Review

A Review on Coagulation/Flocculation in Dewatering of Coal Slurry

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Abstract: Coal slurry is an essential component of mining operations, accounting for more than half of operating costs. Dewatering technology is simultaneously confronted with obstacles and possibilities, and it may yet be improved as the crucial step for reducing the ultimate processing cost. Coagulation/flocculation is used as a dewatering process that is reasonably cost-effective and user-friendly. This paper reviews application of different coagulants/flocculants and their combinations in dewatering mechanisms. In this context, various polymeric flocculants are discussed in the coal slurry in depth. Many operational parameters that influence the performance of coal slurry flocculation are also presented. Furthermore, a discussion is provided on the mechanism of flocculants' interaction, the strategy of combining flocculants, and efficient selection methods of flocculants. Finally, coagulation/flocculation remaining challenges and technological improvements for the better development of highly efficient treatment methods were highlighted, focusing on the intricate composition of slurry and its treatment difficulties.

Keywords: coal; waste; coagulants/flocculants; treatment; optimal flocculants selection; polymeric flocculants

1. Introduction

After coal is mined with its associated impurities, it is sent to a coal preparation plant (CPP), in which the coal is separated from its impurities such as sulfur, ash, clay, and rocks. The main purpose of the CPP, or coal washery, is to improve the quality of coal to make it suitable for the market [1]. Separation technologies are especially effective for treating coal in particle sizes ranging from 10 cm to greater than 0.5 mm. Typical CPPs generate 75–120 kg tailings slurry per ton of coal processed with total solid content between 20% to 35% (*w/w*) [2]. The corresponding coal slurry has become a serious environmental threat in recent years, particularly if disposed of in a tailings storage facility (TSF) or tailings dam. According to the Australian Bureau of Statistics (ABS), coal mining comprised 58% of all water usage within the New South Wales (NSW) mining industry between 2008 to 2009 [3]. In 2019, coal mining in NSW and Queensland utilized water equal to 5.2 million people's annual domestic use [4]. This is equivalent to the water requirements of Sydney, a city with a population of 1.3 million people. Another source of generating coal slurry is the aspiration-engineering unit. Pure water is used to remove dust particles and the purification of air to ensure the safety of workers [5]. The most conventional method for coal waste disposal is using TSFs where there are high potential areas to cause serious environmental problems. In order to reclaim or reuse water for processing operations, slurries

are reserved on the top surface of TSFs. These facilities often have very low surface bearing strengths, making them hazardous areas to humans and wildlife over a long time. Tailings dam failures have always been a serious environmental threat to the contamination of surface waters and aquifers due to seepage, blockages, and insufficient capacity of spillway systems which leads to overtopping [6,7]. Sustainable alternatives proposed for tailings dam disposal includes various combinations of mechanical dewatering methods of sedimentation followed by filtration. These innovative methods provide multiple advantages, including water conversation, reduced percolation into the environment, and simple and efficient water management [8]. A rehabilitation process of the tailings storage facility can be commenced before mine closure much more quickly compared to the original conventional tailing dams [9]. The efficiency of the flocculation process depends on the selection of efficient coagulants and flocculants, and the ways they are applied within the system. This effectiveness of the above-mentioned process can be described through three main criteria; solids settling rate, supernatant turbidity, or clarity, and sediment compressibility [10].

The limitations for the concentration of discharged pollutants from CPPs or their associated areas have been established by the Environmental Protection Agency (EPA). According to EPA, the quality of pollutants which may be discharged by any existing CPPs associated areas must meet the condition before discharging point. As given the detailed information in Table 1 [11], total iron and manganese values must not reach the maximum of 7 and 4 mg/L for any 24-h period. Furthermore, the total suspended solids cannot be more than 70 mg/L. These limitations apply to discharges from any coal mine at which the extraction is taking place or is planned to be undertaken and to coal preparation plants and associated areas. To meet effluent limitations guidelines, the proper degree of effluent reduction attainable by applying economically achievable technology such as coagulation/flocculation.

Table 1. EPA limitations for the concentration of discharged pollutants by coal preparation plants [11].

Pollutant or Pollutant Property	Maximum for Any One Day [1] (mg/L)	Average of Daily Values for 30 Consecutive Days (mg/L)
Total Iron	7.0	3.5
Total Manganese	4.0	2.0
Total suspended solids	70	35
pH	Nl [2]	nl [2]

[1] The term maximum for any one day means the maximum concentration allowed as measured by the average of four grab samples collected over a 24-h period that are analyzed separately. [2] nl = Within the range of 6.0 to 9.0 at all times.

Effective flocculation of washery has become a critical step in recycling high-quality water and improving thickening underflow solids concentration. This increases the operation of coal/mineral processing equipment in plants and improves the performance of tailing dams. Nonionic, anionic, and cationic polymers are employed in new-generation flocculants for flocculation. Even though the flocculation with novel polymers has been recently used, inorganic salts of multivalent metals such as ferric chloride, poly aluminum chloride (PACl), ferrous sulfate, magnesium chloride, and alum are still commonly used. As there is no detailed review paper regarding coal slurry treatment by coagulation/flocculation, this paper aims to review the recent studies on the use and application of different coagulants and polymeric flocculants in the coal slurry flocculation process. Furthermore, the role of different factors in the coal slurry flocculation process was explained followed by a discussion on the flocculants' interaction mechanism. It was also discussed the strategy of combining flocculants and their efficient selection methods. Finally, the remained challenges and conclusions for better development of highly efficient treatment methods were highlighted.

2. Coagulation

A combination of coagulation and sedimentation of suspended particles has been widely used for wastewater treatment purposes for many years. Inorganic salts of multivalent metals such as ferric chloride, ferrous sulfate, magnesium chloride, and alum are commonly used as coagulants [12,13]. It is generally accepted that inorganic salts are subjected to hydrolysis into the corresponding cations and anions when they are added into the aqueous environment. Under this circumstance, they form a wide variety of monomeric and polymeric products, depending on the temperature, solution pH, type, and dosage of ions [14]. Therefore, the primary mechanism in the coagulation of coal tailings slurry is the adsorption of metal ions on the coal surface and the neutralization of the electrical double layer (EDL) charges [15]. In this context, a small amount of positively charged metal ions could neutralize the negatively charged suspended coal particles and reduce the repulsion force between them; therefore, particles will form floc together due to the domination of Van der Waals forces. However, an excessive amount of coagulants reverses the charge of particles from negative to positive, which results in the dispersion of the non-coagulated particles [15].

The low-cost market price is the key factor for choosing coagulants, as given in Table 2. According to the literature, electrolytes cannot coagulate suspended particles larger than 75 μm in size in coal slurry; as a result, small particles form in the coagulation process of coal slurry using electrolytes flocs, and the coarser materials are entrapped in them [16].

Table 2. The market price for bulk sales of coagulants [17,18].

Chemical Material	Coagulants				
	$FeCl_3$	Lime	Alum	PACL	$Fe_2(SO_4)_3$
Price, €/tonne	250–450	130	175–200	250–400	250–350

3. Flocculation

The aggregation of fine particles by polymeric flocculants has been broadly used in mineral processing [19]. The conventional flocculants widely applied in coal preparation plant processes are organic polymeric materials. Synthetic polymers can improve flocculation efficiency significantly. Commercial organic flocculants are mainly water-soluble polymers produced by repeating units of different monomers such as acrylamide and acrylic acid [12]. Table 3 lists the names and market prices for some of the commercial flocculants, including AN 934, FLOCAN, FO-4350, and FO-4700. These materials are usually derived from oil-based and non-renewable raw materials [20]. The particles have different shapes, and behave differently in the dissolution and swelling process. The experimental result showed that using a homogeneous solution could quicken the coal processes and reduce the consumption of flocculants 3–5 times [21].

Table 3. The market price for bulk sales of chemical flocculants [17,18].

Chemical Material	Anionic Flocculants		Cationic Flocculants	
	AN 934	FLOCAN	FO-4350	FO-4700
Price, €/tonne	2550	2500	2800	2980

The most used polymeric flocculants in CPP processes are polyacrylamides that can be classified based on their charge types into four categories: Anionic (negatively charged), cationic (positively charged), nonionic (roughly neutral), and amphoteric (contains both anionic and cationic groups). These polymers can vary in molecular weight (low, medium, and high), amount of charge (low, medium, and high), and structure [22]. Moreover, structural modifications can be induced on flocculants to achieve specific properties such as the temperature-sensitive poly (poly-NIPAM) (N-isopropyl acrylamide) [23,24]. The application of polymeric flocculants for industrial purposes has some significant advantages.

These include high solubility in aqueous systems, not affecting the pH of the medium, high efficiency at low dosage, and producing large, strong, and stable flocs.

On the other hand, polymeric flocculants can lead to environmental consequences and health hazards. Since most commercial polymeric flocculants are derived from petroleum-based materials, they are generally not environmentally acceptable. The majority of them are non-biodegradable, and their by-products release monomers that might have carcinogenic effects [22]. However, the reported research experimental results have asserted that the normally used anionic and nonionic polyelectrolytes have a low toxicity rate. Still, cationic types are usually more toxic, especially to aqueous organisms [25]. The polymers applied in flocculating clays, and coal slurries are discussed below.

3.1. Cationic Polymers

Cationic polyacrylamides (CPAM) are made by copolymerizing acrylamide with quaternary ammonium derivatives of acrylamide. They include 10 to 80 mol% cationic monomer, with higher molecular weights containing just 10% cationic monomer that may operate as flocculants [26]. Commercially available methacrylate copolymers are also available. Poly(diallyl dimethyl ammonium chloride), or polyDADMAC, is typical of low to medium molecular weight; however, higher molecular weight copolymers containing acrylamide are also available. Cationic polymers are essential for aggregating low solid clay suspensions. Their primary use as flocculants is thickening fine coal or coal tailings [27]. Because they struggle to reach high settling rates, they are not generally employed in high-throughput applications.

Cationic polymers use a charge neutralization process to adsorb onto negatively charged small particles. When this happens with higher molecular weight CPAMs, tails may still extend beyond the surface, allowing bridge aggregation by colliding with negative patches on adjacent particles [28]. On the other hand, the CPAM's long-chain operates over a longer distance, resulting in bigger and looser kaolin flocs, lowering the flocculation effectiveness of fine kaolin particles (<10 μm) [29].

Recently, numerous research works have been carried out related to the development of novel biopolymeric flocculants based on polysaccharides. Patra et al. (2020) reported using cationically functionalized amylopectin as an efficient flocculant for treatment of coal suspension [30]. The cationic portion of this flocculant, which may readily neutralize and destabilize the negatively charged coal suspension, is one of the two primary processes by which it operates. Second, it has a high molecular weight, which aids in quicker settling even faster as compared to a commercially available flocculant 883E [30].

3.2. Anionic Polymers

The acrylamide homopolymer is partially hydrolyzed or copolymerized with acrylic acid to produce water-soluble polymers with specified anionic character. Anionic polyacrylamide (APAM) products are available in various charge densities and molecular weights. With various substrates, the monomer sodium 2-acrylamido-2-methylpropane sulphonate (AMPS) may be copolymerized with acrylamide to produce products with similar flocculation activity to APAM, but with a lower molecular weight [31]. The AMPS functionality stays unprotonated at lower pH because it is stronger than acrylic acid. Chen et al. (2021) found that the adhesion force measured in the presence of Magnafloc5250 was 2.71 nN at pH 4, which was higher than that at pH 10 for the flocculation of ultrafine coal suspension [32]. At pH 10, however, the strongest flocculation force (1.87 nN) and the widest range of action (45 nm) were recorded, revealing that the settling tests and floc size measurements were well supported [32]. Although AMPS-containing polymers are less susceptible to calcium and other divalent solution cations, they may be precipitated by aluminum at pH 5 [33].

Anionic polymers are widely utilized in mineral processing applications to flocculate clays. Charge neutralization is thus either irrelevant or a minor component, with the polymer bridging process taking precedence [34]. High molecular weight APAM effectively flocculates negatively charged particles, resulting in bigger aggregates and quicker settling in the treatment of coal tailings [35]. Furthermore, excessive polymer adsorption is far less likely to stabilize kaolinite colloids [36]. Only a few spots of polymer adsorption to each clay particle are possible due to electrostatic resistance between the polymer's COO^- groups and negatively charged surfaces (even at basic pH values) [37]. Simultaneously, the polymer's enlarged conformation caused by charge repulsion creates loops and tails. When combined with probable steric hindrance caused by APAM chain branching, results in the creation of loose, open, and brittle aggregates [38].

3.3. Nonionic Polymers

To improve dewatering, nonionic synthetic polymers are widely utilized, which is generally favored in the presence of multivalent cations or at high ionic strength [39]. Flocculation of -75 μm coal fines in coal slurry is achieved using nonionic Nalco-83370$^+$ flocculant [40]. The flocculation performance results in a maximum settling rate of 0.3222 cm/s with a turbidity reduction ratio of 99.02% (having residual turbidity 41.7 NTU) [40]. When the flocculant is used alone, the quality of flocs generated by CPAM and NPAM in coal tailings slurry flocculation [41]. The quality of the flocs formed by the flocculants, nonionic polyacrylamide (NPAM), is superior to that produced by APAM when employed alone. The combination of trivalent cations has a significantly greater impact on the NPAM effectiveness. The flocs grow bigger and more compact in these conditions due to electroneutralization and bridging flocculation [41].

4. Role of Different Factors in Coal Slurry Flocculation Process Using Polymeric Flocculants

Flocculation characteristics, including floc size and structure, cake resistance, and moisture content in CPPs, are influenced by different factors such as coal slurry composition, charge density and molecular weight of flocculants, polymer structure, polymer dosage, the hardness of water, suspension pH, etc. [42]. The characteristics of flocs produced in the flocculation process are very important because they can affect subsequent operations such as dewatering and filtration in CPPs. Filtration cake with high moisture content can cause many problems such as lower fuel heat value and higher transportation costs [43]. The experimental results showed that anionic flocculants produced large and strong flocs with less porosity; hence, they increased the filtration rate. On the other hand, cationic flocculants small and tight flocs that decrease the filtration rate due to the poor permeability of the filter cake [8,42,44,45].

4.1. Composition of Coal Tailings

Coal tailing slurries can contain variable amounts of coal depending on the applied beneficiation approach. Metallurgical coals of higher market value are normally treated in fines treatment processes, including gravity and flotation methods. Thermal coals are often only treated to 0.25–0.50 mm with the ultrafine passing into the tailing stream. According to the literature, the composition of coal tailing slurry significantly affected the flocculation process [8]. Chemical analysis results of CPP tailings indicated that they usually contain organic matter (coal), quartz, metal oxides, sulfides and carbonates, mica, predominantly muscovite, and different clay minerals such as kaolinite, illite, montmorillonite, etc. [8,46–49]. Generally, in run-of-mine coal, clay particles can occur as 60–80% impurities [50]. Therefore, it is necessary to understand how clay particles can influence coagulation, flocculation and sedimentation, and filtration of coal tailings solids. In clay particles, the face charges and irregular edges significantly impact flocculation mechanisms and efficiency [8].

Regarding a coal-kaolinite suspension, it is reported that the repulsive electrostatic force between the suspended particles can be decreased by adding Ca^{2+} ions. This makes the Van der Waals attractive force the dominant interaction force that results in the aggregation of particles [51,52]. Several experimental results have shown that anionic polymers with high molecular weight are generally desirable for flocculation and dewatering of negatively charged kaolinite and smectite clay particles [53–57]. On the other hand, some experiment results indicated that repulsive electrostatic forces between anionic groups of polymers and negatively charged kaolinite particles limit the polymer adsorption. Furthermore, variations in pH and ionic strength can change the stability of these long-chain polymers [53,58–60]. In another study, montmorillonite suspensions formed clay platelet networks and captured coal particles [61]. Scanning electron microscopy (SEM) for clay minerals results reveal that the house-of-cards structures formed by permanent contact of clay platelets with surrounding particles have high porosity and low settling rate, attributed to the attractive forces keeping the platelets together [62]. The house-of-cards structure comprised edge-to-edge (EE) and edge-to-face (EF) contacts, as shown in Figure 1. Edge-to-face attraction results from attractive double-layer forces between negatively charged faces and positively charged platelet edges [63]. On the other hand, EE contact results from the coalescence of nanobubbles attached to platelet edges [62].
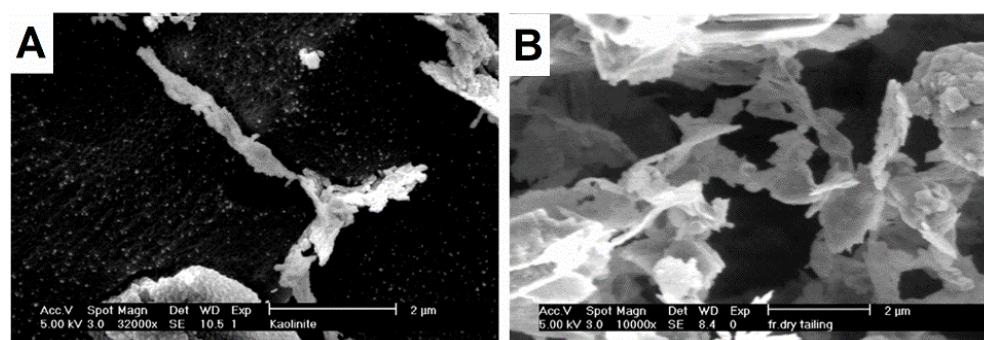
Figure 1. Edge to edge orientation of kaolinite platelets in dilute aqueous: (**A**) kaolin separate platelets in the freeze-fracture micrograph and (**B**) EE oriented kaolinite platelets in freeze-drying coal-associated kaolin (Reproduced from Żbik et al. (2003) [62], Copyright©2021, with permission from the publisher, License No. 5217490592881).

4.2. Effects of pH on the Performance of Polymeric Flocculants

Lignite coal and rock particles may carry a negative charge in an aqueous medium resulting from hydrogen ions dissociating from the alumina-silicic acid surface depending on the pH of the solution [15,16]. Consequently, applying any change in the pH of the medium or the concentration of electrolytes can alter the properties of the EDL, the stability of the suspension, and subsequently the settling rate in the flocculation process with or without flocculant [64,65]. The influence of pH change on the zeta potential of coal particles can be associated with the presence of pH-dependent ionizable functional groups on the surface of particles. The protonation of basic nitrogen-containing functional groups created a positive surface charge on coal particles. In contrast, the negative surface charge is attributed to the dissociation of acidic surface functional groups such as carboxylic [66]. Sabah and Erkan (2006) showed that decreasing the acidic pH value decreased the zeta potential by increasing the H^+ ion concentration; as a result, coagulation occurs due to the van der Waals force domination [65]. Some researchers suggest that in pH value above the natural pH of plant water, inorganic ions such as Ca^{2+} and Mg^{2+} stemmed from water hardness or pH adjustment become active and act as a bridge between negatively charged particles and increase the settling rate [50,65].

Moreover, pH can influence the structure of flocs and change the polymer adsorption and conformation because for most mineral particles, i.e., coal, quartz, and clay, OH^- and H^+ ions are the potential determining ions (PDI) [48]. For example, face-face and edge-face interactions form different structures at different pH values in a kaolinite suspension. Kaolinite particles at low pH carry a positive charge on their edge and a negative charge on their basal surfaces due to proton loss/gain face-edge. Therefore, edge-face electrostatic interaction between clay particles form flocs in the three-dimension house-of-cards structure [60,65,67,68]. On the other hand, both the basal and surfaces of kaolinite particles become negatively charged at high pH values and form a Bandermodel arrangement [60]. The pH also contributes to the conformation of polymers, which changes the final strength of flocs. For instance, anionic polyacrylamides have a coil shape conformation in low pH while they are extended at high pH due to electrostatic repulsion between the charged groups [60,69,70]. Another researcher investigated the effect of pH on the adsorption of polymeric flocculants and indicated that the increasing the pH value increased the negative charge of kaolinite particles. This would improve the flocculation using CPAM and deteriorate the process using anionic polyacrylamide due to the increase and decrease of electrostatic attraction force between negatively charged particles and ionic groups of polymers [60,71]. However, this explanation contradicts the experimental results using anionic polymers undertaken by Ciftci and Isik [72]. According to their flocculation experiments, the anionic groups of polymers become ionized in acidic pH, weakening the bridge formation and flocculation efficiency [72].

The acquired electrical charge by particles, or adsorbed films on their surface, causes aggregation resistance in the fine-particle suspensions. The electrical charge of particles can be controlled through the solution pH. At some pH (isoelectric point), particles have no electrical charge. They are unstable enough for the coagulation process to occur; however, this method could be impractical if the isoelectric point occurs in an unconventional pH range. Moreover, these ions can reverse the zeta potential in which the system is destabilized, according to Hogg (2000) [56]. This destabilization close to this range may be attributed to charge reversal and destabilization of colloidal particles [73]. Polymeric substances are very effective for this purpose since their molecules absorb on the oppositely charged surface (charge-patch mechanism) and aggregation occurs subsequently through the interaction of patches with regions of bare surface on other particles. High molecular weight polymers are most frequently used for floc development, while low molecular weight is used for destabilization purposes [74].

4.3. Water Hardness

Since the water in a tailing slurry is generally recycled and reused in CPPs, the concentration of suspended particles should be at the lowest level. Otherwise, they would harm the efficiency of coal washery processes [50,75]. Water hardness in coal tailings can be characterized approximately with the concentration of multivalent cations, including Ca^{2+} and Mg^{2+}, which are brought to coal tailings through the clean water and leaching from minerals [76]. The results of the research study showed that the mineralogical composition of run-of-mine coal directly affected the water hardness of recycled water. Zhang et al. (2017) has asserted that carbonate minerals, especially gypsum, increase the water hardness because they can release ions including Ca^{2+} and Mg^{2+} ions, while the clay minerals can adsorb these ions and decrease the water hardness on the contrary [76].

4.4. Properties of Polymers

For desirable flocculation results, characteristics of the polymer flocculant such as molecular weight, charge density, and structure have crucial roles [56,77]. For a specific type of polymeric flocculant, the increase in the molecular weight achieved by increasing the length of the molecular backbone would speed up the sedimentation rate due to improving the bridge-binding of small particles [78,79]. Although increasing the charge density enhances the settling velocity, an excess increase in charge density adversely

affects the flocculation process in floc size and floc density [80]. A research experiment investigating the effect of polyacrylamide polymers on floc characteristics showed that increasing the charge density from 10 to 35% increased the adsorption rate by increasing the electrostatic attraction force between the negatively charged kaolinite particles and the positively charged polymer chains. Increasing the absorption rate resulted in decreased floc size by reducing the available sites for bridging [81]. This experiment also exhibited that both the adsorption rate and bridging decreased by increasing the charge density in the case of the anionic polymers. This occurs by increasing the electrostatic repulsion force between the negatively charged surface of the particles and anionic polyacrylamides (PAM) chains (see Figure 2).
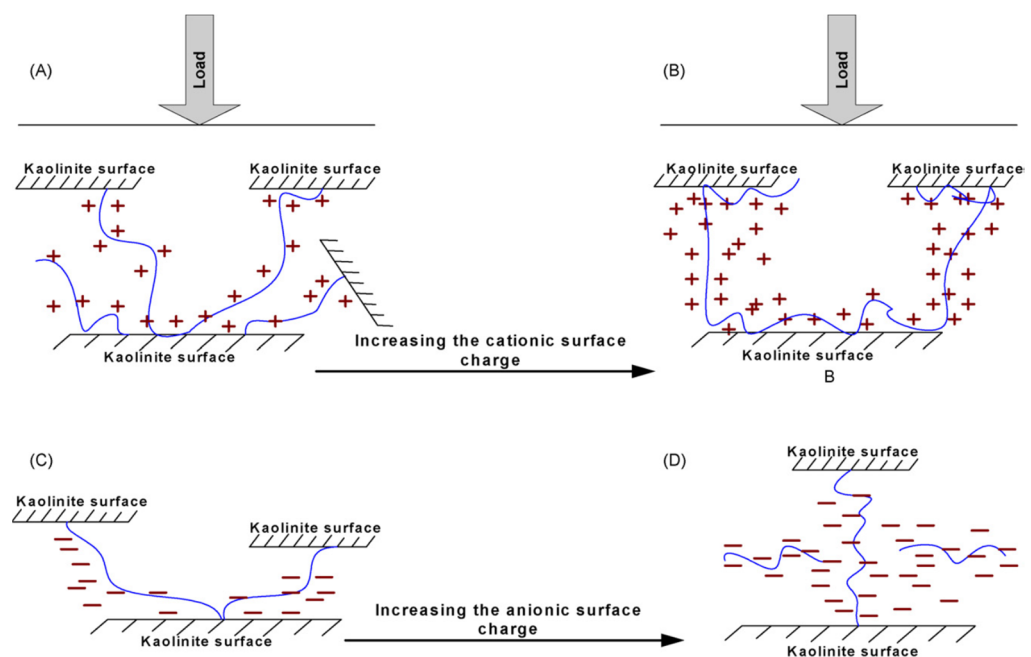
Figure 2. The effect of charge density on the bridging mechanism and adsorption rate in flocculation of kaolinite suspension using anionic polyacrylamides (PAM) of similar molecular weight: (**A**,**B**) the increase of cationic PAM led to the dominance of strong adsorption and loss bridging; (**C**,**D**) anionic PAM caused the decrease in the adsorption rate due to the increased electrostatic repulsion between the negatively PAM chains and the negative kaolinite surface. (Reproduced from Nasser et al. (2007) [81], Copyright©2021, with permission from the publisher, License No. 5217490898472).

Polymer conformation is another factor that contributes to the adsorption of polymeric flocculants onto the suspended particles. It depends on different factors such as the solvent nature, the structure of the polymer itself, the position and number of active groups, and the number of available sites on the surface of solid particles. Alagha et al. (2013) have described several possible conformations for polymeric flocculants after adsorption on solid surfaces as demonstrated in Figure 3 [82].
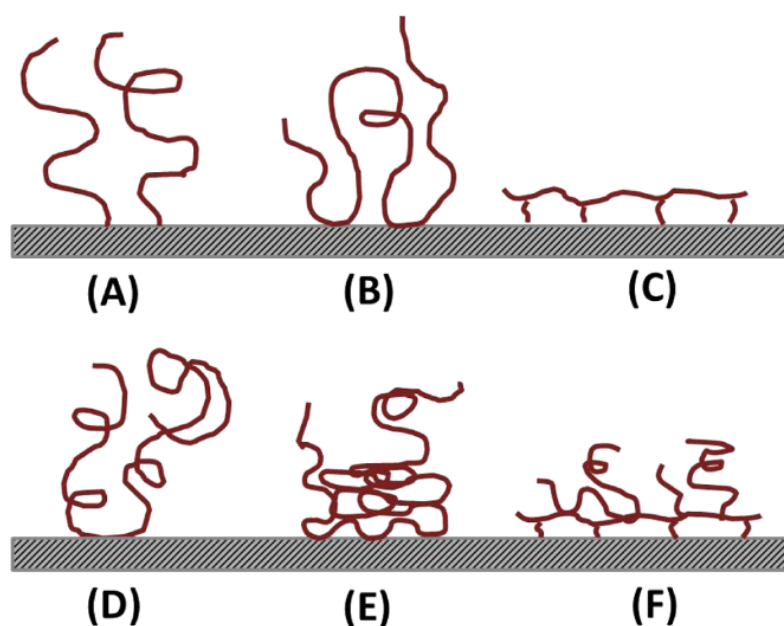
Figure 3. Possible conformations of polymer molecules after the adsorption on solid surfaces: (**A**) single point attachment (weak binding); (**B**) loop adsorption; (**C**) flat multiple site attachments (strong adsorption); (**D**) random coil (high molecular weight polymers); (**E**) nonuniform segment distribution; and (**F**) multilayer adsorption. (Reproduced from Alagha et al. (2013) [82], Copyright©2021, with permission from the publisher).

4.5. Mixing Condition

The optimum mixing time of suspended particles in the flocculation process can be defined as the time needed to coat the half-surface particles by flocculants. The required time must be adjusted to create flocs through the adsorption of flocculants onto the particle surfaces. Long mixing times can hinder flocculation due to the steric effect resulting from overcoating the surface of particles. In contrast, a short mixing time can increase floc touchiness by decreasing the possibility of connecting particles and flocculant molecules and increasing floc breakage rate [83]. Hogg (2000) has asserted that mixing and agitation are the most important affecting factors that contribute to the flocculation process [56]. Moreover, mixing speed is important in breaking or shearing the produced flocs [83].

5. Interaction Mechanism of Flocculants

According to the Derjaguin and Landau, Verwey, and Overbeek (DLVO) theory, the interaction potential between colloidal particles in aqueous media is controlled by the Van der Waals (attractive) and electrical double layer (repulsive) forces [78]. A study carried out by Gustafsson et al. (2003) suggested that the surface charge of particles affects the sedimentation process. Therefore, the low surface charge results in a fast settling rate and a porous cake with high moisture content. However, the high surface charge results in a slow settling rate, and a compact cake with low moisture content [84]. The formation of flocs results from several consecutive steps, including dispersion and diffusion of the flocculants, adsorption of the flocculants on the particles' surfaces, particle collision, formation, and the growth of micro-flocs by consecutive collision and adsorption [12]. The interaction between anionic, cationic, and nonionic flocculants with coal tailing slurry involves several mechanisms, including charge neutralization, polymer bridging, and electrostatic patch, which depend on adsorption of flocculants onto the surface of suspended particles [25,46].

Moreover, the adsorption rate is controlled by the available sites on the surface of particles, and the adsorption rate in flocculated systems typically lies between 0.05 and 0.5 mg/g solids [60]. Generally, high molecular weight polymeric flocculants produce large and loose flocs, while low molecular weight polymers create small and compact flocs [56,85,86].

The optimum flocculant dosage is crucial in a flocculation process before sedimentation and filtration since a low dosage may decrease floc formation rates. In contrast, higher dosage can increase filtration resistance and/or higher moisture content [44,87]. Another dual flocculation experiment using cationic flocculant followed by nonionic flocculant shows that cationic flocculant adsorbs onto the particle surfaces and forms micro-flocs. The subsequent addition of nonionic flocculants leads to floc growth through the bridging mechanism. This combination significantly improves the clarification of suspensions that contain both coal and clay particles [64].
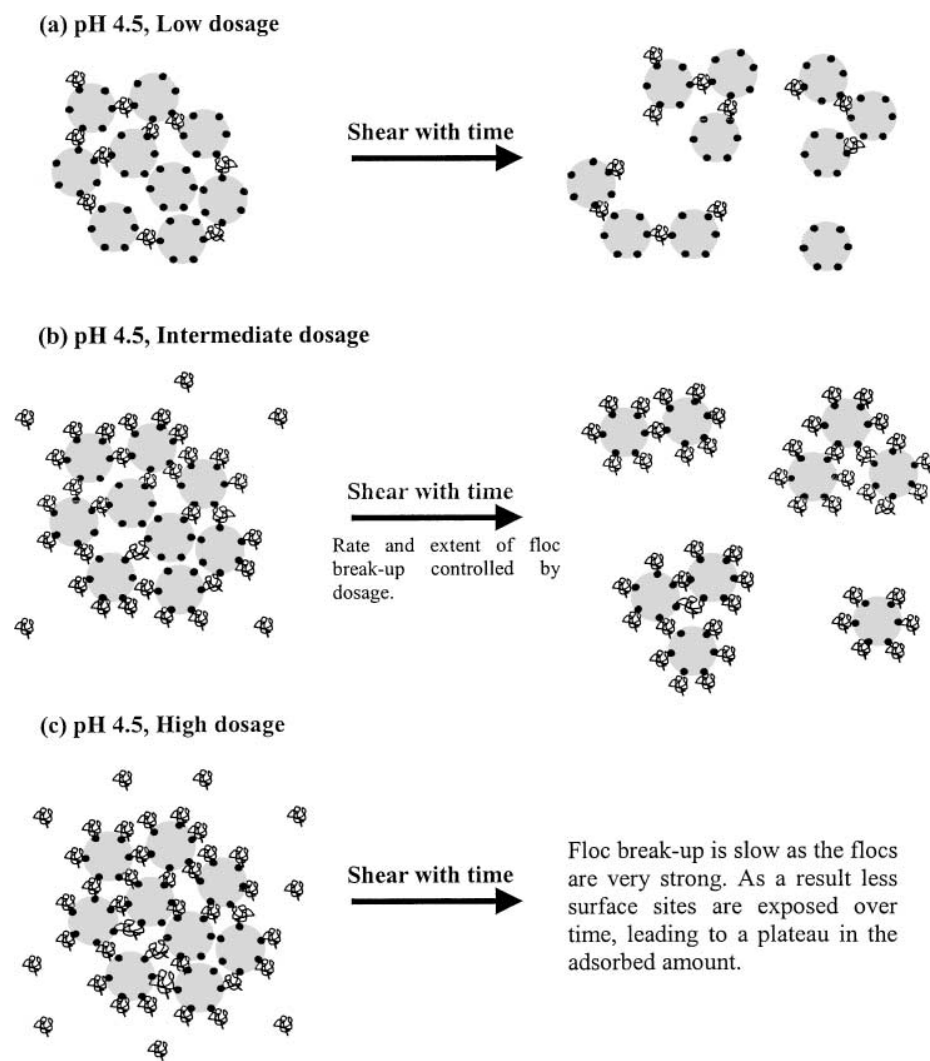
5.1. Interaction Mechanism for Anionic Flocculants

High molecular weight anionic flocculants with low to medium charge density provide high settling rates even at low dosages compared to cationic and nonionic flocculants [8,46]. According to the literature, increasing the charge density increases the settling rate due to producing larger flocs. At the same time, anionic flocculants with low ionization degrees show better clarification of clay-ash suspension [88]. In the flocculation process between coal slurry and low charged anionic flocculants having high molecular weight at a neutral pH, polymer bridging is the dominant mechanism for the formation of flocs [38,46,48,89,90]. Polymer bridging produces larger and stronger flocs that are more resistant to breakage [8,12].

Regarding molecular weight, high molecular weight flocculants provide better efficiency for occurring bridge formation compared to low molecular weight ones due to having larger chains that can be extended from one particles' surface to another [91]. In this process, flocculants adsorb on the surface of particles through the hydrogen and/or chemical bonds [92,93] in a way that hydrocarbon chains of flocculants stretch and increase the possibility of particles attaching [46,94–96]. Choosing an optimum dosage of flocculants plays a critical role in reaching maximum efficiency. An excessive amount of polymer decreases the suspension's stability. It prevents the bridging formation since there will be no available site on the surface of particles to bridge with other particles [72,97].

Moreover, the increased negative surface charge of particles increases the electrostatic repulsive force that leads to reversing the order of flocculation known as a steric disability at high dosage [85,93,98]. In this regard, Taylor and his colleagues [60] present a pattern for the kinetic adsorption of anionic polyacrylamide at pH 4.5 onto kaolinite [60]. As shown in Figure 4, the most common particle in the minerals waste industry, including coal waste tailings. According to this pattern, the two following patterns can occur at low flocculant dosage. Firstly, minimal polymer contacts produce weak flocs that can break easily. Moreover, complete adsorption occurs due to a large number of unoccupied adsorption sites at intermediate flocculant dosage. Secondly, polymer molecules occupy more kaolinite surface sites with increasing mixing time so that kaolinite particles are trapped within the flocs. In this stage, flocs are weak and sensitive to breakage, resulting in a higher adsorption capacity than the initial dosages.

Strong flocs are formed at high dosages through a bridging mechanism with a slow breakage rate. No significant changes are observed in the adsorbed amount because polymer molecules occupy most of the adsorption sites.

(a) pH 4.5, Low dosage

Shear with time

(b) pH 4.5, Intermediate dosage

Shear with time

Rate and extent of floc break-up controlled by dosage.

(c) pH 4.5, High dosage

Shear with time

Floc break-up is slow as the flocs are very strong. As a result less surface sites are exposed over time, leading to a plateau in the adsorbed amount.

Figure 4. Flocs behavior under constant shear as a function of flocculant dosage at pH 4.5 (Reproduced from Taylor et al. (2002) [60], Copyright©2021, with permission from the publisher, License No. 5217491437114).

5.2. Interaction Mechanism for Cationic Flocculants

Flocculation experimental results of coal tailing slurry using cationic flocculants show that a high dosage of cationic flocculants is needed to obtain a high settling rate. For this reason, these flocculants are not extensively used in coal preparation plants for solid-liquid separation purposes. Moreover, cationic flocculants produce small and weak flocs that can break during filtration [8]. However, they result in clearer suspensions with low turbidity rates even at low dosages compared to anionic flocculants due to capturing ultra-fine clay particles [8,46,48]. The schematic illustration of flocculation of coal tailings slurry with cationic flocculants is shown in Figure 5 [65,99]. Flocs are formed via two interaction mechanisms in this process, including charge neutralization and electrostatic patch [100]. Charge neutralization occurs where the flocculants and the adsorption sites are of the opposite charge. Since the colloidal particles in coal tailings carry a negative charge at a neutral to slightly alkaline pH range, the adsorption of cationic flocculants onto their surfaces reduces their surface charge and decreases the repulsive electrical force between suspended areas particles [93]. Thus, van der Waals attraction force becomes dominant, which leads to the formation of micro-flocs [12].
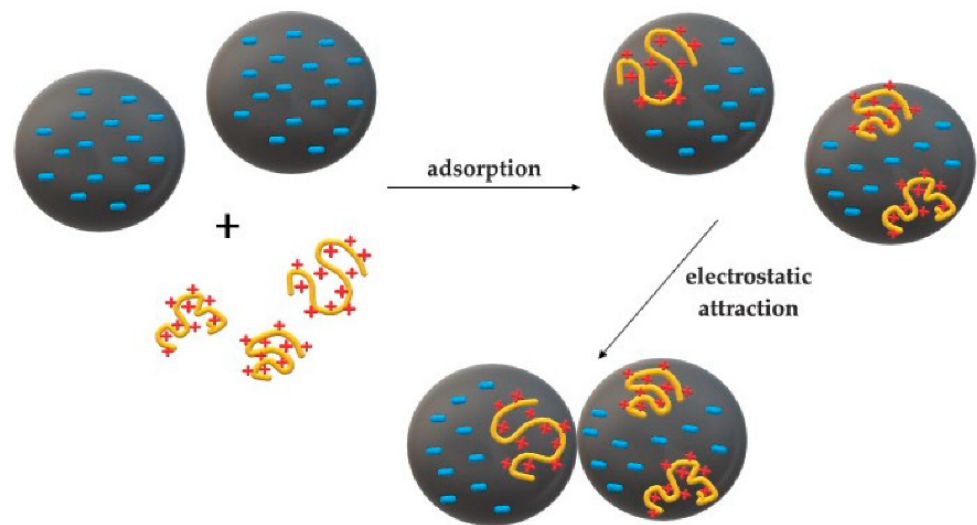
Figure 5. Charge-patch mechanism for cationic polymers according to Maćczak et al. (2020) [99].

For cationic flocculants with high charge density, an electrostatic patch mechanism called mosaic holding is crucial in flocs formation [12,48,90,101]. When highly charged cationic flocculants adsorb on negatively charged surfaces, they cover very small parts of them [46] and form cationic patches or islands between uncoated negatively charged surfaces [102]. Under these circumstances, as particles move towards each other, they can be attached via electrostatic attraction between uncoated negative areas of positive islands [25]. Literature reports that the charge patch mechanism forms small flocs with a low settling rate [101,103]. If too much cationic flocculant is added to the suspension, all the particles become positively charged. Therefore, the electrostatic repulsive forces become dominant, and they will be dispersed again in effect called re-stabilization [12,48].

The use of cationic surfactant, stearyl trimethyl ammonium chloride (STAC), significantly increased the dewatering impact of coal tailings, according to the findings of Chen et al.'s study [104]. The results of the molecular simulation matched the dewatering experiment well. According to the molecular simulation, STAC molecules decreased the connections between water molecules and coal/kaolinite. Additional water molecules were present between the kaolinite 001 surface and STAC due to the –OH functional groups on the kaolinite surface, and they may have worked as a bridge in the adsorption of STAC on the kaolinite 001 surface. Compared to the rest of the STAC molecule, the nitrogen atoms were adsorbed closer to the particle surface. Consequently, the alkyl chains of STAC protruded into the water, allowing water molecules to travel more freely over the particle surface. As a result, coal and kaolinite's hydrophobicity rose, improving the dewatering impact of coal tailings [104].

5.3. Interaction Mechanism for Nonionic Flocculants

Experimental reports reveal that a very high dosage of nonionic flocculants should be consumed to reach optimum settling rate and turbidity compared to anionic flocculants. The interaction mechanism between coal slurry components and nonionic flocculants can be attributed to hydrogen bonding [46,93,105,106].

6. Combination of Coagulants and Flocculants

The coagulation-flocculation is usually conducted by using the cationic inorganic metal chloride salts as a coagulant combined with long chains of nonionic or anionic polymers as flocculants [107]. It is generally known that most of the mineral particles in coal slurry carry a net negative surface charge [8]. The addition of metal salts as a coagulant provides cationic species after hydrolysis, which are adsorbed by negatively charged suspended particles, contributing to the formation of micro-flocs by reducing

double-layer repulsive force between particles [20]. In this stage, the addition of an anionic-nonionic flocculant enhances the sedimentation process via a bridge mechanism between micro-flocs [93,95]. The application of flocculants after coagulants increases the size and density of flocs, decreases the required amount of coagulant, and leads to efficient turbidity removal [93,108]. A research experiment investigating the aggregation mechanism of coal slime water containing illite shows that the combined use of $CaCl_2$ as a coagulant and anionic polyacrylamide as a flocculant has a great performance in turbidity removal [49]. In this process, calcium ions acted as bridges between anionic groups of flocculant and suspended particles [49].

Recently, the influence of cations, particularly trivalent ones like Al^{3+}, and flocculants on colloidal particle flocculation and solid-liquid separation of fine coal tailings was investigated in detail [109]. In this study, Al^{3+} was found to neutralize the surface charge of clay particles and increase their aggregation. Moreover, the combination of MPAM-1, a salt-tolerant anionic flocculant, with Al^{3+} increased the settling of montmorillonite particles greatly, making it a potential strategy for dewatering coal tailings with high levels of swelling clays and inorganic divalent cations [109]. The appropriate use of chemical reagents (flocculant, surfactant, and coagulant) in the dewatering iron tailings, according to the research conducted by Mamghaderi et al. (2021) [110]. This research sheds light on an essential chemical pretreatment that aids in dewatering iron tailings by altering particle surface characteristics and the structure of produced flocs. The employment of Ca^{2+} and Na^+ ions as pH regulators was ideal for filtering because it neutralizes the electrical charge of the particle surface, causing compression of the double electric layer on the particle surfaces. The filtering time was reduced to 7 and 12 min by adding $CaCO_3$ and NaOH (from 15 min). The addition of a polymeric flocculant (A-56 anionic acrylamide) improves filtering kinetics while simultaneously increasing cake moisture owing to water trapping in floc structures [110].

As given in Table 4, the flocculation performance is improved in coal preparation plant tailings by using the combination of flocculants. The main purpose is to make the solid-liquid separation process more economical and effective as the study conducted by Duong (2000) found flocculant or coagulant alone was inadequate to reduce the suspended solids to an allowable limit for recycling or discharge [93]. The interaction mechanism of dual polymers depends on nature and solid surface and solution chemistry that can affect the charge properties and the conformation of polymers [96]. Since anionic flocculants can produce stronger and bigger flocs than cationic and nonionic ones, an increased settling rate is expected [111]. As presented in Table 4, Ciftci et al. (2017) reported a faster sedimentation rate by using anionic flocculant compared to nonanoic and cationic ones [72].

The combination of anionic and cationic flocculants would also be efficient and desirable in terms of improving sedimentation characteristics in coal tailing processes [8]. As presented in Table 4, dual flocculants combination is conducted based on the charge type of flocculants and the order of their addition [48,106]. Dual flocculation test results undertaken by Sabah et al. (2004) showed that the combination anionic and nonionic flocculant had no significant synergic effect on settling rate compared to mono-anionic and flocculant. Still, it greatly improves the turbidity removal rate compared to mono-nonionic flocculant. This improvement can be associated with the polymer conformation in dual flocculation systems [106]. It also shows that regarding the combination of cationic and anionic flocculants, the best performance in terms of settling rate and turbidity removal is obtained by adding low molecular weight cationic and high molecular weight anionic flocculant, respectively. Firstly, polycations neutralize the surface charge of particles and form small flocs. The addition of anionic flocculant enhances the flocculation and sedimentation rate through the bridge mechanism [96,106].

Table 4. Application of single and dual polymeric flocculants for coal slurry components removal.

Flocculant Name	Charge Type	Molecular Weight	Parameter	Optimum Results	Reference
Magnifloc 591-C	Cationic	200,000 relative molecular weight		98.7% removal	
Superfloc 218 plus	Anionic	1,000,000 relative molecular weight	Suspended solids	64.7% removal	[93]
Superfloc 127 plus	Nonionic	1,000,000 relative molecular weight		88.2% removal	
Magnafloc 525	Anionic	Low-medium	Max Sedimentation rate	0.41 cm/s	[90]
Magnafloc 1440	Cationic	High		0.55 cm/s	
Magnafloc 5250	Anionic	Low	Change in volume of the sediment bed		[8]
Magnafloc LT425	Cationic	Low			
Praestol 2540	Anionic	Medium		450 mm/min	
Praestol 2515	Anionic	Low	Optimum sedimentation rate at special dosage	400 mm/min	[72]
Magnofloc 351	Nonionic	-		130 mm/min	
Praestol 857 BS	Cationic	High		50 mm/min	
CMX	Cationic	102,000 g/mol		Removal of 75% Kaolin & removal of 96% bentonite	[112]

7. Efficient Selection of Flocculants

The automation of coal mining activities globally results in huge consumption of water supplies that nowadays is a cause of major environmental concern. Therefore, developing a cost-effective method for cleaning up the process water to make it suitable as return water in CPPs is of great importance. The clarification of recycled water can influence the coal preparation processes such as slurry thickening and dewatering. In this regard, different types of synthetic flocculants and coagulants are used widely to increase the efficiency of the process and improve the clarification of water. The appropriate selection of flocculants in CPPs is specified by the final purposes such as sedimentation speed and water clarification [113].

Based on the theoretical calculations regarding flocculation, there is no need for the particle surface to become completely covered with the polymer [98]. An ideal flocculant should just be able to neutralize a part of the surface charge, which causes repulsion and act as a bridging agent between particles [71]. Using reagent modifiers is one of the efficient methods for improving the selectivity of the flocculation process. For example, introducing sodium silicate in coal-clay suspension can change the surface electrical properties and increase the surface hydration [64]. The efficient selection of flocculants must be conducted based on the molecular weight, charge density, and functional group type to react with the surface sites of mineral particles [56].

Moreover, it must also be stretched and have a flexible (elastic) configuration in solution because, in this way, it can show better involvement in bridge mechanism and produce larger flocs [38,114]. Somasundaran et al. (1988) asserts that this feature greatly improves the flocculation of negatively charged kaolinite dispersions [114]. The dispersion behavior of the coal and suspended clay particles such as kaolinite with the effect of anionic polyacrylamide polymer (APAM) is of great significance in selecting the flocculants [115].

Response surface methodology (RSM) based on central composite rotatable design (CCRD) is a useful technique for optimization the interactive effects of experimental factors. In this context, multi-component coal waste slurry was treated by the flocculation process was performed by hybrid polymer consisting of biopolymer/inorganic [116]. The metal salt and the interactive effects, including polymer dosage, suspension pH, and mixing time

to minimize residual turbidity (RT) and settleable solids volume (SSV) and to maximize the settleable solids speed (SSS), were optimized successfully through the RSM method [116].

8. Conclusions

The current dewatering performance for CPPs is still relatively poor, which results in high-cost treatment. A major reason is the lack of a well-established structure-activity relationship due to coal slurry's highly complicated and multilevel structural features. Little work has been done on the quantitative or semi-quantitative investigation of the structure of flocculant. To understand coagulation/flocculation in dewatering better, the characteristics of coal slurry should be studied thoroughly. However, little work has been conducted on the quantitative or semi-quantitative investigation of the structural information of coal slurry, which might be further examined by using neutron scattering, synchrotron radiation-based techniques, and so on [117,118]. In-depth investigation of the condensed structure of dewatering depends on the development of advanced characterization techniques and highly sophisticated instruments.

The majority of the studies were conducted in surface water treatment facilities or labs. There is limited research on coal slurry in underground coal mines [119]. Therefore, the research on the treatment of the underground coal slurry produced during the coal cutting process is necessary to consider.

In CPP facilities, flocculation is a necessary pretreatment for dewatering due to its low cost and high mobility. New coagulants/flocculants with high dewatering efficiency, cheap cost, and environmental friendliness should be developed rapidly to enhance dewatering performance. The structure-activity connection is fundamental in the development of new coagulants/flocculants. Dewatering mechanisms should be researched in depth based on sludge structural and coagulant/flocculant features. The effects of various metal species of inorganic coagulants and multilevel structural characteristics of organic polymeric flocculants on different targets should be studied in detail.

Various inorganic and organic conditioners, including coagulation/flocculation and composited coagulation/flocculation, may be used to utilize their unique advantages and ultimately improve dewatering performance fully. The electrocoagulation method for electrochemically introducing coagulants is also still waiting to be used in the dewatering of coal slurry. The use of this method to remove color, COD, and turbidity from municipal solid waste leachate has been shown satisfactory results [120]. The electrochemical technique followed by flocculation has been used effectively to treat aquaculture effluent [121]. The future potential of this method for coal slurry treatment could lead to industrial up-scaling.

Nanotechnology enables the manipulation of materials at the nanoscale to achieve desired characteristics and functionalities. This enables the material to be regulated and used in a wide range of applications, including coagulation/flocculation [122]. Nanotechnology, advanced oxidation process, and biotreatment have the potential to be developed and employed in dewatering. However, synergistic and compensatory mechanisms, such as composite applications of inorganic and organic coagulants/flocculants, should be further studied. They are vital in boosting their combination usages and achieving optimal dewatering performance.

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