Investigation of flocculation properties and floc structure of coal processing plant tailings in the presence of monovalent and divalent ions

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Abstract: Low-rank coals are generally processed with wet methods including washing, flotation, etc. Fine-sized tailings of these processes are discharged to tailing ponds with a significant amount of associated water which contains a high amount of dissolved ions. These tailings should be dewatered employing coagulation/flocculation in terms of technological and environmental aspects. In this study, the coagulation/flocculation behavior of coal processing plant tailings obtained from Manisa, Turkey was investigated in the presence of monovalent (Na^+, K^+) and divalent (Mg^{2+}, Ca^{2+}) ions and an anionic flocculant (SPP-600). First, the coagulation properties of coal tailings were determined. Then, the flocculation experiments were carried out, and the turbidity values of the suspensions were measured. Moreover, the sizes of the flocs were determined using a laser diffraction particle size analyzer to analyze the strength of the flocs. The results of the coagulation experiments showed that while divalent ions were more effective at 10^{-1} mol/dm³, higher settling rate and lower turbidity values were obtained in the presence of monovalent ions at 1 mol/dm³ concentration. The optimum flocculant dosage was obtained as 150 g/Mg from the flocculation experiments. The floc size and strength measurements indicated that the larger flocs were obtained with Na^+ than Ca^{2+} in the presence of the flocculant. The strongest flocs were obtained at 10^{-1} mol/dm³ Ca^{2+} + 150 g/Mg flocculant. It can be concluded from this study that the coagulation followed by the flocculation method can be employed to obtain fast flocculation behavior and low turbidity for the dewatering of coal tailings.

Keywords: coal tailings, coagulation/flocculation, floc structure, colloidal particles, monovalent/divalent ions

1. Introduction

Generally, coals are separated from their ash and sulfur-containing minerals using wet coal processing methods including washing (Kong et al., 2018), heavy medium separation (Aktas et al., 1998; Zhao et al., 2019), or flotation (Gungoren et al., 2019). As a result of these processes, a significant amount of tailing is generated, and the fine fractions are discharged to tailing ponds with associated water, which causes important storage and environmental problems such as water pollution, acid mine drainage, and dam structure failure. Therefore, the dewatering of these tailings should be considered for both technical and environmental reasons (Patra et al., 2020).

The suspensions of fine particles generally show high stability, and hence they resist aggregation. This can be attributed to the electrical charge of the dispersed fine particles in aqueous media, where the electrochemical interactions occur between the solid and the surrounding aqueous solution.

Coagulation and flocculation are two widely used methods to destabilize the suspension (Li et al., 2013). In the coagulation process, oppositely charged ions with the charge of the particle surface are used to decrease the electrostatic repulsive forces between the charged solid particles in a suspension. Therefore, short-range van der Waals interactions lead to coagulation (Palomino et al., 2012).

Meanwhile, in the flocculation process, the destabilization of fine particle suspensions is accelerated using long-chain polymers (flocculants) via binding the pending particles for an easier and faster settlement (Gregory and Barany, 2011).

In the literature, there are various studies on the flocculation and coagulation of coal. Alam et al. (2011) investigated flocculation followed by filtration of coal plant tailings. Their results showed that while cationic flocculant (MAGNAFLOC LT 425) at a high dosage was needed to obtain a clear filter cake with low moisture, optimum sized flocs were produced in the presence of an anionic flocculant (MAGNOFLOC 5250). Duzyol and Sensogut (2015) obtained lignite flocs with 90% combustible recovery and 9.8% ash content at optimum conditions of 1 kg/Mg sodium silicate and 16 kg/Mg kerosene dosages at pH 4. Furthermore, they observed a strong correlation between the results for hydrophobic flocculation and ignition temperatures of lignite. The experimental results of Zou et al. (2019) showed that the recovery of selective flocculation flotation of fine coal particles could be enhanced with hydrophobically modified polyacrylamide P(AM-NaAAC16DMAAC) at a lower dosage of the collector. Lin et al. (2020) used a fluidized bed flocculator with a decreasing fluid shear intensity in steps and reported that this flocculation was promising in the flocculation of coal-slime water.

In the studies on the coagulation of coal, Galloux et al. (2015) studied the coagulation of coal mining wastewater (CMWW) with polytitanium tetrachloride, titanium tetrachloride ($TiCl_4$), and ferric chloride ($FeCl_3$). Their results showed that Ti-based coagulants were effective and promising coagulants for CMWW. Li et al. (2017) reported that in the presence of NaCl, the decrease in zeta potential, which is caused by a decrease in electrostatic repulsion among the particles, was responsible for the increase in particle size in the coagulation of coal particles. The results of Lin et al. (2017) indicated that while electrostatic energy plays a dominant role and manifests repulsive force in the long-range (>4 nm), the leading role becomes a hydrophobic force determined by the polar surface interaction energy in the short-range (<4 nm). They used Ca^{2+} ion to decrease the surface electric potential and make the coal particle coagulate.

During the flocculation process, various flocs at different sizes (Johnson et al., 2000), structures (Guerin et al., 2019), and strength (Hermawan et al., 2004) are formed depending on the flocculation conditions such as the pH of the medium (Hermawan et al., 2004), flocculant type and dosage (Alam et al., 2011), surface chemistry of the particles (Ozkan et al., 2016), etc. The success of the flocculation process is highly dependent upon the floc properties, and therefore it should be optimized to generate suitable flocs for different dewatering methods. For example, strong and high-density flocs are favorable in the filtration, but not in sedimentation processes (Hermawan et al., 2004).

Flocs under a range of stresses may break down into smaller particles. Although this process can play a positive role in the redistribution of particles and reagents, it is generally considered detrimental for flocculation (Hogg, 2000). Smaller particles will generally settle more slowly than larger particles of similar density. Therefore, floc strength is a very important parameter for dewatering (Jarvis et al., 2005).

In general, larger and stronger flocs can be obtained with the flocculation process compared to the coagulation process (Ozkan et al., 2016). The high molecular weight flocculants serve primarily as binding agents, enhancing floc strength and reducing degradation rates, thereby permitting floc growth to proceed to substantially larger floc sizes (Hogg, 2000). Meanwhile, the use of flocculants in combination with ions produces a synergism, and therefore it is an important aspect of flocculation and dewatering of suspensions, effectively (Sabah et al., 2004). The addition of small amounts of these polymers to a previously destabilized system can increase the limiting floc size even in a highly turbulent environment (Hogg, 2000).

As known from the literature, different chemicals can be used for the flocculation of coal tailings. Some researchers studied the effect of only non-ionic chemicals such as diesel oil (Ucbeyiay, 2013), kerosene, and fuel oil (Song and Valdivieso, 1998). Sabah et al. (2004) used dual-flocculant systems in the dewatering of coal tailings. In addition to flocculant type and dosage, Sabah and Cengiz (2004) studied the effect of suspension pH on the flocculation of coal tailings. Lemanowicz et al. (2011) investigated the use of ultrasound in dual polymer systems. Ejtemaei et al. (2019) used mixtures of surfactants and flocculants to increase the particle settling rate and reducing filter cake moisture. Bioflocculants was also used as an alternative technique in the flocculation of coal tailings in the absence (Yang et al., 2017) and the presence of a surfactant (Yang et al., 2019).

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Therefore, in this study, it was aimed to investigate the specific ion effect and reveal the mechanism of monovalent and divalent ions on the coagulation and flocculation of coal tailings in terms of processes kinetics, floc characteristics (size and strength), and suspension turbidity. As coagulants, since they are readily available and also present in coal processing plant waters widely, monovalent and divalent ions of Na^+, K^+, Ca^{2+}, and Mg^{2+} were used. To make the process more efficient, flocculation after the coagulation method was used with an anionic flocculant. In the context of this study, the size and strength of the formed flocs were determined with floc size measurements as a function of time using a laser diffraction particle size analyzer.

2. Materials and methods

2.1. Materials

The coal tailing sample used in this study was collected from the tailing pond of coal (lignite) processing plant in Manisa, Turkey. The particle size and ash analyses of the sample are seen in Fig. 1. As seen in Fig. 1(a), the maximum size of the sample was 150 µm, and 70.6% of the sample was under 38 µm. The results of the ash analyses, seen in Fig. 1(b), showed that while the ash content of the -38 µm-sized particles was 62.5%, it decreased with the increased particle size.
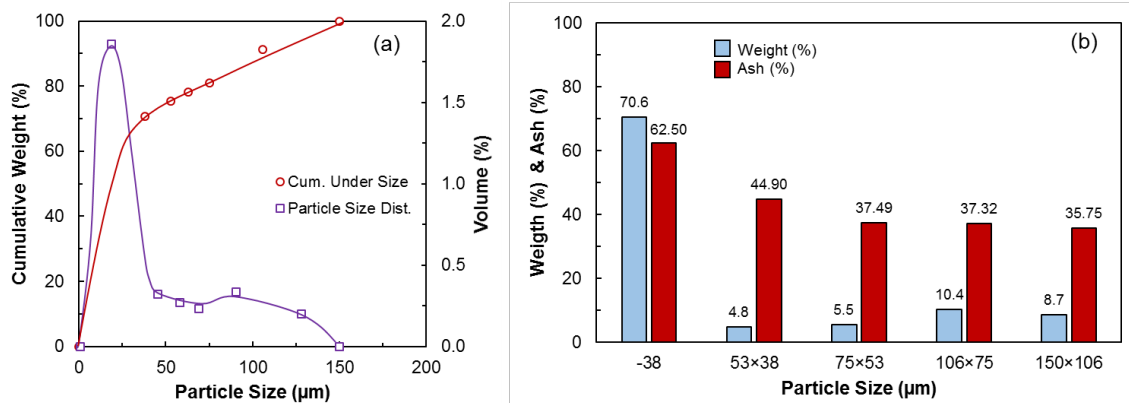

Fig. 1. Results for the (a) particle size and (b) ash analysis of the sample

Meanwhile, the zeta potential measurements of coal particles (-38 µm) were carried out using a zeta meter (ZetaPlus, Brookhaven Instruments, USA) to determine the electrophoretic mobility of charged suspensions. The solids ratio of the suspension was 1% (w/v). For pH adjustments, analytical grades of HCl and NaOH (Merck, Germany) were used. Ten measurements at each pH value were performed, and the average value of the measurements in mono-distilled water (2302, GFL, Germany) was obtained for the coal tailing particles. An average error of these measurements was about 2-3 mV. The experiments were carried out at room temperature (23°C). As seen in Fig. 2, the zeta potential of coal tailings was obtained as negative at all pH values. This result agrees with literature that low-rank coals (lignites) exhibit negative charges along with their gangue minerals such as quartz, clay, etc. Ozkan et al. (2019) reported that the zeta potential of lignite was -15 mV at pH 2 and -37 mV at pH 12. In accordance, Huang et al. (2016) stated that the zeta potential of lignite becomes more negative at higher pH values.

The analytical grade monovalent (NaCl and KCl) and divalent ($CaCl_2$ and $MgCl_2$) salts were obtained from Carlo Erba (Italy) and Merck (Germany), respectively. An anionic commercial flocculant (SPP-600 from SNF, France) was used for the flocculation experiments. The turbidity values of the samples were measured using a turbidimeter (AQUAfast II, Thermo Scientific, USA). The floc size and strength measurements were performed with a laser diffraction particle size analyzer (Mastersizer 3000, Malvern, UK). All solutions and suspensions were prepared with mono-distilled water (2302, GFL, Germany).

2.2. Methods

The coagulation/flocculation experiments were carried out with the coal tailing sample at 5% solids
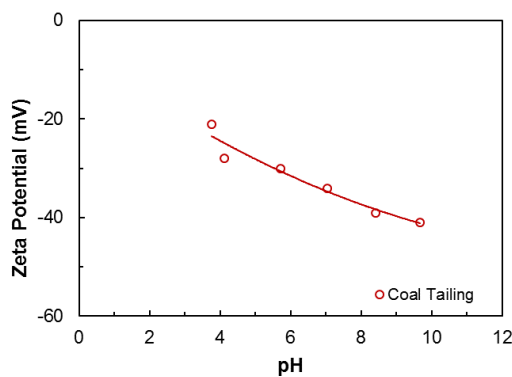
Fig. 2. Zeta potential-pH profile of coal tailing sample

ratio (w/v) at room temperature (23°C). 10^{-3}, 10^{-2}, 10^{-1}, and 1 mol/dm^3 ion concentrations and 50, 150, and 300 g/Mg flocculant dosages were used in the light of the results of Gungoren et al. (2018). The experiments were carried out at natural pH (~6.87). First, 12.5 g of coal tailings sample was mixed in 250 cm^3 distilled water using a magnetic stirrer (C-MAG HS 7, IKA, Germany) at 200 rpm for 10 min. Then, the flocculant at the desired dosage was added to the suspension after transferring it to a graduated cylinder, and it was stirred for a further 1 min. Then, the suspension was left for settling. The settlement experiments were carried out in graduated cylinders with 250 cm^3 volume. The height of the suspension (h_0) was 22.3 cm. As the suspension settled, the height of the turbid layer (h_1) was measured as a function of time. Then, the settling rate was calculated via Eq. 1, where Σt is the total time (min) passed from the beginning of the settlement process.

$$\text{Settling Rate} = \frac{h_0 - h_1}{\Sigma t} \tag{1}$$

The settlement distance was recorded at each 1 min for the first 10 min, and at each 5 min for the next 20 min for calculating the settlement rate of the particles. Meanwhile, the turbidity of the residual solutions was measured at each 10 min up to 30 min.

In the floc size and strength measurements, 0.5 g sample in 50 cm^3 distilled water was stirred using a magnetic stirrer at 500 rpm for 10 min. The flocculant at the desired dosage was added into the suspension during the stirring process, and the stirring process was continued for an extra 2 min. A small amount of floc-containing suspension was taken with a Pasteur pipette from the bottom of the beaker. In this process, a wide-diameter pipette was used in order not to break the flocs. The taken suspension was added into the water at 1 dm^3 volume for the floc size measurements. The suspension was stirred gently at 800 rpm with an overhead stirrer (RW20, IKA, Germany) to keep the flocs pending in the suspension during the measurements. The size distribution of the flocs was determined with a laser diffraction particle size analyzer (Mastersizer 3000, Malvern, UK) with respect to time for observing the change in the floc size, and hence floc strength. The experimental setup for the floc size and strength measurements is given in Fig. 3. The similar floc size and strength measurement set-up were used by Lemanowicz et al. (2011) previously.

3.   Results and discussion

3.1. Coagulation experiments

The settling rates of the coagulation experiments for the coal tailings were determined at 10^{-3}, 10^{-2}, 10^{-1}, and 1 mol/dm^3 ion concentrations, and the results are shown in Fig. 4 along with the results of the turbidity measurements. Since the turbidity of some suspensions was above the measurement range of the turbidimeter, their turbidity was recorded as 1000 NTU.

As seen in Fig. 4(a), in the case of 10^{-3} mol/dm^3 ion concentration, the settling rates of the particles increased in the presence of Mg^{2+} and Ca^{2+} ions. These results indicated that Mg^{2+} and Ca^{2+} ions at 10^{-3} mol/dm^3 concentration helped the bridging formation between anionic groups of the polymer (Sabah and Erkan, 2006) and negatively charged coal, quartz, and clay minerals (Alam et al., 2011). On the other hand, there was no significant change in the settling rates of the particles in the presence of Na$^+$ and K$^+$
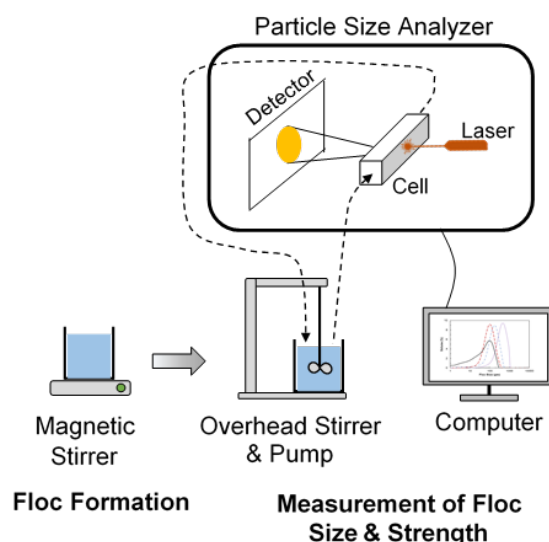
Fig. 3. Experimental set-up for the floc size and strength measurements

ions (Fig. 4(a)). Additionally, Fig. 4(b) shows that the turbidity values of the suspensions decreased in the presence of divalent ions as a function of time while the monovalent ions caused no change in the turbidity values. At 10^{-3} mol/dm^3 concentration, it is seen that the valance and therefore the ionic strength of the ions is the dominant mechanism. Divalent ions with a higher ionic strength compressed the electrical double layer and thus coagulated the particles more effectively than monovalent ions.

Apart from the influence of the valance of an ion, several other factors can also affect the change of the zeta potential including the hydration ability of the ions. In the aqueous solutions, ions can interact with surrounding water molecules to form a hydration shell around themselves (Wang et al., 2017). This interaction is ion-specific and depends on the physicochemical properties, such as the electron structure, atomic weight, and ionic radius, which determines the ion charge density. The ionic radii of K^+, Na^+, Ca^{2+}, and Mg^{2+} are 1.38 Å (Zhu et al., 2019), 1.02 Å (Zhu et al., 2019), 1.00 Å (Kanchana et al., 2013), and 0.72 Å (Kanchana et al., 2013), respectively. Small ions have a high charge density and cause a strong electrostatic ordering of nearby water molecules. On the other hand, large ions with low charge density lead the surrounding water molecules to be largely hydrogen bonded. Therefore, salt ions are classified as chaotropic (water structure breakers) or kosmotropic (water structure makers) according to their hydration behavior (Wu et al., 2016). The cations used in this study are ordered as $Mg^{2+}>Ca^{2+}>Na^+>K^+$ according to their kosmotropism. More kosmotrope ions have a stronger interaction with water. Therefore, it is seen in Fig. 1 (a) and (b) that more kosmotrope ions are more successful in the coagulation of particles.

In the case of 10^{-2} mol/dm^3 ion concentration, as seen in Fig. 4(c), the effect of divalent ions in the settling rate of the suspensions was more significant than the monovalent ions. This can be attributed to the effective adsorption of divalent ions on to the coal particle surfaces compared to the monovalent ions. Wang et al. (2017) reported that according to Coulomb's law, the electrostatic attraction of divalent ions is much stronger than that for monovalent cations. As a result, a divalent cation can be more competitively adsorbed on a solid surface. Therefore, divalent ions can have a stronger role in the decrease of zeta potential compared to monovalent ions. In addition to this, lower turbidity values were obtained in the presence of the divalent ions; however, the monovalent ions again showed no change in the turbidity values (Fig. 4(d)).

At 10^{-1} mol/dm^3 ion concentration, while the settling rate of the suspensions almost showed no change in the presence of divalent ions, the monovalent ions considerably increased the settling rate as seen in Fig. 4(e). In line with the results of the settling rate, the turbidity values of the suspensions also decreased significantly in the presence of monovalent ions rather than the divalent ions (Fig. 4(f)).

Finally, it is seen in Fig. 4(g) that when the ion concentration increased up to 1 mol/dm^3, the settling rate of the coal particles decreased considerably in the presence of divalent ions. The turbidity measurements indicated that the turbidity values also increased significantly in the presence of divalent
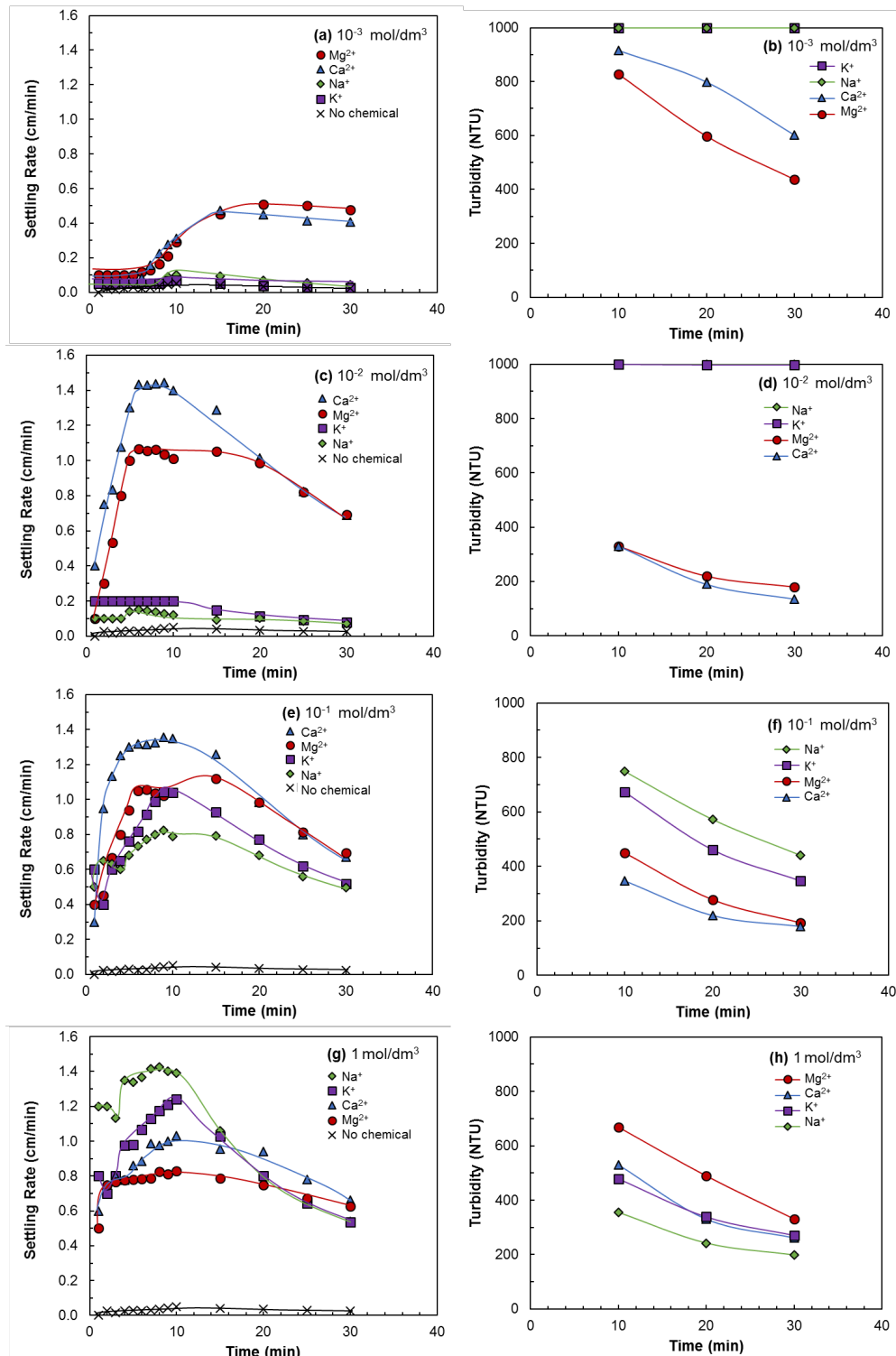
Fig. 4. Results for the coagulation experiments

ions as shown in Fig. 4(h). Moreover, the highest settling rate results were obtained in the presence of monovalent ions at this concentration. Similarly, Chen et al. (2017) stated that the positive effect of Na$^+$ on the coagulation of coal suspensions occurred due to the compression of the electrical double layer, and this led the electrostatic attraction among the coal particles.

Ionic strength can also play an important role in the adsorption of the chemicals (Li et al., 2012) and on the settling rate of the coagulation process (Morshedi et al., 2013), as well as optimum flocculant dosage (Borchate et al., 2014). In this study, the ionic strength of the solutions was also calculated using Eq. 2:

$$I = 1/2 \cdot \sum_{i=1}^{n} c_i(z_i)^2 \tag{2}$$

where i and n are the number of ions, I is ionic strength (mol/dm³), c is the concentration of the solution (mol/dm³), and z is the valance of the ions.

Based on the ionic strength values of the solutions calculated using Eq. 2, the ionic strength of divalent ion solutions was 4 times higher than that of monovalent ions. At 10^{-3} mol/dm³ and 10^{-2} mol/dm³ ion concentration, divalent ions were much more effective in the flocculation of coal tailings due to their higher ionic strength values on the contrary to monovalent ions. At 10^{-1} mol/dm³ ion concentration, the ionic strength of monovalent ions increased sufficiently, and therefore the settling rate increased. For the same reason, the settling rate continued to increase at 1 mol/dm³ concentration for monovalent ions. On the contrary, the excessive adsorption of the potential determining divalent cations of Ca^{2+} and Mg^{2+} on to the negatively charged coal particles changed the charge of coal surface positive. Therefore, an electrostatic repulsion among the coal particles significantly decreased the settlement rate. For these reasons, the optimum ion concentrations for monovalent and divalent ions were chosen as 1 mol/dm³ and 10^{-1} mol/dm³, respectively.

3.2. Flocculation experiments in the absence of ions

The settling rate results of the flocculation experiments and the turbidity measurements at 50, 150, and 300 g/Mg flocculant dosages in the absence of ions are seen in Figs. 5(a) and 5(b), respectively. Meanwhile, Figs. 5(c) and 5(d) show the particle size distribution and d_{90} floc sizes at these flocculant dosages, respectively.

It is a well-known fact that the dosage of flocculant has a significant role in flocculation (Tao et al., 2000a). A low dosage of flocculant may result in inefficient flocculation while higher dosages can increase the filtration resistance (Rushton et al., 2000; Tao et al., 2000b). Duzyol (2016) used Taguchi (L16) experimental design to determine the optimum conditions for the turbidity removal from fine coal suspensions and found that the most influential factor was the polymer dosage. Therefore, the flocculant dosage should be optimized for an effective flocculation process (Gungoren et al., 2018).

As seen in Fig. 5(a), there was no considerable change in the settling rate of the coal tailings as a function of flocculant dosage. However, at the beginning of the flocculation process, the effect of the settling rate in the presence of 50 g/Mg flocculant was slightly higher compared to the other dosages. However, Fig. 5(b) shows that the turbidity values decreased with a decrease in the flocculant dosage, and the lowest turbidity was obtained at 50 g/Mg flocculant. On the other hand, the sizes of the flocs formed at 50 g/Mg were considerably smaller than the flocs form at higher concentrations (150 g/Mg and 300 g/Mg) as seen in Fig. 5(c) and Fig. 5(d). Therefore, 150 g/Mg was chosen as the optimum flocculant dosage in this study.

3.3. Flocculation experiments in the presence of ions

The settling rate and turbidity results of the flocculation experiments in addition to the particle size distribution and d_{90} sizes of the flocs are given in Fig. 6(a-d), respectively for the various ion and flocculant combinations. The size distribution of the flocs is also presented in Table 1. Additionally, the coagulation/flocculation behavior and structures of the flocs are schematically illustrated in Fig. 7 depending on the results seen in Fig. 6.

It is seen in Fig. 6(a) that the use of ions alone slightly increased the settling rate of the coal tailings and decreased the suspension turbidity moderately (Fig. 6(b)). Meanwhile, the flocculant addition showed a great influence on the settling rate of the particles (Fig. 6(a)). However, since the flocculant alone was not efficient to settle down the colloidal particles (Fig. 7(a)); it was not effective in decreasing the turbidity of the suspension (Fig. 6(b)). Additionally, the results, seen in Fig. 6(c) and Table 1 indicated that large flocs were formed in the presence of the flocculant. However, the flocs were loose as illustrated in Fig. 7(a), and they were broken apart into smaller pieces under the shear stress applied during the experiments (Fig. 6(d)) in line with the literature (Hogg, 2000).

Meanwhile, Fig. 6(c) and Table 1 indicated that the flocs formed in the coagulation followed by the flocculation method were not as large as the flocs in the presence of the only flocculant, but still, they were large enough to settle down quickly as seen in Fig. 6(a). Furthermore, these flocs were more

compact (Figs. 7(b-c)), and therefore they were more stable under shear stress (Fig. 6(d)). Additionally, since the ions were capable of binding of the colloidal particles in the suspension (Figs. 7(b-c)), the turbidity of the suspension decreased significantly (Fig. 6(b)).
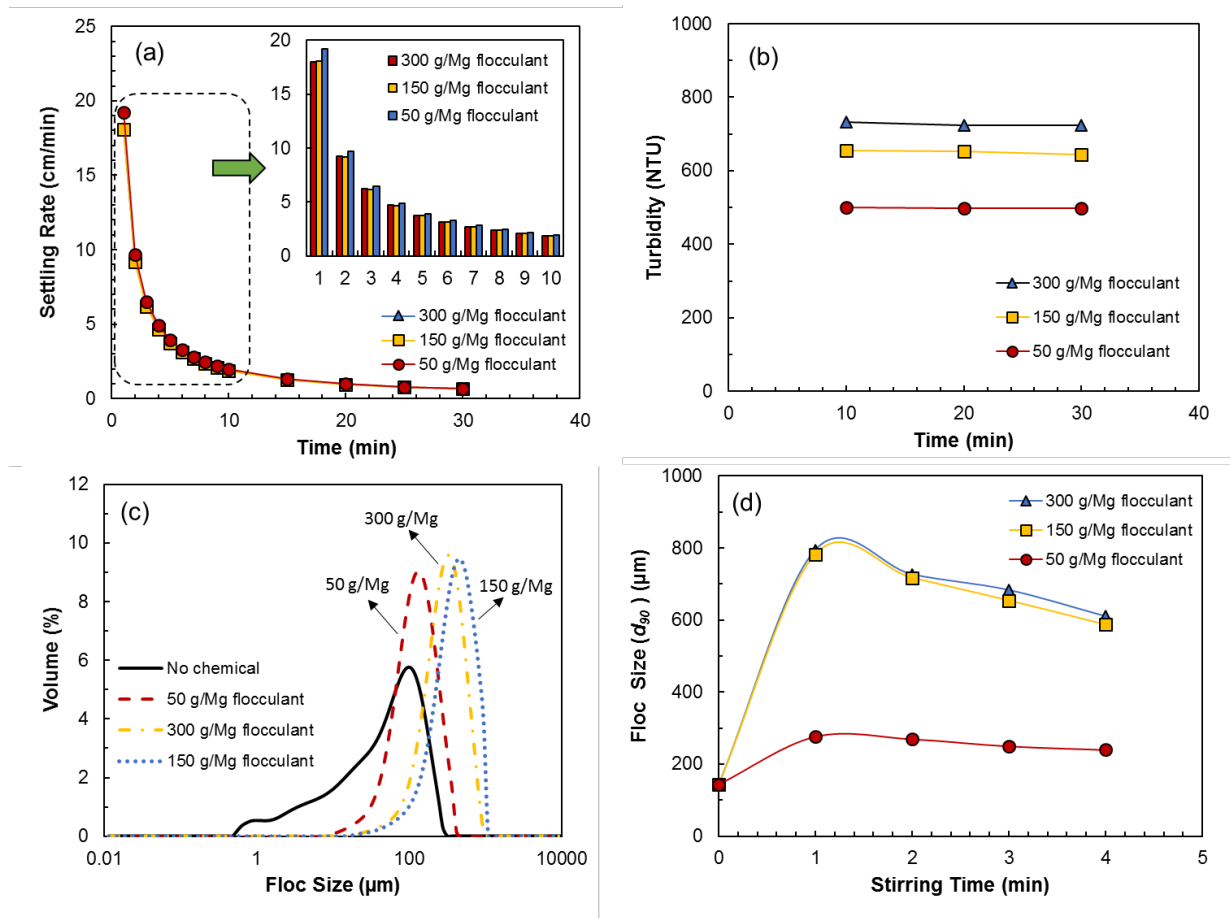

Fig. 5. (a) Settling rate (b) turbidity results of the flocculation experiments along with the (c) particle size distribution and (d) d_{90} sizes with flocculant

Table 1. Floc size distribution at the end of 4 min flocculation at various conditions

Ion Concentration (mol/dm³)	Flocculant Dosage (g/Mg)	d_{10} (µm)	d_{50} (µm)	d_{90} (µm)
-	50	48.191	116.947	239.631
-	150	121.438	297.432	587.061
-	300	125.497	306.455	610.118
1	150	49.71	144.244	291.06
10⁻¹	150	38.32	88.6	180.773

Furthermore, it is seen in Figs. 6(a-d) and Figs. 7(b-c) that although the effect of Na^+ and Ca^{2+} ions in the settling rate of the particles was negligible, smaller but more compact flocs were formed in the presence of divalent Ca^{2+} ion than monovalent Na^+ ion which caused more strength flocs and lower suspension turbidity.

Therefore, it can be inferred from the results of this study that coagulants are needed particularly to settle down the colloidal particles. Additionally, it is also clear that neither the optimization of settling rate nor the size of the formed flocs guarantees the compact consolidation of the flocs (Ofori et al., 2011). The flocculation success and floc structure are strongly dependent upon various parameters including the molecular weight, (Gray and Ritchie, 2006), charge (Cheng et al., 2011), and dosage (Nasser and James, 2006) of the flocculant, as well as the ionic composition of water (Alam et al., 2011).
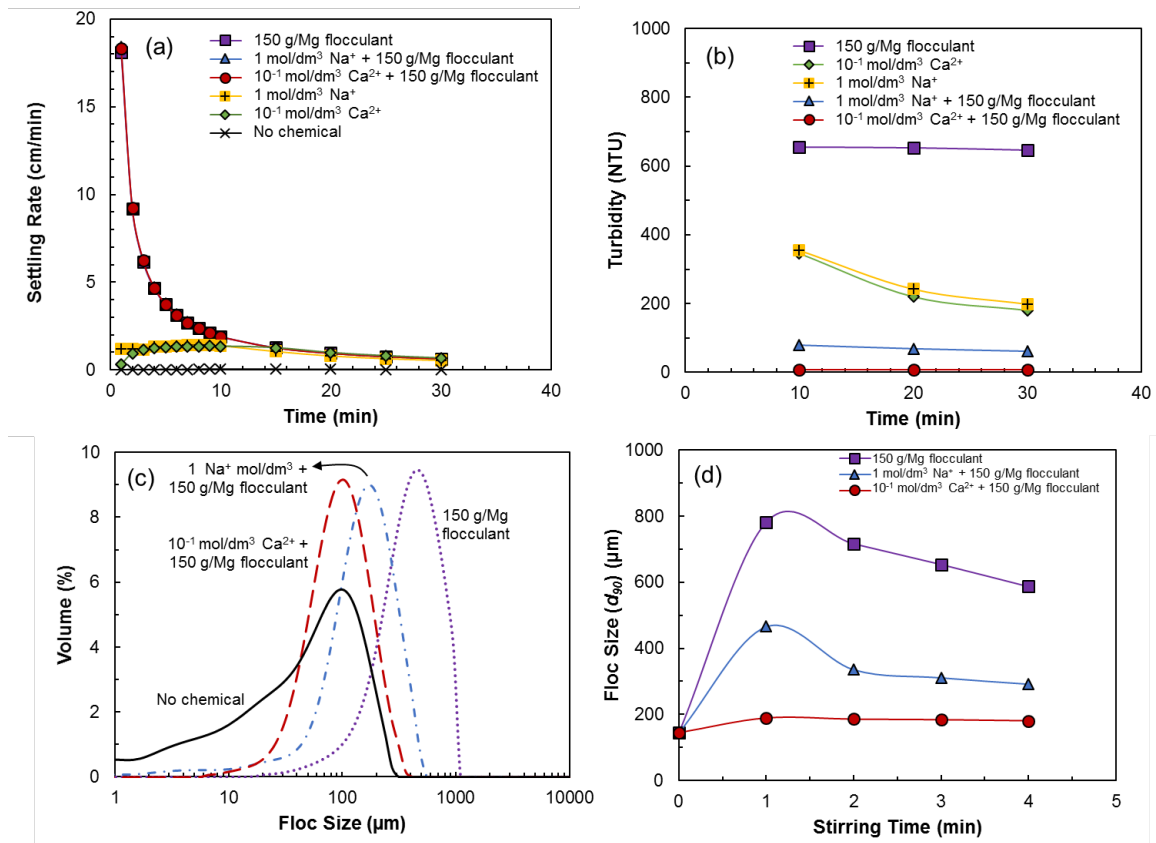
Fig. 6. (a) Settling rate and (b) turbidity results of the flocculation experiments at various conditions along with the (c) particle size distribution and (d) d_{90} sizes in the presence of Na⁺ and Ca²⁺ ions with flocculant
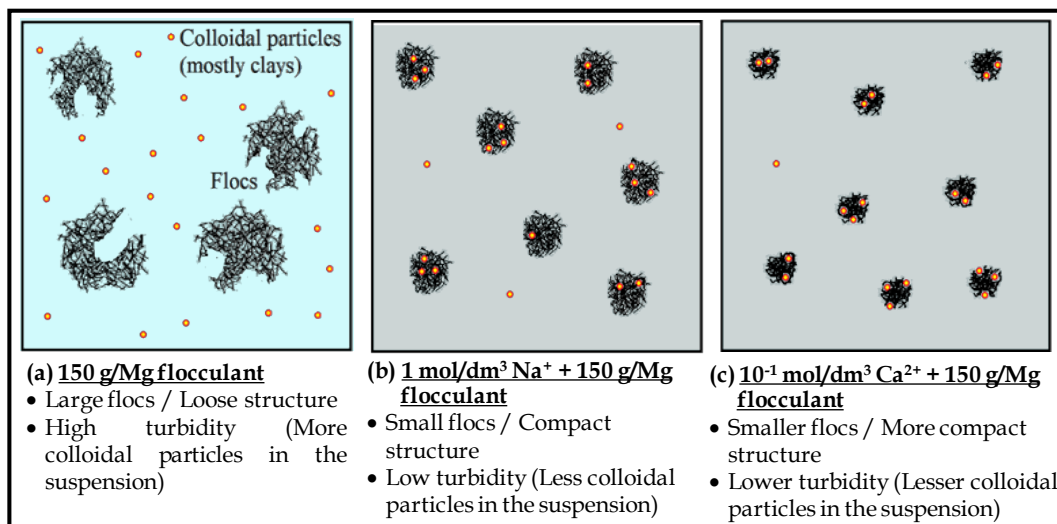

Fig. 7. Schematic illustration of coagulation and flocculation process for the coal tailings (a) 150 g/Mg flocculant (b) 1 mol/dm³ Na⁺ + 150 g/Mg flocculant, and (c) 10⁻¹ mol/dm³ Ca²⁺ + 150 g/Mg flocculant

4. Conclusions

This study aimed to investigate the coagulation/flocculation behaviors of coal tailings in the presence of monovalent (Na⁺ and K⁺) and divalent ions (Mg²⁺ and Ca²⁺) along with an anionic flocculant. For this purpose, the coagulation/flocculation experiments and turbidity measurements were carried out, and the size and strength of the flocs were determined. The coagulation experiments showed that the dissolved ions accelerated the settling rate of the particles at all concentrations. At lower ion concentrations (10⁻³, 10⁻², and 10⁻¹ mol/dm³), the higher settling rate values were obtained in the

presence of divalent ions. The maximum settling rate was obtained as 1.1 cm/min for Mg^{2+}, it was 1.4 cm/min in the presence of Ca^{2+} at 10^{-2} and 10^{-1} mol/dm^3 concentrations. However, at higher ion concentration (1 mol/dm^3), the highest settling rate was obtained in the case of monovalent ions (Na^+ and K^+) which were 1.2 and 1.4 cm/min for K^+ and Na^+, respectively. This can be attributed to the specific ion effect on the particles. While the divalent ions were more effective on the surfaces at low concentrations, the monovalent ions showed an influence on surfaces only at higher dosages. It is also important to note that after 10^{-1} mol/dm^3 Ca^{2+} and Mg^{2+} concentration, the effect of the ion concentration on the settling rate of the particles were reversed and the settling rate decreased from 1.1 cm/min to 0.8 cm/min in the presence of Mg^{2+} and from 1.4 cm/min to 1.0 cm/min for Ca^{2+}. This negative influence was caused by the excessive adsorption of the ions on coal surfaces which changed the zeta potential of particles from negative to positive. Moreover, the turbidity values decreased with the increased settling time and ion concentration up to 10^{-1} mol/dm^3 concentration. The turbidity values were 193 NTU and 180 NTU in the presence of Mg^{2+} and Ca^{2+}, respectively at 10^{-1} mol/dm^3 at 30 min. However, the turbidity values in the presence of 1 mol/dm^3 divalent ions increased in line with their decreasing settling rate. At this concentration, the turbidity values were 271 NTU and 198 NTU in the presence of K^+ and Na^+, respectively at 30 min. For these reasons, the optimum ion concentrations for monovalent and divalent ions were determined as 1 mol/dm^3 and 10^{-1} mol/dm^3, respectively.

Additionally, the flocculation experiments were carried out as a function of flocculant concentration. It was revealed that the concentration of the flocculant showed a minor role in the settling rate. However, since 150 g/Mg flocculant was determined as the minimum dosage for obtaining the sufficient floc size (d_{90} of 143 µm) and strength, coagulation followed by the flocculation experiments were carried out at this dosage.

The results of these experiments indicated that the flocculant was the dominant chemical for the settling rate. According to the results of the floc size measurements, the presence of ions decreased the floc size slightly. However, the main effect of ions was on the turbidity of the suspension. The turbidity decreased from 645 NTU to 61 NTU and 6 NTU when 1 mol/dm^3 of Na^+ and 10^{-1} mol/dm^3 of Ca^{2+} ions were used with 150 g/ Mg flocculant, respectively. Since the ions could bind the colloidal particles in the suspension more effectively than comparatively larger flocculant molecules, the turbidity values decreased considerably. Additionally, it can be inferred from the floc size and strength measurements that while large and loose and therefore weak flocs formed in the presence of the flocculant alone. Smaller but more compact and strong flocs were formed in the combination of ions and flocculant. Overall, it can be concluded from this study that the coagulation followed by the flocculation method can be employed to obtain fast flocculation behavior and low turbidity.

Acknowledgments

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