# Studies on Clarification of Coal Washery Effluent Using Polymeric Flocculants and Settling Kinetics

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## Abstract

Settling tests were conducted on the washery effluent using three types of flocculants namely cationic (Telfloc-3674F), anionic (Magna-1011) and non-ionic (Nalco-83370$^+$). For the study purpose coal washery effluent (having pH of 8.72) was collected from a newly commissioned plant-thickener. Tests were conducted by varying the pH of the pulp at three levels of acidic (4.0), alkaline (11.0) and the natural pH (8.72) of the as collected effluent, besides the flocculent dosages varied at four levels (2, 4, 6 and 8 gpt) for each of the flocculants stated. The results of these tests, estimated in terms of initial settling rate and turbidity indicated that; among the three flocculants tested Telfloc-3674F and Magna-1011 gave best results as compared to Nalco-83370$^+$ flocculent at a washery water pH 8.72. The effect of molecular weight of the flocculants on settling of solids in effluent has been established in terms of the kinetics with a characteristic number for each of the type of flocculants used.

## Introduction

With advancements that have taken place in the field of mining, proportion of fines generation in the ROM coal has gone up appreciably. This resulted in numerous environmental problems related to air-water pollutions. Further, Indian coals possess difficult-to-wash property which needs finer size reductions for improved liberation prior to washing. This has resulted in generation of excess fines in the coal being sent to washing circuits. Coal (hydrophobic) along with other mineral fines (hydrophilic) like shale, slate, clay and several other impurities are generated during stacking, handling, transportation, and dumpling at different points in CPP [1]. Coal washing involves wet processes where coal gets mixed with water, and requires efficient dewatering and clarification techniques. Coal being hydrophobic in nature, at finer sizes the particles remain suspended in water and do not settle even after several days, particularly in tailing ponds. This pollutes the ground water and also deteriorates the agricultural land/crops surround it. Besides this the unclarified, when recirculated to coal washing plants, spoils the overall performance of the operating washery, because of accumulation of colloidal sized particles in excess. These problems are not limited only to the Indian coal washing circuits, but it is noticed globally in all the coal washeries [2–5].

To get-rid of all these problems, one alternative is to enhance the settling rate of particulate solids using flocculants [6]. Polymer flocculants show higher efficiency and acceptability in wastewater/effluent treatments [7–10] especially for removing suspended particulate matter that are accountable for high turbidity [11]. Flocculants are high-molecular long chain water-soluble polymeric compounds that bind the surfaces of the dispersed particles physically and combine them to form agglomerates known as flocs that settle rapidly. The widely used flocculants are; the polyelectrolytes of anionic or cationic or non-ionic types having high molecular weight with different structures of macromolecules which intensify the solid-liquid separations in coal washing plants [12]. Long-back Slater and Kitchener reported that the application of certain polymers as flocculants helped in promoting the settling rates of solids in industrial disperse systems [13].

Water clarification plays a major role in the overall economics of the coal preparation plants (CPP). As per the present environmental policies no effluent/slurry is allowed to be discharged outside the washery premises. Under these circumstances, water clarification using flocculants will help to abide by the guidelines set by MoEF, GoI, 2010 [14], wherein the CPP are to operate the plants on a closed system water-circulation basis, and limit the fresh water consumption not exceed above 1.5 $m^3$. Nowadays, the washeries are designed for closed-circuit system, where the water used in washing circuits to wash the raw coal is recycled and reused. Since this water detains appreciable percentage of colloidal size coal fines and clay particles, need to be clear-off dirt and contain only negligible amounts of suspended particles. Otherwise, huge volume of water would be required to process the coal. But, the removal of these colloidal fines (or water clarification) from the tailing slurry has posed number of challenges.

As a general norm, fines having size less than 0.50 mm are generally responsible for forming slurry in the washery [15]. Thus, an appropriate solid-liquid separation has become an essential part of a coal washing plant. In practice, the prevalent method adopted is sedimentation with aid of flocculants in thickeners, using polymeric flocculants. This method has two significant strictures that evaluate flocculation performance [16]. The first is the low water-turbidity, since water recovered at the thickener overflow is recycled to the plant. The suspended colloidal particles in the recycled water should be at the lowest level, eliminating any negative implications to the process. The second is, settling rate of the flocculated particles, has a direct effect on thickener capacity as well as flocculent performance. Thus, the challenge is dual; precise determination of various properties of the washery water effluent, this includes mineralogy of the gangue particles, physic-chemical properties such as pH, conductivity, pulp density, TDS, alkalinity, hardness etc. besides electro-kinetic properties of the solid matter in washery effluents.

Achieving the lowest water turbidity level while maintaining high settling rate typically influenced and controlled by polymeric flocculent properties, its dosages and the pH value of the washery effluent. Moreover, the efficiency of the process is dependent on the use of accurate type of flocculants (i.e. anionic, cationic and non-ionic polymer) as well as the addition of their dosage [17–18]. On the other hand, water is becoming a scarce commodity, and several governmental slogans are heard every day to save water under the government's national policy. Still, the problem of water purification persists and supply of good quality water remains as a major problem. Thus, coal-water slurry handling has become an integral part of a coal beneficiation plant. This is because, the amount of fine-coal tailings generated annually is very high. To overcome the difficulties faced, the alternatives left are (i) Development of efficient solid-liquid separation systems, (ii) Selection and addition of the correct flocculent and (iii) Understanding of the interaction between the flocculent and the slurry is vital in achieving optimum condition.

In view of the above, in this study the influence of flocculent types, their dosage effects and effect of pH of the pulp on the settling of fine coal fines has been attempted after the physico-chemical and mineralogical characteristics of an effluent collected from a thickener of an operating plant (Dahibari, India).

## Materials And Methods

**2.1 Sample Collection and plant details**: Coal washery effluent form a tailing thickener of Dahibari coal washing plant operating under Bharat Coking Coal Limited, Dhanbad, was collected from the feed-well pipe of the thickener. Collection of the effluent sample was made in large capacity plastic containers with their lids fitted air-tight and stored intact as per guidelines given by American Public Health Association (APHA 2012) [19]. Among the several containers, one of the container was selected, the slurry was filtered and dried. The solids obtained thereof were analysed for the characterisation studies in detail.

**About Dahibari coal washing plant**

Dahibari washery was designed for washing of high-ash Indian coals, that are recently classified and categorised as washery grade IV (with 28 to 35% ash) and washery grade V (with 35 to 42% ash). This is a standalone-type coal washery commissioned in the year 2018 with a treatment capacity of 1.6 MTPA of coal that produces small quantity of washed coking coal (of 19% ash) and the power coal (middling) as its final products. Both washed coal (of 19% ash) and the middling (with 33.5 ± 0.50% ash to captive power plants) are sent to SAIL steel plants. Since the washery was designed to receive coals from different collieries, it falls under the category as NLW (Non-linked washery). Hence the feed ash of raw coal to the washery varies very widely ranging from 28 to 40%. Raw coal crushed to 30-mm is washed with the help of heavy media cyclones and thickeners installed for the collections of comparatively large-sized fraction of fines. The supernatant water of the thickener impounded is re-circulated to the plant while the sludge of the thickener is store in tailing ponds. The satellite location map (latitude = $23^{o}$72'91.4"N and longitude = $86^{o}$77'92.0"E) of Dahibari is given in Fig. 1.

**2.2 Characterization of Sample**: Characterization studies on the collected effluent sample was carried out to know the physico-chemical parameters of slurry viz. pH, conductivity and TDS were measured onsite while the other parameters in the laboratory. The collected effluent showed a natural pH of 8.72 and high turbidity value of 1370 NTU, which may be because of presence of colloidal fines necessitating addition of flocculent for improved clarification. All the physico-chemical properties of the effluent are presented in Table 1. For other characterization studies of coal in effluent, a small amount of slurry was dried at $40^{o}$C and the results are presented in Table 2. Details of the major instruments used for characterization studies are mentioned in Table 3 in supporting information.

**2.3 Water and Flocculants used**: The washery-water slurry of natural pH 8.72 was used to study settling test. To study the effect of pH of pulp (4.0 and 11.0), the same washery-water was induced by addition of required amount of 1N Hydrochloric acid (HCL) supplied by M/s RFCL Ltd., New Delhi, India and 1N Sodium Hydroxide (NaOH) supplied by Merck Specialities Pvt. Ltd., Mumbai, India. For experimental work three types of flocculants were selected namely viz., Cationic flocculent – Telfloc-3674F (TF), Anionic flocculent - Magna-1011(MF) and Non-ionic - Nalco-83370$^{+}$ (NF). Settling tests were performed by varying each of the above stated flocculants at three levels. TF is a medium molecular weight cationic polyacrylamide was supplied by M/s Ion Exchange India Ltd., Patancheru, India. MF is a high molecular weight anionic polyacrylamide supplied by M/s BASF, India. Whereas, NF is a non-ionic polymer supplied by M/s Nalco, India as presented in Table 4. For each test desired amount of freshly prepared flocculent was used after diluting it to 0.1% w/w homogeneous stock solution to study the dosage variations. Fresh flocculent solutions were prepared at an interval two days to improve the precession of results.

**2.4 Flocculation tests and Experimental Studies**: A total of 36 Settling tests were performed using three different flocculants. For each type of flocculent, its dosages were varied at four levels of 2 gpt (0.06 mg/l), 4 gpt (0.12 mg/l), 6 gpt (0.18 mg/l) and 8 gpt (0.24 mg/l) and for each dosage of the flocculent, three pH levels were studied. In all these tests a fixed pulp solids concentration of 3.0% w/w was kept constant (as per prevailing practice at the plant). All these tests were performed at the room temperature varying between 25–30°C. The details of the test conducted along with the levels of the variables studied are summarised in Table 5 in supporting information. Each of these settling test were performed in a 1000 $cm^3$ graduated measuring cylinder as per ASTM 2008 [20] standard jar-test method. For homogeneous mixing of slurry, a constant mixing time of 3min was applied to the collected grab sample prior to each tests. The desired amount of flocculent was added to the slurry, followed by manual stirring for 30 sec. The change in the interface heights as a function of time was recorded for plotting of the settling curves. The interface heights of slurry for the chosen time intervals of 0, 15, 30, 45, 90, 120, 180, 300, 600 seconds were noted. Using this data, settling rates were established graphically from the slope of the straight line of settling curve obtained as per standard procedure (Fig. 2c). After 600 sec of settling time, an aliquot of the supernatant was taken for the turbidity measurements using turbidimeter.

Table 1
Physico-chemical characterization of Dahibari washery effluent sample

| Parameter | Dahibari washery effluent | Permissible Discharge Limit IS:2490 (1981) [46] |
|---|---|---|
| Colour | Black | Colourless |
| pH | 8.72 | 5.5-9.0 |
| Temperature, $^{o}C$ | 29.4 | < 40 |
| Conductivity, µS/cm | 386 | - |
| Turbidity, NTU | 1370 | - |
| COD, mg/l | 300 | 250 mg/l |
| Oil & Grease, mg/l | 5.2 | 10.0 mg/l |
| Total Hardness as mg/l $(Ca + Mg)CO_3$ | 310 | - |
| Calcium Hardness as mg/l $CaCO_3$ | 306 | - |
| Total Alkalinity as mg/l $CaCO_3$ | 340 | - |
| Total solid, mg/l | 7521 | - |
| Total suspended solids, mg/l | 7120 | |
| Total dissolve solids, mg/l | 401 | 2100 mg/l |
| Chloride as mg/l NaCl | 450 | 1000 mg/l |
| Fluoride, mg/l | 1.15 | - |
| Sulphate as mg/l | 144 | 1000 mg/l |
| Nitrate as mg/l | 2.76 | - |
| Iron (Fe), mg/l | 1.7 | - |
| Aluminium (Al), mg/l | 0.2 | - |
| Copper (Cu), mg/l | 0.1 | 3.0 mg/l |
| Lead (Pb), mg/l | BDL | 0.1 mg/l |
| Zinc (Zn), mg/l | 0.8 | 15.0 mg/l |
| Cadmium (Cd), mg/l | BDL | 2.0 mg/l |
| Arsenic (As), mg/l | BDL | 0.2 mg/l |
| Chromium (Cr), mg/l | BDL | 2.0 mg/l |
| BDL – Below Detection Limit i.e. -0.001 mg/l | | |

Table 2
Characterization of Dahibari effluent coal

| Properties | Unit | Values |
|---|---|---|
| Proximate Analysis (Air dried basis) | | |
| Total Ash content, | % | 44.96 |
| Volatile matter | % | 17.38 |
| Moisture | % | 1.91 |
| Fixed carbon | % | 35.75 |
| Ultimate Analysis (Air dried basis) | | |
| Carbon | % | 33.26 |
| Hydrogen | % | 7.56 |
| Nirogen | % | 13.90 |
| Sulphur | % | 0.036 |
| Oxygen | % | 0.28 |
| Other properties | | |
| $GCV^{\#}_{(EB)}$ | Kcal/kg | 3967.2 |
| Specific Gravity | $kg/m^3$ | 1568.0 |
| LTGK Grade | - | G12 |
| Loss of Ignition (LOI), | % | 55.04 |
| Particle size (D80p), | µm | 60 |
| Pulp density (solid concentration) (as received basis) | % w/w | 3.0 |
| Major gangue mineral | Kaolinite, quartz, muscovite | |
| # Goss Calorific Value estimated under equilibrated condition (at Temp = 40°C and RH = 60%) | | |

Table 4
Properties of the polymers

| Name | Telfloc3674F | Magna1011 | Nalco83370$^{+}$ |
|---|---|---|---|
| Type | Cationic | Anionic | Non-ionic |
| Charge density | High charged | High charged | Medium charged |
| Molecular Weight | Medium | High | Low |
| Supplier | Ion Exchange India (Ltd.), Patancheru, India | BASF, India | NALCO, India |

To identifying a most suitable type of flocculent for improved clarification of coal washery effluent, the results of all the jar settling tests conducted have been analyzed in terms of (i) initial settling rates and (ii) the turbidity of the aliquot supernatant liquid. These two responses were determined as stated below:

**Estimation of Initial Settling rate**

This was determined graphically (as per the standard practice) by plotting the height of the slurry-water interface measured as function of time. The value of the slope of the settling curve estimated graphically in the near straight-line region of initial settling periods is considered as the 'initial settling rate'. This is shown in Fig. 2c as a typical example (for a test done at 4 gpt of dosage at a pH of 8.72 of the flocculent TF). Together with the settling curve (Fig. 2c), a comparison of settling data with the zones noticed in thickeners corresponding to the interfaced seen in a jar test is made in Figs. 2 (a and b).

**Suspension Turbidity**

Turbidity of the aliquot drawn from the supernatant liquids at the end of 600 seconds were measured by Turbidimeter. These results were used in conjunction with the initial turbidity of the washery effluent to measure the 'Turbidity Removal Efficiency' given as [21–23]

$$\text{Turbidity removal efficiency, \%} \quad = \quad \left[1 - \frac{T_f}{T_o}\right] * 100 \qquad \text{Eq. (1)}$$

Where, $T_o$ - is the initial turbidity (Nephelometric turbidity unit, NTU) of the washery effluent, $T_f$ - is the final turbidity of the supernatant liquid obtained after flocculation at the end 600 sec.

### Settling Kinetics

The effect of flocculants (TF, MF and NF) on clarification of Dahibari effluent has been assessed for the rate of natural pH (8.72) using a standard second-order kinetic model given as [24]

$$\text{Second Order Rate, } K_2 = \left[\left(\frac{1}{(a*t)}\right) * \left(\frac{x}{(a-x)}\right)\right] \qquad \text{Eq.(2)}$$

Where 'a'- is the initial height of effluent in a jar test, and '$x$'- is the final interface height of effluent after addition of flocculent measured at time 't'.

From Eq. 2, the efficiency of flocculation can be estimated by plotting the second order rate constant $K_2$ ($cm^{-1}$ $sec^{-1}$) against time-'t'. Gregory [25] described it as second-order rate equation based on collision theory for flocculation.

## Results And Discussion

# 3.1 Characterization

The following characterization studies were carried out on the high-ash Dahibari effluent fines:

**a) Granulometric analyses of coal washery effluent**: The particle size distribution patterns expressed in both differential and cumulative forms (by volume percentages) washery effluent are shown in Figs. 3a and 3b respectively indicating about 80% of the particles are below 60 µm in the effluent (Fig. 3b).

**b) Zeta potential studies**: The zeta potential of the suspension plays an important role in flocculation. It is a measure of surface charge acquired on the particles in washery effluent. The results of Zeta potential of Dahibari washery effluent as a function of pH is shown in Fig. 4. The zeta potential value of the particles at natural pH of 8.72 was 10.3 mV exhibiting positive surface charge at all pH values except at pH 12. The addition of $OH^-$ ions (from NaOH) is accountable to revert the positive surface charge into negative at alkaline pH 12 of effluent. The positive surface charge may be due the presence of alumino-silicates along with sodium and potassium. However, in the presence of flocculants at a pH of 8 the value of the zeta potential gets increased to -70.1 mV, -69.1 mV and − 52.8 mV for TF, MF and NF flocculants with its dosage 8 gpt respectively. According to the ASTM D-4187 Standard Test Method, if the zeta potential of colloids (colloidal particles) in water or waste slurry is above − 60 mV, the stability of the system is classified as 'perfect' [3]. Since, the present case zeta potential for the coal slurry was observed to be 10.3 mV at the pH 8, this was classified and considered as highly unstable condition, suggesting the possibility of increase in settling characteristics through flocculation.

**c) XRD analysis of coal**: The adsorption of a flocculent depends on the mineralogical assemblages of the suspended particulate matter, in addition to the prevailing aqueous environment i.e., in the present case the quality of effluent collected from the washery. Therefore, it was necessary to identify the gangue mineral components present in the feed coal. The XRD pattern of the washery effluent coal is represented in Fig. 5, which indicates the presence of muscovite, kaolinite and quartz as the gangue minerals present in the order of increasing intensity of XRD.

**d) TG-DTA analysis of feed coal**: To confirm the results of proximate analysis of coal TG-DTA test were conducted at a heating rate of 10 K/min in oxygen atmosphere on the coal washery effluent. The TG-DTA peaks shown in Fig. 6 depicts a drastic weight loss over 300–600$^{o}$C temperature range in the TGA curve is due to decomposition of carbon, volatile matter and moisture of the coal. Similar observations were also made by Sabah et al [26].

# 3.2 Experimental

# 3.2.1 Effect of flocculent type and its dosages on initial settling rates

In flocculation, the molecular weight of a flocculent affects the performance as it controls the inter-particle bridging mechanism, and so the clarification. Literature cited on this aspect revealed that [1, 3, 27–29] higher molecular weight results in improved bridging mechanism, despite the evidences where, increase in molecular weights beyond certain limit, results in deleterious effects. This in fact may be because; very high molecular weight flocculants generally are more viscous and do not mix properly or get distributed throughout the slurry. This affects the adsorption, which has to be very rapid. In view of this in the present study, three different molecular weight flocculants (of high; MF, medium; TF and low; NF) were selected as specified in Table 4.

Figures 7 (a to c) are plotted to analyse and compare the influence of the three flocculent types (TF, MF and NF) by considering the initial settling rates of the flocs at varied flocculent dosages (varied from 2 gpt to 8 gpt), for the tests conducted at a constant level of pH in each of these figure. The maximum initial settling rate observed is for the flocculants TF and MF with the initial settling rate values of 0.4178 and 0.3333 cm/sec respectively. Whereas, with low-molecular weight flocculent NF the highest initial settling rate noticed is 0.2960 cm/sec when analysed at a fixed dosage of 8 gpt at a natural pH of 8.72. This established clearly the influence of molecular weight and the iconicity of the flocculants studied (Table 4).

Further, the effect of dosage of the flocculants added is also illustrated in these figures, where; an increase in the settling rate of coal (together with mineral impurities) also increases gradually and touches a highest value [30–31, 3] with increased flocculent dosage. The variations noticed in the settling rates are significant only after 6 gpt of flocculent addition, for all the three types of flocculants tested. However the reason for low settling rates at lower dosages for a given pH may be due to the inadequate concentration of polymer for adsorption onto the surface of the particles [32–33].

## 3.2.2 Influence of pH of effluent on settling rate

The pH value of an effluent plays a significant role on adsorption of a polymer onto the surface of particle and size-growth of flocs in slurry [31–32, 34–37]. Figures 7 (a to c) are plotted to study the effect pH variations clearly depicts that at natural pH (pH = 8.72), initial settling rates observed are of high values than that of acidic (pH = 4.0) and alkaline (pH = 11.0) pH levels of the effluent. This implies that, in acidic and alkaline pH levels, excess of $H^+$ and $OH^-$ ions occupy the surface of oppositely charged mineral impurities associated with coal fines and also resist the extension of long-polymer chains in slurry, despite of its high dosages which negatively affects flocculation process & lowers down the rate of settling [38].

Incidentally, the cationic polymer (TF) has positive charge patch of quaternary ammonium, sulphonium or phosphonium ions [29] that adsorb through long chain polymer bridging onto the positive charge surface of particles present in effluent. Simultaneously, the negative charge patch of carboxylic group on the anionic polymer (MF) gets adsorbed on the positively charged particles present in the washery effluent through charge neutralization. While, the non-ionic polymer (NF) gets adsorbed through hydrogen bonding or hydrophobic interactions [32, 39] during floc formation of the particles present in Dahibari washery effluent. This implies involvement of different mechanisms at different pH ranges in clarification of Dahibari washery effluent. Thus resulting retarded settling rates in acidic and alkaline pH conditions of the effluent. Therefore a natural pH 8.72 is found to be effective for all types of flocculants used in this study to enhance the settling rates.

## 3.2.3 Effect of turbidity analogous to settling rate

Since the Dahibari coal washery effluent consisted of kaolinite (clay) and muscovite minerals. Both being flaky/lath shaped particles, do not settle easily and remain suspended, leading to high turbidity of the aliquot. Turbidity of Dahibari washery gave a value of 1370 NTU at natural pH of 8.72 imparting black colour to the effluent (Table 1). Figures 8 (a to c) shows a maximum turbidity removal of 99.19% (11.1 NTU), 99.28% (9.8 NTU) and 93.20% (93.1 NTU) for TF, MF and NF respectively at 8 gpt of flocculants dosage and natural pH of 8.72. This analogous to the initial settling rates mentioned in Sect. 3.2.1. A highest turbidity reduction of 9.8 NTU was noticed with MF because of oppositely charged physical bonding between the particles in effluent and the anionic surface charge of flocculent. Besides this, the variations noticed in turbidity results is due to high molecular weight of polymers leading to formation of large sized but less compact flocs, while the low molecular weight polymers show a reverse phenomenon resulting in formation of small and more compact flocs [32, 40–42].

In general, at slow initial settling rates, the colloidal particles in effluent get more time to interact with polymer and also more inter-particle collisions to form strong flocs resulting in more clarity of supernatant. But in the present case, for the cationic and anionic flocculants, even with higher initial settling rates the turbidity removal efficiencies noticed are high.

However Figs. 8 (d to f) and 8 (g to i) clearly represent that even with reduced initial settling rate values (noticed at acidic and alkaline pH levels) the turbidity removal efficiencies did not improve. This observations is noticed at all the dosage levels of the flocculants. In other words, even with increased flocculent dosage, the turbidity removal efficiency do not meet the high values observed with that of natural pH of 8.72. This is mainly because of the presence of excess of $H^+$ and $OH^-$ ions that hinder the polymer adsorption activity onto the surface of particles present in Dahibari washery effluent. It can be concluded from Fig. 8 that high supernatant clarity does correspond to high settling rate.

A comparison of settling rates and turbidity removal values (NTU) for coal washery effluents carried out by different researchers in their previous studies using different polymer flocculants with the results of the present study has been made and shown in Table 6. The table clearly reveals that the present study results achieved are comparable and efficient, as it gives a maximum settling rate and turbidity removal values for a minimum duration of 600 sec at lower levels of flocculent dosages even with very fine size particles of -60 μm ($D_{80p}$).

Table 6
Comparison of settling rate and turbidity removal specifically for coal washery effluents by polymer flocculants from studies by some investigators (A true extra the information cited from the literature)

| Investigator | Name of Polymer flocculants | Type of Polymer Flocculants | Molecular weight of Polymer flocculent | Flocculent dosage | Maximum Settling rate achieved | Solid content / Pulp density | Effective pH of slurry | Particle size in slurry | Initial Turbidity | Maximum Turbidity removal | Time turbid measu |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sabah and Cengiz 2004 [17] | Praestol 2540 | Anionic (Medium) | 15–20 million | 34.19 g/ton-solids (2.0 mg/l) | 300 mm/min | 5.85 % solids | 8.3 | -0.18 mm | - | 18.8 NTU | After 1 minut |
| | Praestol 2515 | Anionic (Low) | 15–20 million | 51.28 g/ton-solids (3.0 mg/l) | | | | | | 8.0 NTU# | |
| | Magnafloc 351 | Nonionic | 16 million | 102.56 g/ton-solids (6.0 mg/l) | | | | | | 6.3 NTU | |
| | Praestol 857 BS | Cationic | 12–15 million | 119.66 g/ton-solids (7.0 mg/l) | | | | | | 12.0 NTU# | |
| Moyakhe et al 2017 [38] | Senfloc 5310 | Nonionic | High | 193 g/ton | 1110 mm/min | 4.71 % | 3.8 | - | 60.0 NTU* | 41.0 NTU* | After 1 minut |
| | Senfloc 5330 | Nonionic | Medium | 193 g/ton | 745 mm/min | | | | | 18.0 NTU* | |
| | Senfloc 5150 | Anionic (Low) | High | 97 g/ton | 305 mm/min | | | | | 10.0 NTU | |
| Shravan Kumar et al 2014 [48] | Magnafloc1011 | Anionic | High | 32.50 g/t solid | 178.15 mm/min | 8.0 % solids (w/w) | 8.0 | -600 mm (1.1–700 µm) | 30 NTU$ | 7.42 NTU | After 1 minut |
| Deniz 2013 [49] | MagnaflocLT27 | Anionic | - | 0.04 % (4.0 mg/l) | 19.63 cm/min | 6.0 % | 8.0 | -0.038 mm | - | - | - |
| | Magnafloc1011 | Anionic | | 0.04 % (4.0 mg/l) | 12.74 cm/min | | | | | | |
| | MagnaflocLT25 | Anionic | | 0.05 % (5.0 mg/l) | 3.489 cm/min | | | | | | |
| | Magnafloc155 | Anionic | | 0.1 % (10.0 mg/l) | 6.481 cm/min | | | | | | |
| | SuperflocN300 | Nonionic | | 0.3 % (30.0 mg/l) | 10.422 cm/min | | | | | | |
| Present study | Telfloc-3674F | Cationic | Medium | 8 gpt (0.24 mg/l) | 0.4178 cm/sec | 3.0 % solids (w/w) | 8.72 | -60 µm (4.4–142 µm) | 1370 NTU | 11.1 NTU (99.19 %) | After 1 minut (600 s |
| | Magna-1011 | Anionic | High | | 0.3333 cm/sec | | | | | 9.8 NTU (99.28 %) | |
| | Nalco-83370+ | Nonionic | Low | | 0.2960 cm/sec | | | | | 93.1 NTU (93.20 %) | |

# Estimated from Fig. 4 of the quoted reference [17] * Estimated from Fig. 3 of the quoted reference [38] $ Estimated from Fig. 7 of the quoted reference [48]

## 3.2.4 Settling kinetics

The Plots shown in Figs. 9 (a to c) represent the settling curves at varied flocculent dosages for three different flocculants (TF, MF and NF) obtained at the natural pH of Dahibari washery effluent (pH = 8.72). Figures 10 (a to c) represent their corresponding second order kinetic plots. It can noticed from the settling curves of TF and MF that, all the curves show almost a linear variation with time upto 90 sec, and then deviate with prolonged settling time, finally to remain constant after 120 sec of settling time. Whereas, the low molecular weight flocculent NF although shows the linearity in settling upto 90 sec, but an exponential variation in settling is noticed till 240 sec of settling time which eventually tends to an asymptotic value i.e. after 240 sec of time.

In Figs. 10 (a to c), the discrete settling rate constants (Δh/Δt) estimated at a different settling durations are plotted against time. This was felt necessary because, most of the settling curves overlapped each other indicating almost similar settling pattern in Figs. 9 (a to c). However, the plots shown in Figs. 10 (a to c) clearly depict a distinguishable variations in their linearity following the second order kinetic settling rate for all the three types of flocculants tested. It is interesting to note that, from the slope of these plots, the plotted lines converge and overlap each other with decreased molecular weight of flocculants. This implies the dosage variations made with the low molecular weight flocculent (NF) is marginal and insignificant.

#### Variation in rate constant with flocculent dosage

Further, observing to the slopes of the straight lines shown in Figs. 10 (a to c) with a changed flocculent dosages, their slopes were found to increase with the addition of flocculent quantity (gpt). Higher flocculent dosages gave higher slope values and vice-versa. The variation in slopes noticed is also dependent on the type of flocculent and its molecular weight. Now to understand the effect of flocculent dosage on overall settling rate, Fig. 11 has been plotted by taking dosage in gpt (on abscissa) against the value of $K_2$ (in ordinate) for a given flocculent. In this case also a linear variation of $K_2$ with the flocculent dosage is observed. The values of the slopes of the lines shown in this plots can be taken as the 'characteristic number' which is dependent of the type and molecular weight of the flocculent when tested at a pH of 8.72 for the Dahibari washery effluent. In other words, the values of these characteristic numbers given as 1.9945 for TF (cationic), 1.229 for MF (anionic) and 0.249 for NF (non-ionic) flocculent types.

## 3.3 Particle size analysis of effluent coal and flocs

The particle size analysis performed by laser beam particle size-analyzer on the as obtained effluent sample of Dahibari washery and also of the flocculated flocs obtained with 8 gpt of dosage at natural pH of 8.72 using three different types of flocculants (anionic, cationic and non-ionic) are shown in Figs. 12 (a and b) for comparison purpose. Figure 12a represents differential plots in percent volume. Looking at the peak areas of the plots, the peaks obtained with TF & MF overlap on to each other indicating similar performances. Figure 12b shows that the values for $D_{10}$, $D_{50}$ and $D_{90}$ percent passing sizes of flocs and also of the feed effluent collected from Dahibari washery. The sizes obtained with TF and MF flocs are bigger and overlap, this supported their high initial settling rate study mentioned in Sect. 3.2.1. The particle size distribution of the washery effluent and other minerals particles was observed in the range of 4.4 to 142 µm, this size range of particles in effluent get increased to 52 to 327 µm for TF, 45 to 300 µm for MF and 19.7 to 169 µm for NF which indicate formation of flocs after flocculation. These observations are in accordance with that of Gungoren et al [43].

## 3.4 FTIR analysis of effluent coal and flocs

Figure 13 is the result of FTIR analysis study of the washery effluent and flocculated flocs. The peaks of these plots show only the presence of inorganic Si-O bending vibrations in the region of 1100 – 1000 $cm^{-1}$ [44] subsequently extended its symmetric stretching vibration peaks of Si-O appeared at 802 $cm^{-1}$ which shows its bending vibration at 470 $cm^{-1}$. The peaks in FTIR spectra of coal between 1100 and 400 $cm^{-1}$ can be assigned to clay minerals (Kaolinite) and quartz, [45]. The areas of these spectrum showed noticeable deep stretched peaks after flocculation with polymers (TF, MF and NF) in the present study. The transmittance percentages of Dahibari effluent coal flocs gets shifted upward above the effluent transmittance values after flocculation indicating adsorption of polymers to the inorganic (clay, quartz) associated with the coal surface.

## Conclusion

- Characterization studies conducted on Dahibari washery effluent by various methods indicated effluent is of highly heterogeneous nature witness from its physico-chemical properties.
- The collected effluent showed presence of colloidal fines with D80 percent passing size = 60 µm which results in high turbidity value of 1370 NTU. Thus hindered the natural settling of coal particles in thickener when observed at a natural pH of 8.72 of effluent without the addition flocculent. This lead to conclude that addition of flocculent as a necessary step.
- The results of the flocculation tests indicated that, all the three flocculants tests gave satisfactory results for clarification of the water of Dahibari washery effluent. However, among the three flocculants tested, the cationic (TF) and anionic (MF) polymer flocculants gave better results in terms of initial settling rates and the measured turbidity values.
- Second order kinetic rate constants estimated elaborate the results of effective clarification occurred between polymer flocculants and the suspended particles of Dahibari effluent.
- The order of effectiveness of polymer flocculants is TF > MF > NF. The overall results of the study indicated that, the TF and MF are most suitable for clarification of Dahibari coal washery effluent to reutilize the treated water in coal washing circuits and to reduce the fresh water consumption for coal washing process.

## Declarations

#### Funding

This research did not receive any specific grant from any of the funding agencies.

#### Competing interest

The authors hereby declare that there is no competing interests.

#### Availability of data and materials

The material was obtained officially from the Dahibari coal washery, BCCL, Dhanbad after taking the consent from the washery management. The data presented are results of the tests conducted in the laboratory using a 1000 $cm^3$ jar test as per standard practice.

**Code availability**

Not applicable

**Authors contribution**

Ms Sarika N. Pimpalkar, the first author of this paper has carried out all the experiments in the laboratory under the supervision of Prof Nikkam Suresh and Prof Gurdeep Singh. The supervisors have helped in designing of the experiments, analysis of the data and also in correcting the draft copy of this research paper.

**Ethics approval**

The authors of this paper hereby confirm that all the procedures described, tests performed, studies conducted, data presented and the interpretations made thereof on data are in accordance with ethical standards of the institution. However the site map of the Dahibari washery presented and the thickener diagram (Fig. 6a) from the website for which the reference has been cited.

**Consent to Participate**

Not applicable.

**Consent to Publication**

All the authors of this paper hereby give their consent publish the contents of the paper after its peer review. Authors have no objection in publishing the data or analytical contents of the paper in the journal.

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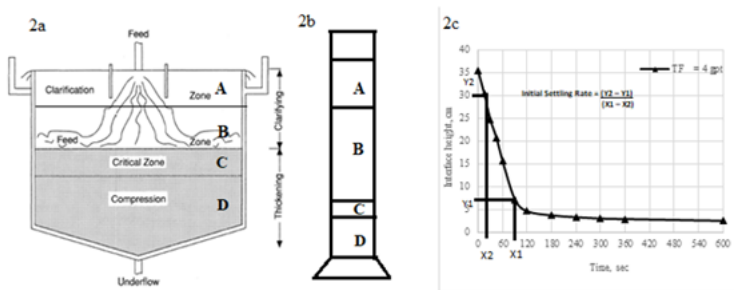
## Figures

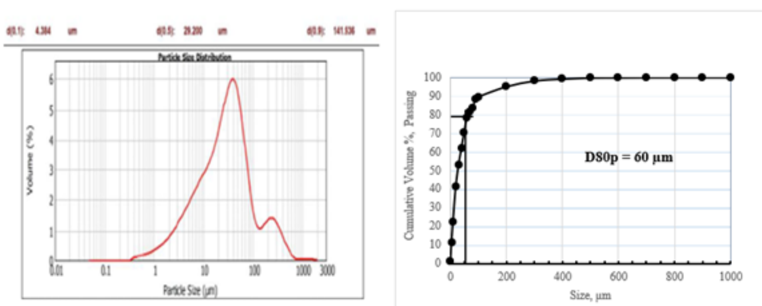

## Figure 1

Satellite view of Dahibari coal washery




## Figure 2

(a) Typical zones in thickener [47] (b) Zone comparison in Jar test (c) Plot showing settling curve and estimation of initial settling rate as a typical example at 4gpt with Telfloc-3674F (TF)




## Figure 3

Particle size distribution plot for Dahibari effluent coal (Using Malvern Particle Size Analyser) b Cumulative particle size distribution plot for Dahibari effluent coal

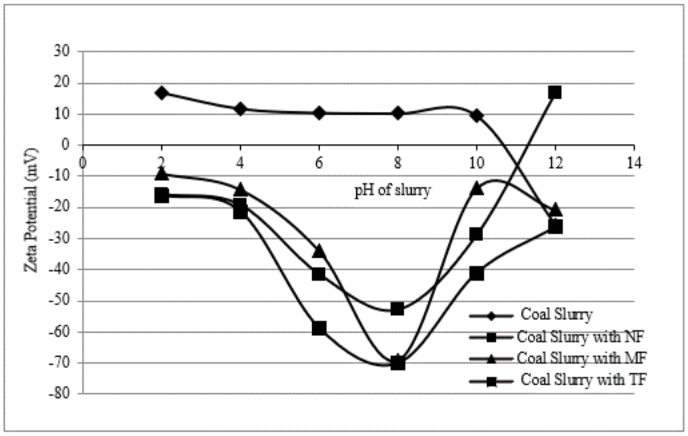



**Figure 4**

Zeta Potential profile for Dahibari washery effluent coal slurry and effluent coal slurry with flocculants dosage of 8 gpt

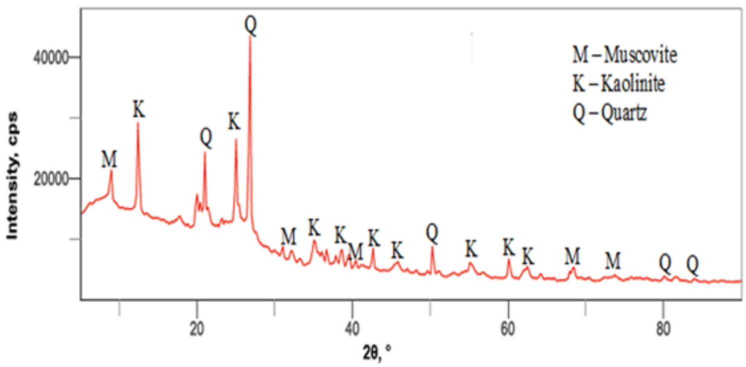



**Figure 5**

X-ray diffractogram (XRD) of Dahibari washery effluent coal

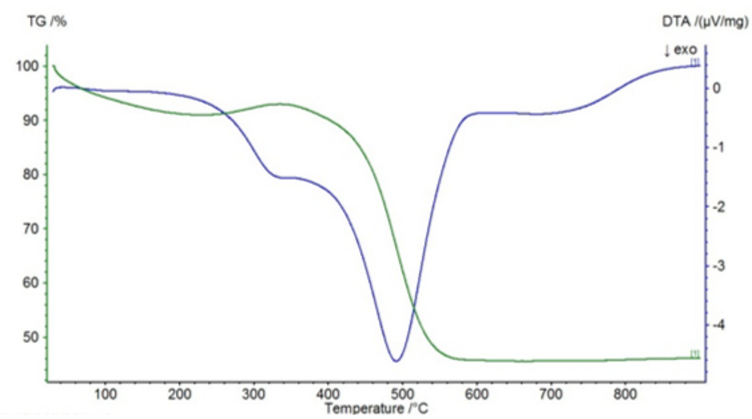
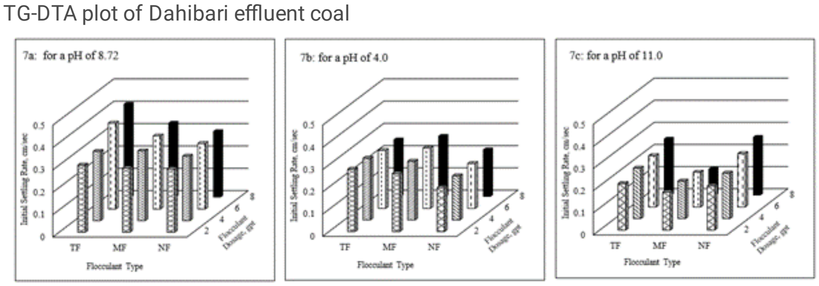



**Figure 6**

TG-DTA plot of Dahibari effluent coal



## Figure 7

(a to c) Effect of variables on settling rates (a) at natural pH of 8.72 (b) at acidic pH of 4.0 (c) at alkaline pH of 11.0

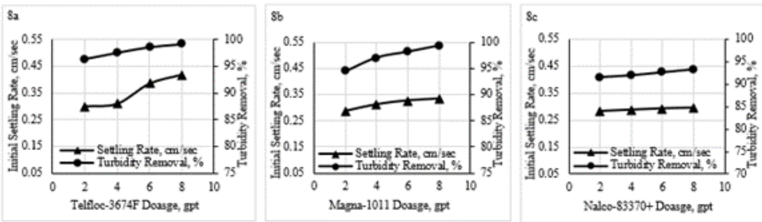



**Fig. 8 (a to c)**

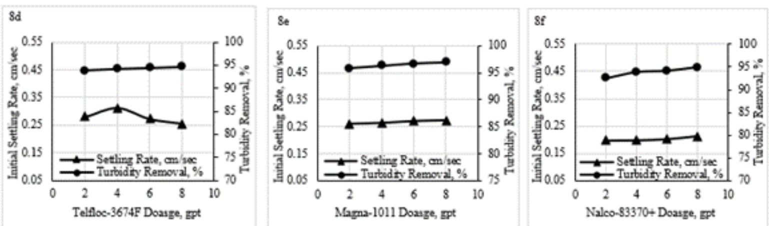



**Fig. 8 (d to f)**

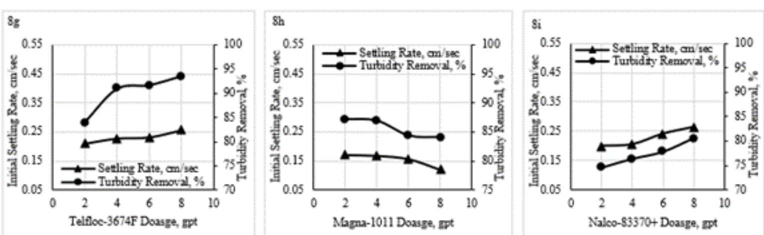



**Fig. 8 (g to i)**

## Figure 8

(a to c) Turbidity removal analogous to initial settling rate at natural pH = 8.72 for (a) Telfloc-3674F (b) Magna-1011 and (c) Nalco-83370+ flocculants (d to f) Turbidity removal analogous to initial settling rate at acidic pH = 4.0 for (d) Telfloc-3674F (e) Magna-1011 and (f) Nalco-83370+ flocculants (g to i) Turbidity removal analogous to initial settling rate at acidic pH = 11.0 for (g) Telfloc-3674F (h) Magna-1011 and (i) Nalco-83370+ flocculants

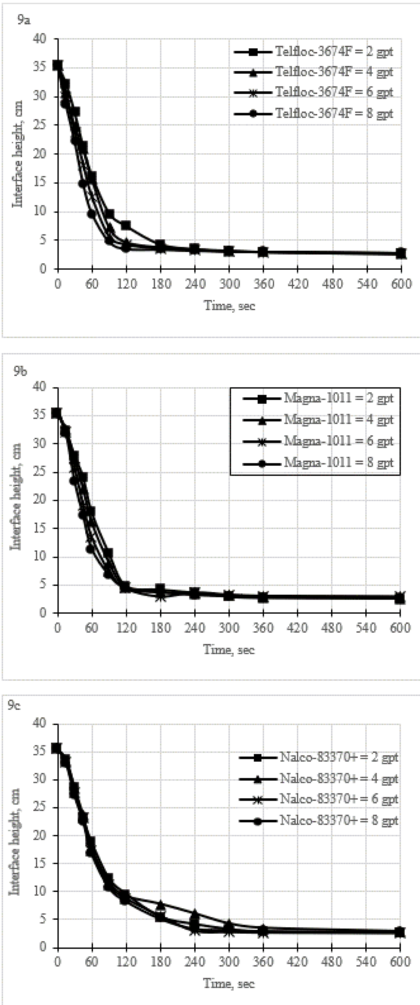



**Figure 9**

(a to c) The settling curves for (a) Telfloc-3674F, (b) Magna-1011 and (c) Nalco-83370+

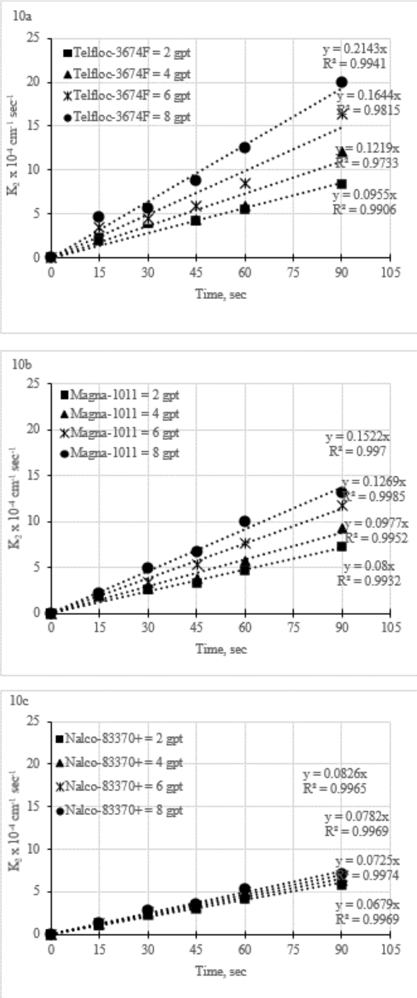



**Figure 10**

(a to c) The second order kinetic rate plots for (a) Telfloc-3674F, (b) Magna-1011 and (c) Nalco-83370+

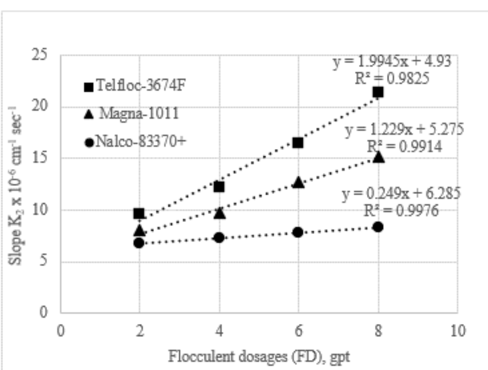



**Figure 11**

Variation in the second order kinetic rate plots with flocculants dosages

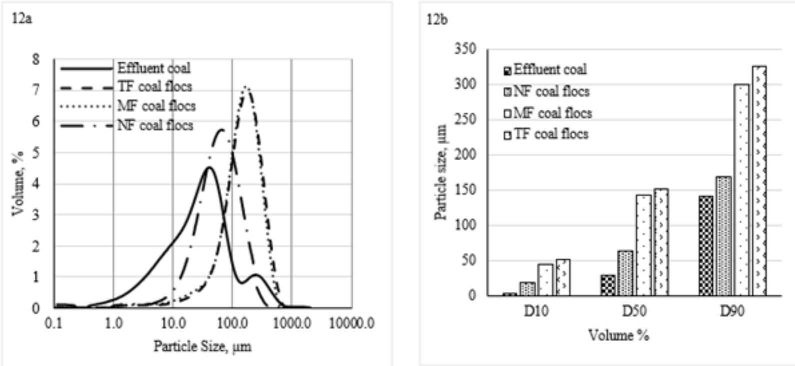



**Figure 12**

(a & b) Comparative analysis of Particle size of Dahibari effluent coal & coal flocs (a) percent Volume peak (b) D10, D50 and D90 particle size

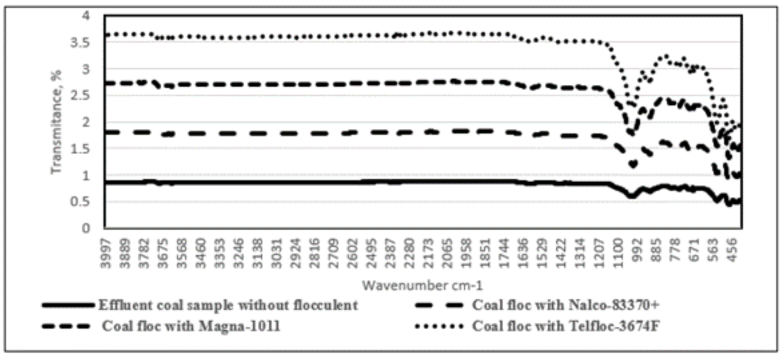



**Figure 13**

FTIR spectra of Dahibari effluent coal before and after polymer flocculation

## Supplementary Files

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- 4Supplementarymaterial.docx