, 78 Color	
3087 COD; 5240 SS (mg/L), 4770 NTU, 7.3-8.3 pH	Inorganic	polyacrylamide (PAM) Cationic polyacrlyamide	Feedstock solutions	0.5-15 mg/L	Charge neutralization	-	200 rpm for 2 min.	40 rpm for 15 min.	30 min.	SVI of 14 ml/g, 5 mg/L dose	95 turbidity, 98 TSS, 93 COD	(Wong et al., 2006)
2900 COD; 6000 SS (mg/L), 4585 NTU, 7.0 pH	Inorganic	polydiallyldimethylammonium chloride (polyDADMAC)	feedstock solutions	0.4-2.0 mg/L	Bridging mechanism, charge neutralization	-	200 rpm for 2 min,	40 rpm for 10 min.	5 min.	9.0 pH	90 COD	(Razali et al., 2011)
3890 COD mg/L, 365 NTU, 7.44 pH	Inorganic	aluminum sulfate	Stock solution	0-2.5 g/L	Charge neutralization	-	150 rpm for 1 min.	50 rpm for 15 min.	60 min.	1.5 g/L dose, 6~8 pH	60 COD	(Yang et al., 2013)
3340 COD mg/L, 360.25 NTU, 7.32 pH	Inorganic	Iron sulphate	Stock solution	2.5-15 mL	Charge neutralization	-	150 rpm for 1min.	50 rpm for 15 min.	60 min.	10 mL dosage	63.6 COD	(Wang et al., 2011b)

450-500 COD mg/L, 1.4-1.5 NTU, 1478-1853 µS/cm, color = 300-360 PtCo, 8.41-8.45 pH	Inorganic	Poly-aluminum Chloride (PAC)	Powder	1-50 mg/L	Sweep coagulation and adsorption bridging	-	-	1-60 min.	8 h	40 mg/L dose, 5 pH, 30 min stirring time	91.18 Color	(Zhu et al., 2013)
3523 COD; 940 BOD_5; 260 TSS (mg/L), 873 NTU, 6.5 pH	Inorganic + inorganic (Hybrid)	Alum + PACl		200-2000 alum; 55-15151 PACl (mg/L)	Charge neutralization	-	50 rpm for 2 min.	40 rpm for 20 min.	30 min.	9.5 Ph 140 ml/g in SVI, 1550 mg/L alum, 1314 mg/L PACl	80.02 COD, 83.23 Turbidity	(Birjandi et al., 2016a)
1453 COD; 841 TSS (mg/L); 7.15 pH	Natural coagulant	natural Cassia obtusifolia seed gum	Stock solution	0-2.0 g/L	Adsorption with interparticle/polymer bridging	-	150 rpm for 5 min.	0–50 rpm for 0-25	5 min.	Initial pH 5, 0.75 g/L	86.9 TSS, 36.2 COD	(Subramonian et al., 2014)

										dose, 10 rpm, 10 min slow-mixing, 1 min settling time		
--	Inorganic + inorganic (Hybrid)	PolyDADMAC + polyacrylamide (PAM)	Powder	0.4–2.0 PolyDADMAC; 0.4–8.0 PAM (mg/L)	Charge neutralization and bridging mechanism	-	200 rpm for 2 min,	30 rpm for 10 min.	5 min.	1.2 mg/L PolyDADMAC dose, and 2 mg/L PAM dose	96.8 TSS, 98 COD, 71.7 Turbidity	(Ariffin et al., 2012)
3 087 COD; 5240 SS (mg/L); 4770 NTU, 7.3-8.3 pH	Inorganic	alum and polyaluminum chloride (PACl)	Dry	200-2000 alum;	Charge neutralization	Cationic polyacrylamide (C-PAM)	200 rpm for 2 min.	40 rpm for 15 min.	30 min.	alum (1000 mg/L), PACl	99.7 Turbidity,	(Ahmad et al., 2008)

				50-1500 PACl (mg/L)		and anionic polyacryl amide (A-PAM) 1-6 mg/L				(500 mg/L), pH 6, SVI (38 mL/g), 12 s. settling time	99.5 TSS, 95.6 COD	
10773 COD, 1572.5 TSS; 13348 TDS (mg/L), 10.35 ms/cm 1044.78 NTU, 27.63°C, 6.9 pH	Inorganic + inorganic (Hybrid)	PAC, $MgCl_2$, and PAC/Polymer, $MgCl_2$/Polymer, $MgCl_2$/PAC, PAC/$MgCl_2$/Polymer	Powder	200-1600 mg/L	Precipitation/adsorption mechanism	cationic polymer (GA4361) (15 mg/L)	100-200 rpm for 2 min.	20-60 rpm for 15 min.	30 min.	PAC/MgCl2/Polymer) at pH 11. 100 rpm rapid and 40 rpm slow	95.43 Turbidity, 25.16 Color, 16.16 COD, 83.33 TSS	(Gholami et al., 2020)

										mixing speeds		
70 NTU, 120 COD mg/L, 7.2 pH	Inorganic	Poly-silicic-cation (PSiCs)	Powder	16 mg/L	Charge neutralization, adsorption	-	150 rpm for 2 min.	30 rpm for 10 min.	30 min.	PSiC with Si/(Al + Fe) ratio of 0.9	67 COD, 95 color, 99 Turbidity	(He et al., 2016)
160-193 SS; 640-872 COD (mg/L) 7.5-7.8 pH	Inorganic	Aluminum sulfate	Powder	669-2931 mg/L	Adsorption, bridging and net capture	PAM copolymer 1.17-6.83 mg/L	200 rpm for 2 min.	50 rpm for 10 min.	22 min.	2,733 mg/L alum, 4.52 mg/L of PAM	89.87 COD	(Ming et al., 2021)
35733 COD mg/L, 3112.33 NTU, 7.05 pH	Inorganic	Poly-ethylene oxide (PEO), PAC and poly-DADMAC	Solution	1200-1714 PEO; 191-364 poly-	Adsorption and charge neutralization	-	-	-	30 min.	poly (ethylene oxide)	66 TS, 75 COD, 95 Turbidi	(Domínguez-Robles et al., 2019)

				DADMAC; 990-2913 PAC (mg/L)						at pH 2.0. 2913 mg/L PAC	ty	
106 SS; 150 COD; 47 BOD (mg/L), 66 NTU, 7.5 pH	Inorganic	Poly-silicic-cation coagulants (PSiCs)	Aqueous solution	80 mg/L	Adsorption and inter-particle bridging	-	150 rpm for 2 min.	30 rpm for 10 min.	30 min.	Si/(Fe + Al) molar ratio; pH are 0.8 and 1.5	96.44 Turbidity 59.77 COD	(Li et al., 2016)
3446 TSS; 2050 COD; 1060 BOD (mg/L), 7.56 pH	Inorganic	PAC, $FeCl_3$.	Powder	50 mg/L	Inter-particle bridging and charge neutralization		-	100 rpm for 20 min.	30 min.	7.5 pH, 18.9 ºC	70 COD	(Boguniewicz-Zablocka et al., 2020)
2350 mgCOD/L, 1480 µS/cm, 155 NTU, 22.8ºC, 4.45-9 pH	Inorganic	Aluminum sulfate	Powder	0.1-2 g/L	Sweep coagulation and charge neutralization	-	130 rpm for 2 min.	30 rpm for 20 min.	30 min.	6.62 pH, 1.25 g/L dose	36 COD, 95 Color, 97	(Öztürk and Özcan, 2021)

											Turbidity	

NTU: Nephelometric turbidity unit, PtCo.: Platinum cobalt units, FTU: Formazin Turbidity Unit,

AOX: adsorbable organic halides, PtCo.: Platinum cobalt units, NTU: Nephelometric turbidity unit, cRFA: chlorinated resin and fatty acids, PAC: polyaluminum chloride

Many parameters can affect the efficiency of the coagulation/flocculation process, including the nature/type and dose of coagulant/flocculant, pH, mixing speed and time, temperature, and retention period, among others. These characteristics can be improved to dramatically increase process efficiency. Optimization approaches that consider the interaction of the elements are advised as an alternative, especially for experimental tasks. Thus, Table 2 depicts the advantages, disadvantages, and application guides for various optimization tools.

Table 2. Advantages, disadvantages, and application guides for various optimization tools

Optimization tools	Advantages	Disadvantages	Guidelines for application
Response surface methodology (RSM).	• RSM is an effective technique for optimizing operating variables while also drastically decreasing time and experimentation expenses. • It can aid in the reduction of workforce, costs, and resources. • The optimized values could be very close to the experimental results.	• They are not ideal for parameter optimization when many experiments are at play. • It has been discovered to have limited use when the data is minimal. • In the classic experimental design procedures employed in RSM, as the number of experimental factors increases, so does the	• In the central composite design, every variable has two levels, but the Box-Behnken design has three levels for each factor. Considering each variable, RSM employs two to five tiers. As the number of parameters increases, so does the number of experiments. • Of all the experimental matrix designs, the CCD is one of the most extensively utilized quadratic design strategies. It is created by employing random experimentation to test for lack of

		number of coefficients in the quadratic model equation, and hence the number of experimental trials. Thus, making the process expensive and more time consuming.	fit with no large number of design points.
Artificial neural network (ANN)	• ANN could well predict the optimized values for the treatment process, when compared with the experimental values. It could certainly pave the way in the water treatment sector for greater efficiency and process automation with coagulation-flocculation. • It could present minimum run time and highest performance.	• Requires lots of data and computational power. • Data preparation needs careful attention. • Requires parallel processing power that is compatible with their structure. As a result, the network's realization is contingent. • Reduced trust in the network since it does not give a clue as to why and how a	• ANN training with little experimental data is conceivable using the central composite design (CCD) and Box-Behnken design (BBD) approaches. With decreased root means square error. • ANN can provide a more precise estimate of the experimental targets. It can perform admirably in experimental data regression and prediction using Design-Expert. In the optimization, ANN might overcome RSM restrictions.

		probing solution can be addressed. • Its structure is determined by no specific rule. As a result, optimal network structure is achieved by trial and error. • The network's lifespan is uncertain.	
Uniform design (UD)	• They are appropriate for research in which numerous experiments can be carried out concurrently. • It has a variable number of levels for each factor. • This process is more robust and requires fewer runs than other optimization strategies. • It minimizes the number of experimental runs by lowering the number of parameter combinations. • Of all experimental designs, it can handle the greatest	• It only considers a uniform distribution of experimental points with excellent representativeness in the experimental region. • The optimization capabilities of a uniform design with a smaller number of experiments are unknown.	• It is based on the principles of fractional factorial design and space filling design. • It defines the number of experimental trials based solely on the level of factors instead of the number of factors.

	number of levels for each factor. • It can choose experimental points equally throughout the experimental region and is very representative of the experimental domain. • It is distinguished by its tiny sample size, which allows it to handle the greatest number of levels with the fewest experimental runs of any design approach. Another benefit is that trials in the studied experimental domain are very representative.		
Taguchi method	• It is preferred in large-scale processes. • Grey relational analysis (GRA) has several uses in determining the best parameters for various treatment procedures. • For the grey relational grade (GRG), optimal arrangements of the	• It is controversial because the underlying statistics have not undergone sufficient peer review.	• It is a grey relational analysis (GRA)-based method. • It is an optimization approach to classify every possible setting in a test regarding many parameters and is strongly based on orthogonal array, which attempts to reduce the variability in the process. The orthogone matrix (OM), a specially developed

	coagulation-flocculation process parameters might be predicted for a variety of performance attributes. • It also lessens the quantity of tests required for optimization. • It constructs the experiment process allowing for the independent evaluation of factors through a limited number of trials, making it one of the most effective techniques for multifactor optimizing circumstances. • The process variability was reduced, and there was a straightforward, methodical way to improve the performance and efficiency of the design, which reduced operating costs.		matrix used for laboratory testing, is used. The method makes use of triangle columns and line graphs. This makes creating the parameters' easy obligations. The results of the laboratory examinations are then analyzed. • The signal to noise ratio (S/N) is used to calculate how far the response functions deviate from the desired values. • The analysis of variance (ANOVA), which was employed for evaluating the significance and validity of the model, is one of the additional optimization approaches utilized by the Taguchi statistical method.
One factor at a time (OFAT) approaches	• One factor at a time can be used to define factors influencing contaminant removal.	• The single-dimensional search is time-consuming, laborious, and expensive.	• To assess each parameter's specific impact on the process, this method entailed changing one parameter at a time while maintaining the other ones.

	• Optimal process parameters that could facilitate the treatment process can be determined.	• Since the interactions between variables are disregarded, the genuine optimum cannot be attained. • They use a lot of parameters and bigger factors at once, and optimizing the independent variables is expensive. • It is no longer advisable and no longer in use.	
Self-directing	• It facilitates maximizing productivity. • It is preferred in large-scale processes.	• It only requires two levels for each factor. • it ignores the influence of interactions among factors in multivariable systems.	• It provides sufficient data on the impact of variables and delivers useful data regarding direct, pairwise interaction, and curvilinear variable effects. • It permits the study of interactive effects amongst operating settings and allows for the determination of the best operating circumstances.

4.7 Classification of coagulants for PPME treatment

One of the finest solutions for contaminant strength of pulping wastewater is coagulation and flocculation. Because of the inclusion of cationic/anionic polymers that interact electrostatically with the lignin component in the black liquors, chemical complexes are formed and precipitated (Domínguez-Robles et al., 2019). For a good coagulation-flocculation process, selecting highly effective coagulants and flocculants is critical. This review identified some categories of materials used as coagulants. They are basically inorganic and organic materials. Where the organic is sub-divided into natural, biopolymers, minerals, waste derived and composite coagulants.

4.7.1 Inorganic coagulants

Inorganic polymer coagulants (IPCs) are often made using a slow alkaline titration process, where a base is introduced to a metal salt solution while it is vigorously stirred. Rapid increases in pH throughout their synthesis often have a negative impact on the hydrolysis-polymerization events, resulting in metal hydroxide precipitation. As a result, weaker bases are favored over strong bases for coagulant production. During the hydrolysis-polymerization events, the basification agent imparts OH- ions, which impacts the rate of polymerization and precipitation. It also has an impact on the species distribution, stability, and performance of metal coagulants that have been produced. The coagulant manufacturing method requires further exploration in order to create a stable coagulant with the necessary basicity and metal species (Lal and Garg, 2019). Because IPCs have a large molar mass and a high density of positive charges, they can diffuse in wastewater and remove negatively charged colloidal particles by electrical repulsion (Wei et al., 2011). IPCs are widely employed as useful coagulants and have been receiving significant attention. IPSCs (inorganic polysilicate coagulants) are commonly utilized to remove residual suspended particles and natural organic materials from wastewater due to their high charge neutralization, adsorption bridging, and sweep coagulation characteristics. Composite polymerization, copolymerization, and synchronous polymerization can all be used to make them (Li et al., 2016).

Polymeric coagulants or polyelectrolytes, particularly those with a large molecular mass, have been increasingly popular in recent times due to their ability to form big, thick, compact, and powerful flocs that can precipitate well and decrease sludge volume (Renault et al., 2009). Because of their inexpensive cost, wider availability, decreased alkalinity consumption and sludge creation, effectiveness beyond a wide pH range, and higher coagulation efficiency than conventional coagulants, polymerized metal coagulants are increasingly being employed for wastewater treatment (Choudhary et al., 2015). Typical examples of inorganic coagulants found in literature are alum, lime, potassium alum, iron-based salts, PAC, polyferric sulfate (PFS), polyacrylamides (PAMs), and poly-dially dimethyl ammonium chloride (polyDADMAC). PACl, $FeSO_4$, $FeCl_3$. epichlorohydrindimethylamine copolymer (PAE), poly (ethylene oxide) etc (Subramonian et al., 2014).

In inorganic coagulants, sludge formation is less, and because of the decreased proportion of inorganics and consequently ash, sludge is a better fuel. Alum and other inorganic coagulants, on the other hand, have been demonstrated in experiments to impair the bonding ability of recycled fibres. This could be due to their low molecular weights and poor water-solubility (Mukherjee et al., 2014). Other drawbacks (see Fig. 10) associated with the prolong and excessive usage (largely applied dosage) of inorganic coagulants include the detrimental effects and risks on human health and living organisms, ineffectiveness in low-temperature water, high procurement cost, low biodegradability, increase of metal content in discharged effluent and significant generation of toxic sludge (Subramonian et al., 2015).

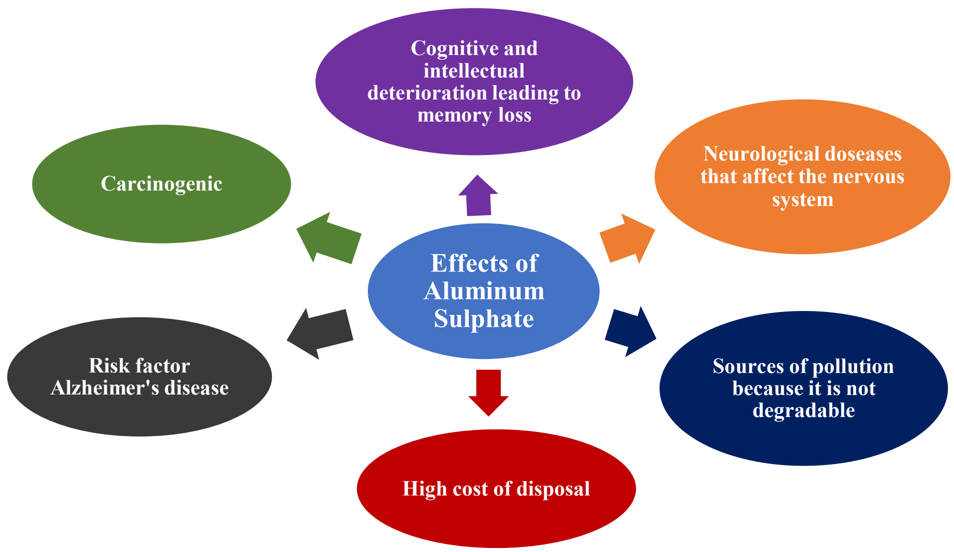


Fig. 10. Environmental effects of inorganic coagulants (Sulaiman et al., 2017).

When inorganic flocculants were dissolved in water, the hydrated reaction occurred, resulting in a complex hydrated ion. Despite the fact that some of these compounds only have one or two positive charges, they are quite potent flocculants. It can be adsorbed on the negatively charged particles' surfaces and act as a charge neutralizer. It may ultimately result in a reduction in the repulsive attraction among suspended particles and generated big particles (Yang et al., 2013). Aluminum sulphate is the most often used coagulant in the PPM. The charge neutralization of negatively charged colloids by cationic hydrolysis intermediates and the inclusion of contaminants in an amorphous hydroxide precipitate, also known as sweep flocculation, are the two methods that it uses (Ahmad et al., 2008). Its insertion into the paper pulp enhances the retention of finely dispersed materials by promoting flocculation, which reduces the turbidity of pit water. However, its use results in highly moistened and difficult-to-filter precipitates, which severely impedes pulp dewatering on the machine wire and degrades the papermaking process (Izmailova et al., 2015). Aluminum contamination of water is also caused through the usage of aluminium sulphate, which has been linked to Alzheimer's disease in humans. Therefore, it become necessary to apply additional purification processes to reduce the remaining concentrations (Leiviskä and Rämö, 2008).

Inorganic coagulants have been frequently employed because of their effectiveness. These traditional coagulants, however, are unable to meet the growing need for organic matter removal, prompting researchers to examine and develop natural and modified natural polymers as coagulants (Zahrim et al., 2015). For PPME treatment, a 5 mg/L dosage of iron sulphate was used as a chemical coagulant. TSS and COD concentrations were found to attain steady state after 15 minutes. This implies that the applied dosage was sufficient for optimal reductions of total COD and TSS levels as there was no additional improvement in the pollutant reductions (Al-Shannag et al., 2012). In a wide pH range and at low temperatures, PAC is a very efficient coagulant with low waste sludge production. It's made from an aluminium hydroxy-chloride aqueous solution. Despite its high cost, it has a 70% efficiency rating. A study found that lower PAC dosages outperformed larger PIX doses in terms of therapeutic outcomes. This shows the effect of distinct anions on coagulation. Thus, it is important to know that PIX is a ferrous coagulant, which includes iron sulphates, chlorides, and iron chloro-sulphates. They're very useful for removing phosphorus from wastewater, hydrogen sulphides binding, and wastewater sludge conditioning. Compared to PIX, the PAX coagulant removed COD levels somewhat better at all coagulant concentrations (Boguniewicz-Zablocka et al., 2020). Generally, the treatments used under the operating circumstances established would permit for the energy valorization of the solid fractions recovered (Domínguez-Robles et al., 2019).

4.7.2 Organic coagulants

Organic coagulants are water-soluble synthetic polymers, with some natural compounds thrown in for good measure. They are classified as cationic, anionic, or nonionic based on their ionic structure (Saraswathi and Saseetharan, 2012). It is preferable to use organic coagulants, such as polyelectrolytes with various structures, which aid in the formation and aggregation of deposits, thereby speeding up the sedimentation process. In comparison to inorganic coagulants, the advantages of organic coagulants are: less reliant of treatment processes on pH, lower dosage requirements, greater efficacy, less dissolved metal ions content after coagulation, lower cost, coagulation sludge is frequently generated in lower volumes, and lack of toxicity (Feng et al., 2021). However, coagulation efficiency and effectiveness are not usually improved by using exclusively organic coagulants. Sludge flocs can be too weak, flocculate poorly, and sediment poorly. Therefore, prior to their industrial application, it is recommended/suggested to carefully investigate their toxicity and biodegradability (Leiviskä and Rämö, 2008). Alternatively, It is strongly advised to employ mixed inorganic-organic coagulants including iron or aluminum compounds as well as organic polymers (Kos et al., 2016).

4.7.2.1 Natural coagulants

Green and natural bio-coagulants/flocculants from renewable biomass resources have received widespread attention for wastewater treatment. Proteins and carbohydrates make up their structure. These polysaccharides are made up of carbohydrate rings linked by glycosidic linkages.

In a charged solution, polysaccharides behave as electrolyte bridges (Mosaddeghi et al., 2020). They are abundant, favorable, and eco-friendly with no pollution as they pose minimal health risk to living organisms. They are highly biodegradable, low toxicity, cost effective, low residual sludge production and may likely not produce treated water with too high a pH. One of the advantages of using natural products/materials as coagulants, is that a decrease in the quantity of chemical coagulant needed (Wu et al., 2010). The majority of natural coagulants are plant-based. Example of these coagulants are: mustard seed extract, rice and cassava starch, guar gum, xanthan gum, banana stem juice, Moringa oleifera seed powder, Nirmali, Native sago trunk starch, Cassava and Cactus leaves, *Ocimum basilicum,* Serratia ficaria, *Opuntia ficus indica*, Okra, Vegetable waste, Lentil extracts, Plantago major L., *Cassia obtusifolia* seed gum, alginate, acacia, chitosan, mucilage, nirmali, tannin, cactus, Jatropha curcas, Mango and Banana peels, and some legumes such as beans (Phaseolus vulgaris), and Adenanthara pavonine, Acanthocereus tetragonus, food waste biochar, have been studied (see Fig. 11).

The coagulation procedure was utilized to treat raw and undiluted PPME with natural *Cassia obtusifolia* seed gum. The efficacy of coagulation with C. *obtusifolia* gum was comparable to that of alum. The method of floc production with C. *obtusifolia* gum and alum was different. C. *obtusifolia* gum and alum went through several stages of heat degradation. Flocs made with C. *obtusifolia* gum were very fibrous-like and aggregated, but those made with alum were irregularly shaped and aggregated. As a natural coagulant, C. *obtusifolia* gum could be a viable alternative to toxic inorganic coagulants like alum in the treatment of PPME (Subramonian et al., 2014). A related study treating PPME with Serratia ficaria, the removal rate of COD and color were up to 72.1% and 99.9%, respectively. The removal efficiencies were similar and even better than those obtained while using chemical synthetic flocculants. Serratia ficaria was able to flocculate several types of real wastewaters, such as brewery, soy sauce brewing, meat processing (wastewater) and river water (Gong et al., 2008).

4.7.2.2 Biopolymers and minerals

Biopolymers are currently being explored for PPME treatment. These include chitosan, Xanthan gum, Locust bean gum, vegetable tannin, *Cassia javahikai* seed gum, okra and *Ipomea dasysperma* seed gum. These biopolymers are biodegradable, renewable, and non-toxic to aquatic species. Secondary contamination caused by an overabundance of biopolymer can also be prevented (Mukherjee et al., 2014). Chitosan exhibits both coagulant and flocculant properties, such as a high cationic charge density, long polymer chains, aggregate bridging, and precipitation. Chitosan has the benefit of being non-toxic and biodegradable, non-corrosive, and safe to handle because it is a biomacromolecule (Renault et al., 2009). Minerals could be used as coagulants as well. This comprises bentonites, talcs, and other similar materials.

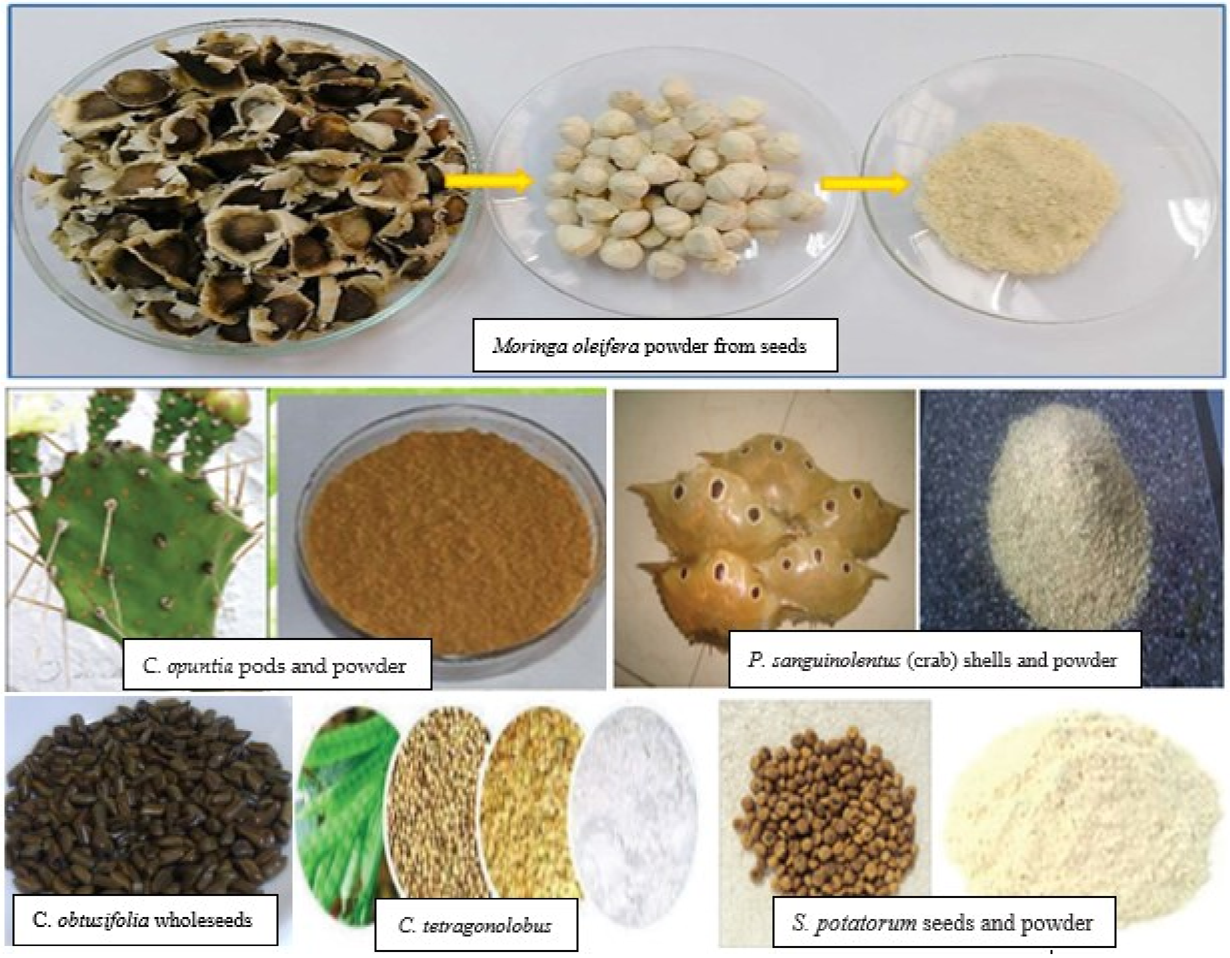


Fig. 11. Natural coagulants for PPME treatment (El Gaayda et al., 2021; Subramonian et al., 2014; Vishali and Karthikeyan, 2018)

4.7.2.3 Waste-derived coagulants

Industrial wastes have also been used to make coagulants. This is to ensure waste reuse and cost reduction (Abioye et al., 2023b; Li et al., 2016; Yang et al., 2019). According to literature, galvanized aluminum slag, papermaking sludge, oil shale ash, pyrite slag, wasted sulfuric acid, fly ash etc. have already been tried (Feng et al., 2021). Polymeric ferric aluminum sulphate chloride (PFASC) produced from waste pickling liquor has been employed as a coagulant for papermaking effluent with a COD of 130 mg/L. When compared to commercially obtainable PAC and polyferric sulphate, the synthesized coagulant performed significantly better (Gray et al., 1995).

PSiCs and PSiCc are poly-silicic-cation coagulants (PSiCs) made from industrial wastes such as fly ash, pyrite slag, and spent sulfuric acid through synchronous polymerization and co-polymerization. The structure, morphology, and performance of PSiCs are better than PSiCc. Coagulants hydrolyze, thereafter intermediates are adsorbed on particle surfaces, hydroxyl complexed in coagulation, and the stable particle structure is destroyed in effluent. PSiC with metal ions also increases adsorption bridging and capture abilities, allowing for the precipitation of stable particles. PSiCs has a considerably better coagulation performance than PSiCc in eliminating COD ($P < 0.05$). PSiCs and PSiCc both have identical iron content and charge neutralization properties. It suggests that the ability to neutralize charges is vital in eliminating turbidity. PSiCs possesses more coagulant-specific linkages, such as Si–O–Al and Si–O–Fe, than PSiCc, and morphological study suggests that PSiCs has a greater adsorption bridging capacity than PSiCc. As a result, PSiCs have a better coagulation performance when it comes to COD elimination (Li et al., 2013).

4.7.3 Hybrid coagulants

Modifying coagulants to improve their efficiency and reduce excess alum contents in treated water is finding widespread application since there is a need to improve the treatment efficiencies of coagulation–flocculation process. This has led to the development of hybrid coagulants (Zheng et al., 2011). Hybrid coagulants can be obtained through different synthesis routes. The methods of preparation vary with the type of hybrid coagulants. One way to prepare hybrid coagulants is by adding other compounds to produce new coagulants such as the polyaluminum ferric chloride (PAFC) (Lal and Garg, 2019), polymeric ferric chloride – polydiallyldimethylammonium chloride

(PFC – PDADMAC), inorganic flocculates polymeric phosphate-aluminum chloride (PPAC), perfluorinated surfactants (PFSs), and polymeric ferric silicate sulfate (PFSiS) which carries a negative charge. Additionally, by adding a modifier, the coagulant's molecular size and aggregating ability can be enhanced, thereby boosting the coagulant's stability and longevity.

The methods for hybrid coagulant preparation can mainly be summarized into five (5) categories. They are physical blending, copolymerization, elevated temperature blending, chemical grafting/crosslinking, and hydroxylation–prepolymerization. Component material type, solubility in water and high aggregating power to molecules, colloids as well as particles of pollutants are among the most important requirements for technological applications of hybrid**.** Material components that are being used to form a “hybrid coagulant” can be found from any or a combination of (i) biopolymer (ii) inorganic, (iii) natural polymer, (iv) organic (see Fig. 12). Thus, the selection of components for hybrid coagulants is based on the characteristics of wastewater.

Hybrid coagulant classifications are based on the combinations that have recently been published in research articles. The combinations that have been produced so far are as follows:

i. Inorganic–inorganic materials
ii. Inorganic–organic materials
iii. Inorganic–natural polymer materials
iv. Inorganic–biopolymer materials
v. Organic–organic materials
vi. Organic–natural polymer materials

The much more developed hybrid coagulant mixtures now employed are inorganic–organic and inorganic–inorganic hybrid. Organic-biopolymer hybrids, natural polymer–biopolymer hybrids, and biopolymer–biopolymer hybrids are all conceivable (Lal and Garg, 2019).

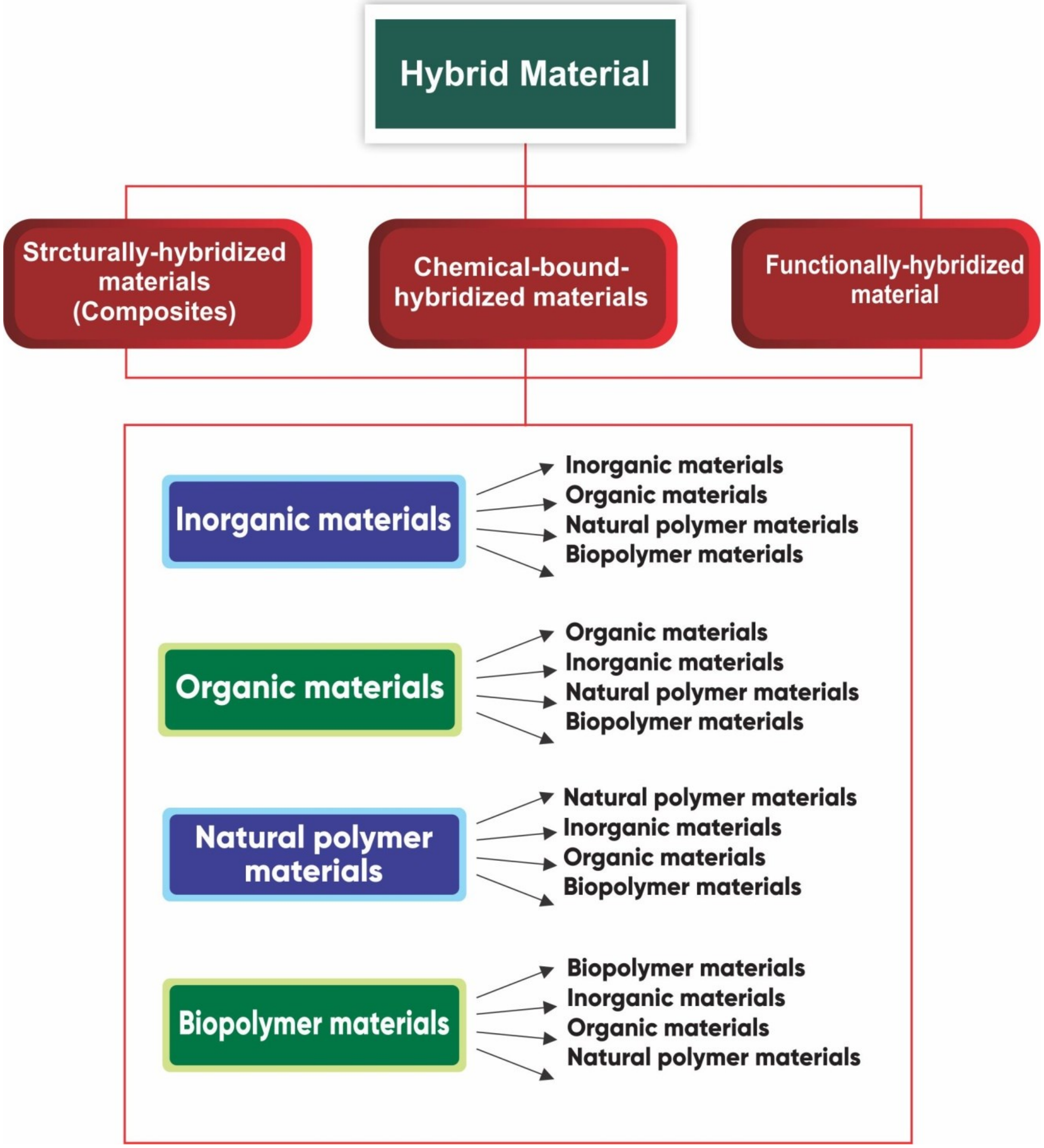


Fig. 12. Hybrid materials classified in a hierarchy for usage in flocculation and coagulation (Lee et al., 2012)

The use of a combination of coagulants may aid in the retention of fine fibres and filler in the paper pulp. In so doing, using mixed inorganic-organic coagulants has a number of advantages, including a reduction in coagulant doses, the formation of larger sludge flocs, easier sediment separation etc. (Zeng et al., 2012). Furthermore, by administering a modifier, the coagulant's molecular size and aggregating ability can be enhanced, thereby boosting the coagulant's stability and longevity. Modified composite and pre-hydrolized coagulants are getting increasingly intricate in terms of composition, but they are also more effective when compared to classic reagents. Plant-based coagulants can totally or partially replace chemical coagulants since inorganic and organic coagulants are complementary to each other to a certain extent (Wu et al., 2010). Waste materials could also be mixed to form a composite coagulant. This was proven by (Li et al., 2013), where pyrite slag, alkali-leached fly ash and wasted sulfuric acid were combined. Sulfuric acid used with coagulants such as alum and lime may lower the amount of coagulants needed for precipitation (Garg et al., 2010).

According to a study, the addition of titanyl sulphate results in ecological safety, no secondary contamination and high flocculation rate. During wastewater clarifying, this results in the development of coarse stable floccules, resulting in a filterable precipitate. As a result, it was hypothesized that it might have binding qualities for paper pulp components used in paper production. It can also be employed as a binder in a composite coagulant that includes titanium and aluminium salt (Izmailova et al., 2015). Irfan et al (Irfan et al., 2017) found that coagulants used in combination were more successful in lowering COD, TSS, and color than coagulants used in solitary form. The coupling of ferric chloride, PAC, and cationic polymer reduced COD by 81% and TSS by 95%, while the combination of aluminum chloride, PAC, and anionic PAM reduced color by 88%. When compared to the concentration of all coagulants, anionic and cationic PAM concentrations play a larger influence. In a related study using a combination of polyaluminum chloride, magnesium chloride, and polymer (PAC/$MgCl_2$/Polymer) in the ratio 100:50:15 at pH

11, 95.43%, 25.16%, 16.16%, and 83.33%, removal efficiencies were achieved for turbidity, color, COD and TSS respectively (Gholami et al., 2020).

Individual coagulants efficacy can be improved by combining alum with a bio-coagulant (basil mucilage) (Mosaddeghi et al., 2020). Experimental findings revealed that, after 10 minutes of the coagulation process, the percentage of color reduced to the lowest level at the optimum alum: O. *basilicum* ratio of 2.8. Thus, in the color reduction process, primary contact time is particularly significant at the start of the mixing, when coagulant adsorption on the suspended particles in the solution is rapid. Nevertheless, as time passed, the number of free active sites reduced, resulting in a reduction in color reduction performance.

A study investigated the flocculation efficiency of polydiallydimethylammonium chloride (polyDADMAC) and polyacrylamide (PAM) as dual flocculants in the treatment of PPME (Ariffin et al., 2012). The flocculants were chosen because of their high charge density and molecular weight, PolyDADMAC and PAM were chosen. PAM acts as a bridger, while PolyDADMAC acts as a destabilizer. Increasing polyDADMAC dosages resulted in particle destabilization and small flocs, whereas adding and increasing PAM increased the size of flocs for a more synergistic flocculation process. Due to the charge neutralization action linked with the bridging mechanism from PAM, which causes an increasing number of flocs, increased dosages of polyDADMAC result in better flocculation. PoyDADMAC in combination with PAM was found to be effective in treating PPME. The treatment of PPME with a polymer or a mixture of inorganic coagulant and flocculant. The use of a PACl coagulant in combination with polyelectrolytes (Organopol WPB20 and WPB40) improved the removal of turbidity, TSS, and COD. Polyelectrolytes were added to enhance the treatment results. Any increase in polyelectrolytes dosage, on the other hand, has no influence on PACl coagulation. From a variety of alternative combinations, PACl in combination with Organopol WPB20 proved to be the most effective in terms of pollutant reduction. 99%, 60%, 92%, and 58% elimination of turbidity COD, TSS, and absorbance were achieved at optimum pH 9, 540 mg/L PACl, and 3 mg/L Organopol WPB20 doses, respectively (Simonič and Vnučec, 2012).

The utilization of combined inorganic-organic coagulants has several advantages as depicted in Table 3. These include lowered coagulant doses, larger sludge flocs, easier sediment separation from the water phase, a smaller sludge volume, the ability to coagulate at lower temperatures, a lower pH of the process, and lower concentrations of iron or aluminum ions in water (Kos et al., 2016). Lentil extracts are low-cost organic coagulants serving as a viable alternative to favor coagulation-flocculation of PPME. The use of modified lentil extract as an aluminium sulphate coadjuvant in the coagulation-flocculation process was found to be beneficial. The lentil extract acts as an efficient coadjuvant at optimal concentrations, resulting in a nearly 50% reduction in alum needs (Ordaz-Díaz et al., 2017). The use of titanyl sulphate and aluminium sulphate coagulants in combination can produce treated effluents that meet regulatory standards, reduce residual aluminium in water, and improve component flocculation efficiency. The load on the flotation installations and filters will be reduced as a result. It will also cut down on a plant's maintenance costs. The composite coagulant's ideal application conditions are a concentration of 10^{-4} M and a pH of 4. Microcrystalline cellulose particles are negatively charged in this pH range, while TiO_2 particles have no charge and titanyl sulphate and aluminium sulphate particles are positively charged, promoting significant heterocoagulation of the component particles. The findings can be applied in paper production to reduce fine cellulose fibre and TiO_2 filler falling through the machine wire and improve pit water quality (Izmailova et al., 2015).

Table 3: Advantages and disadvantages of organic/natural and inorganic coagulants

Coagulant category	**Advantages**	**Disadvantages**
Inorganic coagulants	Proven efficiency	High operational cost
	Short retention time	High sludge management cost
	Low capital cost	Heavy metal accumulation
	Coagulants not easily affected by pH variation and effective of wide pH range	Large volume of hazardous sludge. This results from the hydrolysis process.
	No efficiency loss with long-term storage	Nonbiodegradable
	Reliability	Cause neurological diseases like Alzheimer's disease, Encephalopathy leading to dementia, Down's syndrome and staining of Hippocampal neurons
	Easy availability and storage	
Organic/Natural	Low material/product cost	Lower efficiency
	Low capital cost	Long retention time
	Biodegradable	Inability to manage large pH variation
	Abundance of renewable resource	Inventory and processing costs are high.

	Natural coagulants have medicinal ability	May promote membrane biofouling
	Long storage duration will decompose the natural coagulant which will change the structure of active coagulant agent and become nutrient source for microbial growth	Natural coagulants contain organic matter which may decrease their efficiency over time.
	They are versatile because they can be employed in conjunction with synthetic coagulants to aid in the coagulation process.	Rapid mixing induces cell rupture and furnish the effluent with organic matter
	Non-toxic, biodegradable, and environment friendly	Competitiveness as many natural coagulants have varied applications.
	Supernatant and sludge generated during natural coagulant treatment can be used for variety of reasons, including soil enhancement.	Natural coagulants require a greater dosage, require processing and storage, and are not always available all year.
	Economically attractive alternative to the synthetic coagulants	The absence of source for mass availability
	Easy availability and storage	

Hybrid	High efficiency	High operational cost, depending on the materials and processes utilized.
	Short settling time	Long retention time in the case of biological processes.
	Reduce metal consumption	Large volume of hazardous sludges and their high management cost
	Reduce biofouling potential	Could promote biofouling of membrane in the case of membrane bioreactors.
	Increase floc size	

Sources: (Bahrodin et al., 2021; Gautam and Saini, 2020; Kurniawan et al., 2022b)

Aluminum chloride has proven to be particularly effective at removing color from PPME. Coagulants employed in combination, on the other hand, were shown to be more effective at lowering COD, TSS, and color. The combination of ferric chloride, PAC, and cationic polymer reduced COD by 81% and TSS by 95%, while the combination of aluminum chloride, PAC, and anionic PAM reduced color by 88%. When utilizing a mix of flocculants and coagulants, the concentration of anionic and cationic polymers is more important than the concentration of all sole coagulants (Irfan et al., 2017; Wang et al., 2009). More specifically, it was found that treating PPME using alum and PACl as coagulants improved turbidity and COD removal while also producing less sludge. To come to some agreement between the three solutions, a desirable functional method was adopted. The best results were achieved with 1,550 mg/l alum and 1,314 mg/l PACl at pH 9.5, with 80.02% COD removal, 140 ml/g SVI, and 83.23% turbidity removal (Birjandi et al., 2016a).

5.0 Coagulation-based hybrid treatment systems

Many research studies have been conducted on PPME conventional treatment systems, with varying degrees of success due to high maintenance/operational costs and higher energy needs (Duan et al., 2010). It is obvious that wastewater treatment process based on a single approach is not effective enough to meet the increasingly stringent discharge requirements of PPM (Afzal et al., 2008). This is because all the single treatment methods in use have some drawbacks. The single conventional biological aerobic/anaerobic methods have been reported as not effective in recalcitrant pollutants degradation. Therefore, there is an obligation to explore for other options such as integrating two or more treatment techniques to aid in the decomposition of resistant chemicals in samples before discharge (Eskelinen et al., 2010). This is critical to finding solutions to numerous trending issues in PPME treatment.

The tendency to treat effluent by employing the hybrid or integrated process to obtain improved efficiency and general system compactness has been observed in the past decades worldwide (Amaral et al., 2014). Their use has received a lot of attention to boost treatment efficiency, enhance effluent quality and as well produce less sludge. They are sustainable, energy-saving and provide stable treatment efficiently**.** Hybrid systems can create bioenergy, lowering system operating costs (Ahmed et al., 2021). A hybrid system combines two physicochemical, physicochemical and biological, or two biological processes (Ashrafi et al., 2015). According to literature (Kamali and Khodaparast, 2015), if an effluent contains persistent hazardous pollutants with limited biodegradability, chemical treatments may be required before biological processes to eliminate physical barriers generated by strong interactions in the molecules that may block biological degradation of stubborn pollutants. As a result, a physicochemical pretreatment like coagulation-flocculation should speed up biological stages and reduce reactor volume. Although coagulation is a relatively effective single-treatment process, integrated treatment strategies appear to be more promising (Boguniewicz-Zablocka et al., 2020). Coagulation after biological treatment has been considered a viable method for high-quality wastewater.

For summary, Table 4 also presents an overview of published articles that investigated hybrid coagulants and coagulation processes for the treatment of PPME.

5.1 Hybrid coagulation, adsorption, and primary settling systems

Adsorption is a typical response. It has two primary steps that take time for particle transmission, stabilization, and reaction. The rapid absorption is a surface response, whereas the slow absorption is an organic transfer and disperse to the internal pore. Proper stirring and reaction temperature can aid mass transfer and increase the likelihood of contaminants and adsorbents coming into contact. It could also affect the adsorption equilibrium which will eventually affect the treatment cost. Therefore, it is suggested to optimize the reaction temperature and stirring speed/time-(Kurniawan et al., 2023). Wastewater pH significantly influences adsorption capacity for removing nonbiodegradable products. Increased adsorption efficiency is also enhanced by increasing the size of the solute molecule (Ahmad et al., 2022; Bhattacharjee et al., 2007). To remove contaminants from wastewater, several adsorbent materials have been tested. But the adsorbents' concerns of cost and handling persist.

A combination of adsorption and coagulation is an excellent solution in terms of economic efficiency and usability. This has been proposed by (Duan et al., 2010) using an adsorbent and a coagulant as stated in Table 4 for the removal of dissolved organic compounds (DOC) from PPME. Contaminants were initially adsorbed on the surface and inside of the adsorbent, and subsequently removed by coagulation. The amount of adsorbent used correlated with contaminant removal. However, overdosing the adsorbent may cause problems such as high costs, handling concerns, and chemical waste, despite its benefits in pollution removal. It was discovered that the COD of the treated wastewater declined from 230 mg/L to 90 mg/L, thereby meeting the standard discharge limit. For the treatment of PPME, primary settling, coagulation–flocculation-assisted clarifying, and activated carbon adsorption were used. Alum has a higher effectiveness of pollutant removal than $MgSO_4$ and lime during coagulation. To remove the remaining organic impurities, activated carbon post-treatment was investigated in a batch reactor. The results indicate that a four-hour HRT for plain settling was efficient in reducing the pollutant load by 30%. Pollutant reductions with the three combinations depicted in Table 4 met water quality standards (Mehmood et al., 2019).

5.2 Hybrid coagulation and membrane separation processes

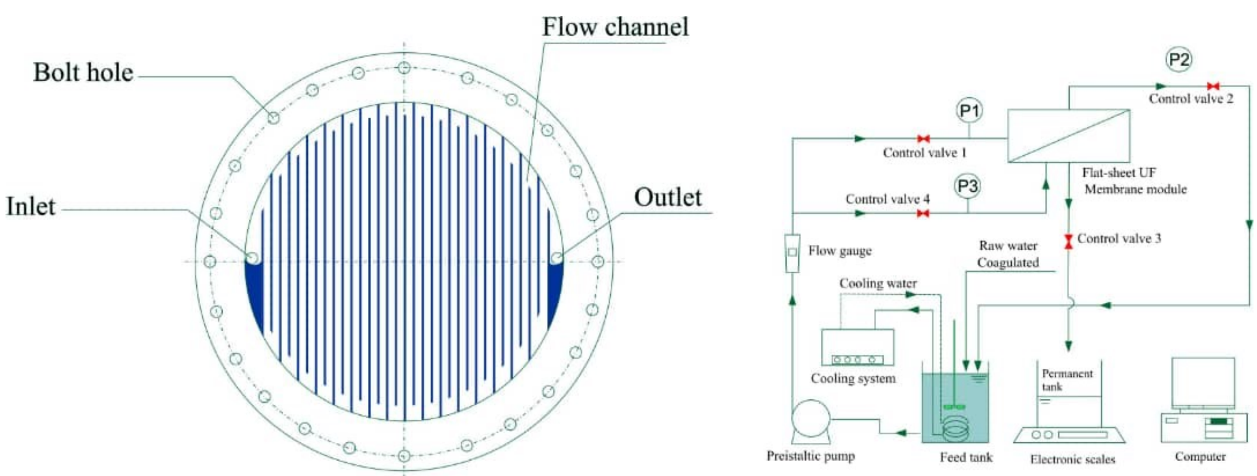
Membrane technologies have proven to be great in treating PPME because they are compact, require less chemicals, are more reliable, produce superior effluent quality, and are not constrained by high temperatures or harmful substances. Membranes can remove AOX, COD, and color from PPM. However, a major challenge with direct membrane filtration is membrane fouling, which reduces permeate flux, increases membrane fouling, and reduces membrane life span (Xu et al., 2019). Pretreatment is recommended to reduce membrane fouling and hence membrane flux. The high flux of nanofiltration membranes is favored, while the high solute rejection of low-flux RO membranes is preferred. Coagulation, nanofiltration/reverse osmosis (NF/RO), and adsorption were all investigated for PPME. Pretreatment with coagulation and adsorption on modified clinoptilolite tuff (MCT) removed practically all organic and inorganic components from the NF/RO process. MCT was best for removing organic pollutants. It is more hydrophobic than non-modified tuff, allowing for easier organic adsorption. Coagulation as a pretreatment to adsorption increased color removal. The size exclusion effect was the primary rejection mechanism for all membranes, causing NF/RO performance. Membrane-solute interactions, dipole moment, and basicity/acidity of solutes all influenced organic rejection (physicochemical properties of the system) (Bennani et al., 2012).

In comparison to nanofiltration and reverse osmosis, ultrafiltration (UF) is significantly superior and has garnered considerable interest because to its ease of operation, small footprint, efficient energy usage, high membrane flux, higher water quality, and excellent antifouling ability. Crossflow UF has been the most extensively employed method for the treatment of PPME. Pretreatment before UF is critical for optimizing membrane performance, minimizing membrane fouling, and maximizing membrane lifetime. Coagulation is a well-established pretreatment process for UF. It aids in the removal of suspended/colloidal particles, as well as inorganic/macromolecule organics from effluent. It mitigates the downward trend in flux. Coagulation improves algal organic matter removal and reduces their fouling potential. According to the literature, when recycled paper mill wastewater was processed with coagulation and then with UF, the COD of the effluent was 95 mg/L and the UV254 was 0.440, indicating a decrease in the effluent's organics content. This was most likely because the addition of coagulants facilitated particle agglomeration and settling, hence reducing the amount of organics to a certain extent. (Xu et al., 2019).

Ultrafiltration was utilized in conjunction with coagulation pretreatment to treat wastewaters from a pulp mill's first-stage caustic extraction and alkaline bleaching operations. Constant transmembrane pressure (TMP) ultrafiltration tests were performed. When the process performance was assessed, it was determined that the coagulant dose was the critical element determining permeate flux improvement. This may be a result of the fast absorption of organic molecules on the membrane surface and the production of cakes. Pretreatment of wastewater with alum or Coagulants such as $FeCl_3$ can greatly reduce the drop in permeated flow during subsequent membrane filtering [36]. A similar study examined filtration following sedimentation by microfiltration followed by ultrafiltration at three different TMPs (1.5, 2 and 2.5 kg/cm^2). The best operation was stated to be the UF operation at a TMP of 2.5 kg/cm^2. Both flux and rejection increased with an increase in TMPs. The concentration of lignin was found to decrease following

UF, which was also seen in the appearance of the permeate color. The significant drop in BOD seen in comparison to COD could be because higher molecular weight species contributing to BOD were rejected more effectively by the membrane, whilst low molecular weight chemicals contributing to COD were retained to a lower extent by the membrane (Kurniawan et al., 2022a).

To treat recycled-paper pulping effluent, a hybrid technique of improved coagulation with a high dose of PACl and UF was used (see Fig. 13). At concentrations ranging from 0 to 2000 mg/L PACl, overall membrane filtration resistance dropped, membrane flux increased, while concentration polarization resistance increased. However, at a concentration of >2000 mg/L PACl, its antifouling activity began to wane. By increasing cross flow velocity, overall membrane filtration, pore blockage, layer, and concentration polarization resistances were decreased, resulting in an increase in membrane flux (Wu et al., 2019).



(a) Structure diagram of the membrane module (b) Flow diagram of the experimental setup

Fig. 13. Hybrid coagulation and membrane separation treatment process for PPME (Wu et al., 2019).

5.3 Electrochemical coagulation, electro-activated peroxymonosulfate (PMS) and acid pretreatment

5.3.1 Electro-coagulation

Electrocoagulation is a technique that utilizes anodic dissolution. The electrocoagulation process is based on the in-situ creation of a coagulant species capable of removing a variety of contaminants from the treated water and wastewater. This approach ensures great treatment efficiency. Nevertheless, its efficiency depends on (i) the electrode type, (ii) the structure of the electro-coagulators, and (iii) the operating circumstances (Bennani et al., 2012). The pH value, the rate of recirculation in the electrochemical cell, and the current density all have a substantial effect on the electrolytic cell's performance (Buzzini et al., 2005). Thus, the electrocoagulation/flotation process can be stated as follows:

- Reactions electrolytic at electrode surfaces
- Coagulation of aqueous phase pollutants,
- Pollutants that are soluble or colloidal adsorb coagulants.
- Sedimentation or flotation of aggregates

Coagulation and electrocoagulation possess mechanical similarity and operate on the same mechanism. However, because the electrocoagulation approach established additional treatment processes through the electrochemistry mechanism in addition to adding coagulants to the wastewater as a pre-treatment step, better removal efficiency values could be obtained (Öztürk and Özcan, 2021). Electrocoagulation experiments with flocculants were conducted to examine the removal of TSS and COD. The hybrid technique was found to remove the most contaminants. The results indicated that using $Fe_2(SO_4)_3$ as chemically assisted coagulants was superior to using

$CaCO_3$ in the electrocoagulation procedure. However, it resulted in a decrease in the amount of time necessary for electrocoagulation to achieve the highest degree of pollutant elimination. Extending the treatment time by up to 30 minutes improves the removal efficiency. This may be because flocculants improve the electrical conductivity of wastewater. As a result, it was established that electrocoagulation using iron salt-based flocculants is more successful than conventional coagulation (Al-Shannag et al., 2012).

5.3.2 Electro-activated peroxymonosulfate (PMS)

Using coagulation and electro-activated peroxymonosulfate (PMS) to treat PPME was studied. Electro-activated PMS was used to treat pretreated wastewater with $FeCl_3$. COD was reduced by 53%. Electro-activated PMS outperformed electro-Fenton in COD elimination and specific oxidant efficiency. Using the BOD/COD index, PMS increased the biodegradability of treated samples by combining coagulation with SRP. Thus, the hybrid method can be employed as a biological pretreatment (Jaafarzadeh et al., 2017).

5.3.3 Acid pretreatment

Coagulation and acid precipitation techniques for COD and color removal in the pretreatment of PPME have been reported to be effective/feasible. Acid precipitation runs were conducted at pH values ranging from 0.5 to 5. The inclusion of H_2SO_4 during the process greatly reduced the residual COD to pH 5.0. From pH 3-5, the rate of COD reduction was shown to be significantly faster. Following that, the pace of reduction slows. COD removal was mostly accomplished by separating non-biodegradable lignin from the wastewater. pH 1.5 was chosen as the optimal value, as it resulted in 61% COD elimination overall. To lower the pH of the effluent to 1.5 or less, a substantial amount of H_2SO_4 was necessary. However, the removal of COD at a pH of 1.5 does not appear to be economically viable due to the substantial increase in treatment costs. Additionally, a greater amount of alkali will be required to elevate the pH of the treated effluent (Garg et al., 2010).

5.4 Chemical oxidation, advanced oxidation processes, microelectrolysis, dissolved air floatation and dielectric barrier discharge ionization technologies

5.4.1 Oxidation and advanced oxidation processes

Advanced oxidation processes (AOPs) convert organic pollutants to short species and even mineralize them by producing extremely reactive free radical oxidants. They are used as a final step in the treatment of industrial wastewaters (Rodrigues et al., 2008). Recently, AOPs like ozonation have been used to turn refractory compounds into innocuous ones. Ozone treatment could reduce toxicity and improve degradability of chlorine-based chemicals (Eskelinen et al., 2010). Processes such as Fenton reaction, modified Fenton oxidation (MFO), combined Fenton oxidation bioflocculation (FBF), and MFBF were employed to treat pulp and paper wastewater. It was discovered that MFBF outperformed all other sequential treatment methods in terms of efficiency by successfully removing organic contaminants, metal ions, lignin, and color. The bioassay test demonstrated the reduction in wastewater toxicity after combinatorial treatment. Thus, the MFBF approach is ideal for treating various contaminants in PPME (Sharma et al., 2020a).

Fenton oxidation, the most popular method of AOPs, has been widely employed to treat PPME because of its high oxidation efficiency, ease of handling, and environmental friendliness. The typical Fenton reaction involves ferrous ions reacting with hydrogen peroxide (H_2O_2) to produce the hydroxyl radical (HO), which has a high potential for degrading stubborn organic contaminants (Fang et al., 2016). The enhanced treatment of papermaking effluent was accomplished using the coagulation/Fenton process indicated in Fig. 14 below. Coagulation effectively eliminated the hydrophobic fraction, which accounted for the majority of DOC in the raw wastewater (60%). The hybrid technique was used to convert the high molecular weight compounds in DOC to low molecular weight ones.

The reduction in COD during the coagulation process resulted in a decrease in the amount of H_2O_2 required for the subsequent Fenton process. The Fenton oxidation method revealed that the hydroxyl radical's oxide electrode potential was 2.80V and has a greater electronegativity and affinity for electrons. Redox reactions occurred rapidly in order to attain a more favorable treatment outcome (Sharma et al., 2020a). As an active oxidation catalyst, $FeCl_3$ was chosen for study because its dissolved amount from earlier treatment stage may help degrade contaminants. So, noncatalytic wet oxidation (WO) was used to improve the wastewater properties after coagulation (Dhakhwa et al., 2012). The technique worked best when the wastewater's biodegradability was improved from 0.22 to 0.96. Although noncatalytic treatment improved biodegradability, the residual color of treated wastewater may still be undesirable to biological processes, necessitating subsequent catalytic treatment.

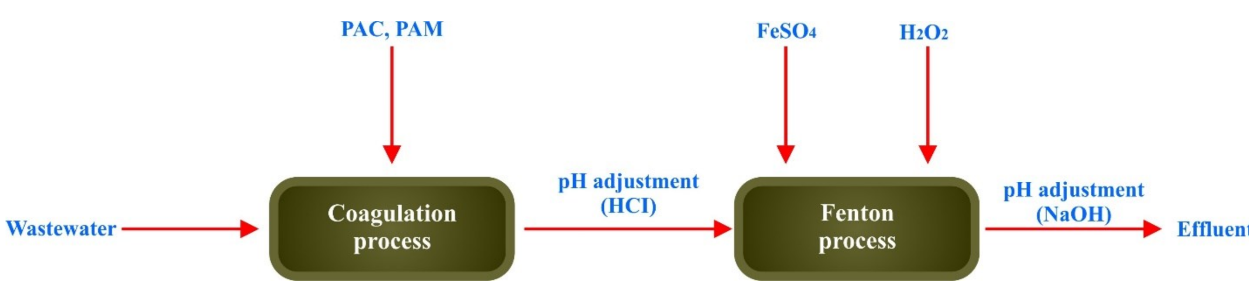


Fig. 14. The flow diagram of the coagulation/Fenton process (Fang et al., 2016).

5.4.2 Micro electrolysis

Pretreatment of pulping effluent included microelectrolysis and fenton oxidation-coagulation. The clearance rate of COD increased significantly over time, reaching 84% in 15 minutes, before fluctuating somewhat (Lan et al., 2013). The pH required by micro electrolysis and Fenton oxidation are nearly the same, so combining the two processes can save acid and alkali consumed in pH correction. The Fe^{2+} produced by micro-electrolysis was utilized in Fenton oxidation. The copious Fe^{3+} produced by Fenton oxidation acts as a flocculant. The optimal pH of the flocculation reaction utilizing Fe^{3+} was 7, removing 41% of COD and 75% of chrominance. Thus, this hybrid system not only improves wastewater treatment efficiency but also reduces treatment costs (Lan and Wu, 2011).

5.4.3 Dissolved air floatation (DAF)

Organic contaminants and TSS overwhelm anaerobic bioreactors in PPME treatment. Using reducing pollutant loads and increasing wastewater bio-treatability, the stage of pretreatment by DAF system with coagulation/flocculation (C-F) process was experimented by (Ansari et al., 2018) (see Fig 15). The decision was made due to tiny particles and the difference in specific gravity of the influent. Using optimal coagulant-flocculant dosages, the C-F/DAF system produces lower COD concentrations and greater BOD_5/COD ratios than raw wastewater. This ratio increased from 0.44 to 0.5 after pre-treatment, while $sBOD_5$/sCOD decreased from 0.65 to 0.53. The treatment removed TSS and VSS. Due to the high concentration of soluble COD in the effluent, connected growth can help prevent malfunctions, poor floc formation, and dispersed growth. This is achieved by improving the bio-treatability of pre-treated wastewater and minimizing clogging and sludge washout.

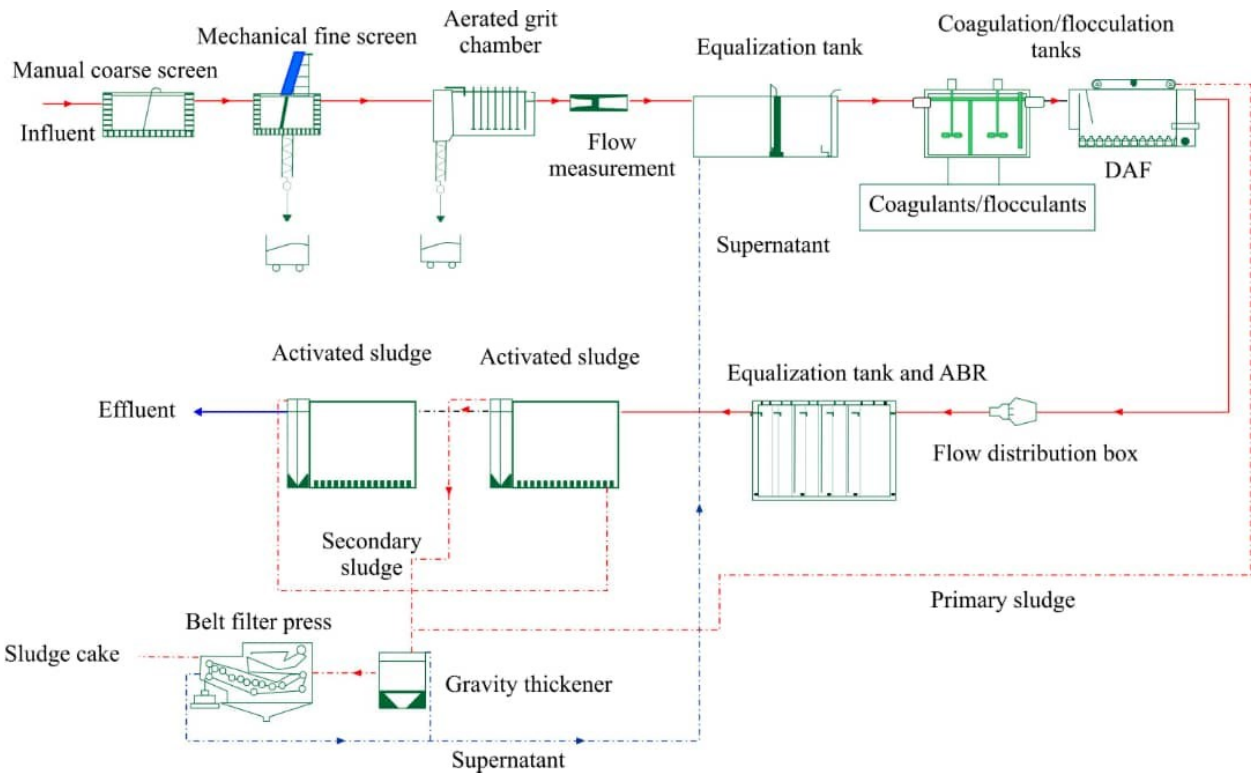


Fig. 15. The flow diagram of the wastewater treatment plant in the paper and cardboard recycling industry (Ansari et al., 2018).

5.5 Thermochemical precipitation and photocatalysis

5.5.1 Thermochemical precipitation

Pretreatment processes such as thermochemical precipitation and coagulation may be used. Thermolysis is a chemical reaction in which a material is broken into its constituents with the use of heat. Catalytic thermolysis of PPME in the presence of a $CuSO_4$ catalyst has demonstrated its efficacy in dramatically decreasing COD and color while recovering a significant amount of energy in the form of solid residue. It has been reported that both fresh and thermally treated wastewater coagulate. Coagulation on catalytically thermally treated effluent removes more COD and color at a coagulant dose of 1 kg/m^3 than at a dose of 5 kg/m^3 for non-thermally treated effluent. Due to the lowered amount of coagulant, the amount of inorganic sludge formed was reduced by 25% (Kumar et al., 2009).

5.5.2 Photocatalysis

Photocatalysis is a photo-activated chemical reaction that occurs when a substance encounters photons of sufficiently high energy levels. It can remove refractory residues. However, for successful photocatalysis, COD values must be greater than 800 mg/L due to light scattering effects caused by a high suspended material content. Additionally, organic matter tends to reclaim the catalyst surface, reducing the quantity of photons reaching photo-reactive sites on TiO_2. When a semiconductor is triggered by light, a photocatalytic reaction occurs. The energy of the light radiation should be equal to or greater than that required to generate the band gap (Marques et al., 2017). Coagulation–flocculation treatment of pulp and paper effluent was performed using $FeCl_3$ as a coagulant and chitosan as a flocculant. The pre-treated aqueous soluble phase was exposed to photocatalytic treatment. The addition of hydrogen peroxide to the UV/TiO_2 combination did not significantly improve degradation yields during photocatalysis. However, it boosted the rate of photosynthesis. The combination technique effectively reduced the organic charge and inorganic pollutant species in wastewater. The treated water had a biodegradability index of 0.71, was transparent, and lacked color and odor. This demonstrates that the final sample is appropriate for biological degradation in its entirety. It was established through toxicity experiments using the Artemia salina bioassay, which demonstrated a significant reduction in harmful contaminants in effluents following treatment with combination procedures (Rodrigues et al., 2008).

5.6 Biological processes

Biological treatment is used for PPME. These procedures can only yield low-quality effluents because DOM contains hydrophobic molecules with high molecular weight (HMW) that resist microbial decomposition and biological treatment (Duan et al., 2010). Thus, pre-, and post-treatment physio-chemical approaches in hybrid processes are required. The biological treatment removes most organic matter while the physical-chemical process polishes. Biodegradable organic fraction can be stabilized by coagulation-flocculation and biological processes.

5.6.1 Biological activated sludge process

For the treatment of PPME, an integrated chemical and biological treatment technique was adopted. Following chemical coagulation, oxidation, and finally the biological activated sludge process, Adjusting the pH during coagulation treatment had no effect on the effluent quality. While coagulation reduced the solids content, the coagulants shown in Table 4 produced low-quality effluents in terms of organic load, turbidity, and dissolved metals. As a result, untreated effluents should not be discharged into surface water systems. Interestingly, the integrated treatment achieved maximum removal of the measured contaminants, with residual concentrations of the effluents far below their maximum allowed limits for safe disposal into water courses (El-Bestawy et al., 2008).

5.6.2 Aerobic stabilization basins (ASB)

Aerobic stabilization basins (ASB) are widely utilized in the PPM for other sophisticated biological treatments. However, ASB treatment efficiency can be significantly lower than more advanced biological systems for pollutant removal. This is due to reduced biomass retention in the ASB, where slow-growing microbes are required to remove significant levels of organic matter, suspended particles, and nutrients (Lewis et al., 2013). So advanced pre-treatment is required before discharge of pulp and paper effluents to an ASB.

The ASB treatment of Pinus radiata (Sulfite) PPME was studied at various scales. Pre-treated alum coagulated wastewaters were subjected to ASB treatment with and without alum sludge. Anhydrous oxide complexes are formed by residual Al^{3+} in the ASB influent wastewater, or by pre-treatment flocs carried over to the ASB (Lewis et al., 2012). Alum pretreatment prior to coagulation eliminated high molecular weight (HMW) compounds (3–8 kDa), and alum sludge addition removed additional HMW components, resulting in a disproportionate loss of aromatics. It does, however, exhibit a low degree of chemical selectivity. Additionally, it exhibits molecular weight selectivity and is effective in removing LMW (300 Da) organics. ASB treatment was used as a final stage of treatment to biologically stabilize organics that remained in the wastewater following coagulation. Significant changes in the composition of the organics, minor/negligible decreases in UV absorbance, and subsequent significant decreases in COD were seen during the treatment. Additionally, the specific ultraviolet absorbance (SUVA) and color of wastewaters rose with the least amount of color production (Lewis et al., 2011).

5.6.3 Bio-electrochemical treatment system (BET)

The bio-electrochemical treatment system (BET) is an emerging technology capable of both waste remediation and energy generation. Using a BET system eliminates the need for an external voltage supply. The in situ biopotential generated by the electrode assembly and the biocatalyst degradation of the substrate is sufficient to refill the energy input. The BET's biocatalyst's ability to use a wide spectrum of organic molecules as substrates is also a benefit. The study examined the efficacy of BET in treating PPME. At pH 7, BET removed nitrates 33.5%, COD 55%, sulfates 58% and phosphates 33%. Interestingly, the BET system recorded color removal. Table 4 shows that post-treatment coagulation increased removal rates. The study indicated that combining BET with chemical coagulation can effectively treat complicated wastewaters without external load (Krishna et al., 2014).

Table 4: Overview of the coagulation-based hybrid processes for PPME treatment

Hybrid treatment system	Influent initial wastewater characteristics	Materials	Coagulation stage	Treatment efficiency	Remarks/findings	Ref.
Adsorption + coagulation	230 COD; 55 SS (mg/L), 25-40°C, 7.2 pH	Bentonite and Polyaluminum Silicate Chloride (PASiC)	Post-treatment	60.87 COD, 41.38 Color	Highest removal efficiency was achieved at 7.0 pH, 400 mg/L coagulant dose, 450 mg/L and adsorbent dose, 30 min. settling, 300 rpm stirring speed for 5 min.	(Duan et al., 2010)
Coagulation + adsorption + NF/RO	209.8 inorganic carbon (IC); 359.2 TOC; 422 COD; (mg/m^3); 7.8 pH, 1427.7 µS/cm; 862 NTU	$AlCl_3 \cdot 6H_2O$, MCT, RO membrane, tight and NF membranes	Pre-treatment	98 TOC, 80 COD, 99 Turbidity	Coagulation was obtained using 2.5 g/m^3 MCT and 0.8 g/dm^3 $AlCl_3 6H_2O$ adsorption. After NF/RO treatment, the solutes were almost completely removed. Membrane pore size was the most important factor in removing IC and TOC.	(Bennani et al., 2012)

Coagulation + adsorption + ultrafiltration	16800 COD; 6600 BOD_5 (mg/L), 12.34 TS; 4.6892 Lignin concentration (g/L), 337 NTU, 8.0 pH	Lime and alum, powdered activated carbon	Pre-treatment	60 TS, 85.7 BOD, 77 COD	Freundlich's isotherm was shown to accurately characterize adsorption isotherms at two distinct pHs (3.2 and 6.1). After adsorption with activated carbon, the KBL's dark color became virtually translucent.	(Bhattacharjee et al., 2007)
Coagulation + ultrafiltration	246 TSS; 733 COD; (mg/L); 7.83 pH, 162 PtCo., 2875 µs/cm conductivity	PAC, CPAM, polysulfone membrane	Pre-treatment	91.81 COD	Pretreatments slowed up the transition from pore blockage to cake filtering, resulting in less fouling. It significantly promotes the UF performance.	(Xu et al., 2019)
Coagulation + ultrafiltration	297 TOC; 3147 COD; 58 SS (mg/L); 46.3 NTU, 10 pH, 2955 TCU Color, 5100 µs/cm conductivity	Alum and $FeCl_3$	Pre-treatment	93.5 Turbidity, 98 Color	Membrane filtration was used to remove COD and color. When compared to alum, $FeCl_3$ produced a higher increase in permeate flux.	(Hong et al., 2007)

Coagulation + ultrafiltration	297.1 COD mg/L, 69 NTU, 7.56 pH, 123.6 mg/L dissolved organic carbon.	PaCl, polyethersulfone (PES) membranes	Pre-treatment	60.1 DOC, 99.1 Turbidity	Adding moderate coagulant dose and simultaneously running at a high cross-flow velocity and a low TMP could be used to control membrane fouling in a cross-flow ultrafiltration process.	(Wu et al., 2019)
Electro-coagulation + chemical coagulation	2950 COD; 3446 TSS; 11571 TS (mg/L), 7.0 pH, 9340 µs/cm	Iron plates, $Fe_2(SO_4)_3$, or $CaCO_3$	Post-treatment	90-97 TSS and COD	The size of the electrocoagulation unit in continuous operations might be determined using an electrocoagulation time of roughly 30 minutes.	(Al-Shannag et al., 2012)
Upflow - Anaerobic Sludge Blanket Reactor (UASB) + Coagulation	210-240 mg/L COD, 600-630 µS/cm conductivity, color (U.C) 1150-1350, 7.0-7.5 pH	Aluminum sulfate, $FeCl_3$	Post-treatment	98 COD, 98 color	Aluminum sulphate at 350–400 mg/L was required for the coagulation-flocculation process.	(Buzzini et al., 2007)

Coagulation + ASB	3400 mg/L COD	Alum and alum sludge	Pre-treatment	~80 Color	During the coagulation step, aromatic and alkyl groups were removed. Additional elimination of aromatic C was seen with ASB treatment.	(Lewis et al., 2011)
Coagulation + oxidation + activated sludge proces	270 BOD; 552-792 COD; 673-1979 TSS (mg/L); 592 NTU, 7.4-7.8 pH	Alum, lime, $FeCl_3$, hydrogen peroxide	Pre-treatment	98.59 TSS, 61.34 COD	Nearly all COD, BOD_5, high molecular weight chemicals, and silica were eliminated. It was able to provide high quality effluent.	(El-Bestawy et al., 2008)
FBR/SBR + coagulation + sand filtration	488 BOD; 2054 COD; 2873 TDS; 145 TSS; 6.6 pH	Alum, SBR, FBR, sand bed	Post-treatment	93 COD, 96.5 BOD	When exposed to the fish for 72 hours, the treated PPME were confirmed to be non-toxic.	(Afzal et al., 2008)
BET+ coagulation	4100 COD; 500 TSS; 2500 TDS (mg/L), 6.10 pH, 4000 PtCo.	Alum, $FeCl_3$, non-catalyzed graphite plates	Post-treatment	95 COD, 100 Color	Individual operation of BET and coagulation both showed lowest performances in terms of color and COD removal.	(Krishna et al., 2014)
Primary settling + coagulation–	975 BOD; 2820 COD; 784 TSS; 2710 TDS (mg/L), 7.61 pH,	$MgSO_4$, alum and lime	Pre-treatment	99.5 Turbidity, 99.1 COD,	Turbidity, COD, TSS, TDS, and color were reduced by > 90% using a blend of primary	(Mehmood et al., 2019)

flocculation + adsorption	6600 PtCo., 1348 µmhos/cm conductivity, 645 NTU			99.4 TSS, 99.5 color	settling and coagulation–flocculation-aided clarifying.	
Coagulation + acid precipitation	700000 COD; 140000 BOD; 724000 TS (mg/L) 11.2 pH	Alum, ferrous sulfate, H_2SO_4	Pre-treatment	64 COD	The solid residue obtained during precipitation has a high heating value and can be utilized to generate power and recapture heat as a sustainable energy source.	(Garg et al., 2010)
Coagulation + sulfate radical-based process	270 BOD; 1300 COD; 790 TSS1110 TDS (mg/L), 6.85-6.94 pH,	$FeCl_3$, electro-activated peroxymonosulfate PMS	Pre-treatment	53 COD	COD elimination was hampered by an overabundance of electro-activated peroxymonosulfate (PMS) and a higher current density.	(Jaafarzadeh et al., 2017)
Catalytic thermal treatment + coagulation	810 COD; 72 BOD_3 (mg/L)	alum, $FeSO_4$, $FeCl_3$, PAC $AlK(SO_4)_2$	Post-treatment	88 COD, 96 Color	pH 12 was found to be the most effective in terms of filtration rate. The steady state operation was achieved with a reaction time of 1 hour.	(Kumar et al., 2009)

Coagulation–flocculation + heterogeneous photocatalysis	1162 COD; 172 BOD (mg/L)	$FeCl_3$, chitosan, $UV/TiO_2/H_2O_2$ system using mercury lamps	Pre-treatment	81 COD	$FeCl_3$ efficiently removed COD. Chitosan increases the speed of sedimentation and compaction. SO_4^{2-} was produced during photodegradation.	(Rodrigues et al., 2008)
Aerated lagoon + coagulation	200-1200 mg/L	PACl and chitosan	Post-treatment	80 COD, 85 Turbidity	Large flocs were generated. Thus, making settling faster. Residual colors and heavy metals were also removed.	(Renault et al., 2009)
Coagulation + Dielectric barrier discharge ionization (DBDi)	3,929.40 COD; 4,185 TSS (mg/L), 17,140 Pt-Co color, 7.4 pH	PACl and chitosan	Pre-treatment	89.81 COD, 99.14 TSS, 99.22 color	COD elimination was better with DBD ionisation processing. When taken alone, however, it proved less successful at removing TSS.	(Purwono et al., 2020)
Coagulation + Ozonation	2380 mg/dm^3 COD, 1250 PtCo color, 634 NTU	MCC (pAA-co-pDMC) and PACl	Pre-treatment	85.6 Turbidity	The hybrid system yielded effective results on decolorization and turbidity removal. The main	(Wang et al., 2019)

					pollution loads were removed by MCC (pAA-copDMC).	
Coagulation + Dissolved air floatation (DAF)	840 TS; 5800 COD; 5200 sCOD; 2600 BOD; 2350 sBOD; 215 TKN; 7.2 pH	PACl, cationic polyacrylamide (C-PAM)	Pre-treatment	98.1 TSS, 39 COD, 33 color	The approach is more effective at improving the biodegradability of particulate organic matter.	(Ansari et al., 2018)
Coagulation + noncatalytic wet oxidation	5120 COD; 1125 BOD_3; 173 TSS; 10951 TDS (mg/L), 13.0 pH	$FeCl_3$	Pre-treatment	77.5 COD, 87 color	Coagulation was not sufficient for color removal. Therefore, noncatalytic wet oxidation was adopted. During the post-treatment, dissolved iron functioned as a catalyst, speeding up the breakdown of organics.	(Dhakhwa et al., 2012)
Coagulation + Fenton process	244 mg/L COD	PAC, PAM, H_2O_2	Pre-treatment	86.5 COD	Coagulation considerably reduced the COD of the PPME, as a result, the succeeding Fenton procedure will require less H_2O_2.	(Fang et al., 2016)

Modified Fenton oxidation and biological flocculation method (MFBF)	880 COD; 2064 TS; 1450 TDS (mg/L), 5514 PtCo., 102.4 NTU, 7.9 pH, 2.5 mS/cm conductivity	$FeSO_4 \cdot 7H_2O$, hydrogen peroxide, bacterial bioflocculant	Post treatment	~94 COD, 96 color, ≥60 heavy metals	Fenton oxidation and bioflocculation may be mutually beneficial in lowering or eradicating one another's unwanted side products.	(Sharma et al., 2020a)

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6.0 Future perspective

The eligibility criteria for an appropriate PPME treatment may be based on several considerations. This includes the sources of water quality, utility capacities, flexibility, environmental compatibility, reliability, and the treatment technique's operating and maintenance costs. As a result of other technologies being used as a pre- or post-treatment, the coagulation-based hybrid processes have shown excellent results in treating PPME that contains several pollutants. However, under such scenarios, achieving complete removal is challenging, as such there is still need for exploring means for achieving higher performances. Even though hybrid systems are gaining popularity due to their success in the treatment of PPME, several developing nations still use traditional coagulation/flocculation and biological treatment methods. These traditional treatment systems have drawbacks, such as mechanical failure, huge footprint, and expensive capital, maintenance, and operational costs. Innovative coagulation-based hybrid technologies with low costs are gaining ground. Hence, this review investigates coagulation-based hybrid treatment systems that integrate different physical, chemical, and biological treatment technologies. Thus, potential future research directions regarding PPME treatment through coagulation-based hybrid systems are proposed as follows:

- Its development, application, and commercialization are all hampered by several issues. The highest of all is the industrial scale-up. Thus, an effective and affordable option might be to deploy sustainable technologies like nanotechnology, microbial fuel cells, and membrane filtering on a large scale.
- Prior to the selection of the coagulant and technology to be attached to the coagulation during hybrid treatment system design, an extensive study of the parameters, functional groups, and compounds that would play a significant role in the process is very important. This is to herness

the high potential of both the coagulant and technology and reduce wastage. Hence, it is necessary to conduct a thorough analysis of the kinetics of reactions, reactor design, the impacts of functional parameters, and the processes for the degradation of PPME pollutants.

- The selection of appropriate materials to be utilized as coagulants in the hybrid system is very important. Nonetheless, since the water and wastewater sectors use a lot of these coagulants, using them effectively is a major difficulty. For the development of natural coagulants, more study is required to find new sources, such as non-edible plants or novel medical plants. More research is also needed to determine the effectiveness of bacteria-based and other natural coagulants in removing micropollutants from dirty water. It is also important to find the elements responsible for the coagulation process.
- Unlike the extensively used chemical coagulants, several natural coagulants' individual coagulation mechanisms were yet to be fully characterized. If a synthetic coagulant is to be utilized, further investigation on their toxic effects expected to be caused on the microbial community of activated sludge is required for the specific relevant model development.
- To further enhance the sustainability option of the coagulation-based hybrid systems in terms of cost, longevity, environmental friendliness, and contaminant removal efficiency, future studies could investigate the production of crosslinked biocoagulants/bioflocculants and the sustainable use of geopolymer materials for coagulation. Modifications to the biocoagulants/bioflocculants' chemical, thermal, and physical properties are also possible. Nevertheless, the chemicals and materials used for the enhancements have prompted questions about biodegradability, cost, health, and safety.

To tackle the issues highlighted above, a thorough analysis is required to establish the validity of the coagulation-based hybrid systems and promote their industrial implementation.

7.0 Conclusion

Contaminants found in PPME that are discharged into water streams have been an increasing source of public health and environmental concern. Despite significant progress in PPME treatment technologies and the identification of associated hazards, existing PPME treatment methods have limits, mainly in terms of efficacy. Thus, additional treatment of the wastewater may be required to remove the hazardous and dangerous by-products created during the single coagulation treatment process. This review discussed the performance evaluation of several single coagulation processes that are extensively conducted, thereby highlighting their removal mechanisms, performance evaluation and design and operational parameters. Hence, the review found that:

- Coagulation processes using different conventional and modified coagulants have shown an overall 55-78% or even lesser removal efficiency for PPME contaminants, is not sufficient to bring down their concentration within the permissible limit.
- Hybrid systems have demonstrated to be more effective in removing PPME pollutants (>97%) and have a higher removal rate, as well as being more suitable for treating heavy organic loads.
- The hybrid systems have also shown promise in the treatment of PPME at the pilot and field scale.

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