COMBINED EFFECT OF NATURAL DISPERSANT AND A STABILIZER IN FORMULATION OF HIGH CONCENTRATION COAL WATER SLURRY: EXPERIMENTAL AND RHEOLOGICAL MODELING

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ABSTRACT

The present study deals with the formulation and stabilization of a high concentration coal-water slurry using a sub-bituminous bimodal coal sample and a dispersant derived from the plant Acacia auriculiformis in the presence of the stabilizer carboxymethylcellulose. For the first time, we investigated the surface activity of A. auriculiformis natural surfactants isolated by chemical and aqueous extraction methods by calculating their critical micelle concentration (CMC) from surface tension measurements. The CMC of the isolated dispersant was found to be 0.021 g/cm3 and 0.010 g/cm3 by chemical extraction method . Four coarse particles of different sizes, such as 217-295 µm, 97-295 µm, 155-217 µm, and 80 -1 5 µm, were mixed with fine particles below 37 µm to form the bimodal coal samples Sa-1, Sa-2, respectively Sa-3 and Sa- . Apparent viscosity of coal slurry was studied as a function of coal particle size variation, different coarse to fine coal ratio, coal concentration (60-67.2%), A. auriculiformis concentration in the area. (0.01-0.021 g/cm3) and stabilizer content (0.001-0.01 g/cm3). The addition of carboxymethyl cellulose as a stabilizer increased the carbon content and durability of the sludge. The effect of the functional group of the surfactant was discussed in explaining the stabilization mechanism of coal-water sediments. A theoretical simulation is given to prove the experimental observation.

Introduction

One of the major factors that decide the socioeconomic growth of a country is the extent of industrialization which in turn solemnly de- pends on the accessibility to power generating sources. Due to the de- pletion of the natural energy sources as a result of climatic change and exhaustive uses by modern society, significant awareness has been per- ceived for the production of alternative energy sources [1,2]. Coal in par- ticular, has been receiving worldwide attention as alternative fuel similar to hydrogen fuel, biodiesel, bioethanol etc. due to its ability to re- place fuel oil in several industrial applications. At this cross road, it is in- evitable to have a controlled utilization through up gradation of quality of coal and minimal expenses with restricting wastage of during trans- portation. Coal is usually, delivered as energy source to many industries in liquid form popularly known as coal water slurry (CWS) due to its low cost, ease in handling and ability to produce large amount of heat

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energy on combustion [3]. CWS is the concentrated solution of coal in water, the effectiveness of which depends on its coal content and free- flowing characteristics. But due to the association of nonpolar coal as re- sult of Vander Waal interactions, CWS splits into two phases obstructing its pouring characteristics. Thus, attempts are being made from time to time to formulate stable CWS with increased coal concentration and du- rability. In order to maintain the smooth flow of concentrated CWS, sev- eral physical and chemical methods have been developed which inhibit the interactions among coal particles. The physical methods like micro- wave irradiation [4], exposure to ultrasonic radiation [5,6], changing the pH [7,8] and temperature of the medium [9].

Surfactant molecules are amphiphilic in nature and consist of a long chain hydrophobic, tail and hydrophilic head. Surfactant has the unique property to reduce the surface tension of water on mixing with it. Above a particular surfactant concentration when air-water interface is satu- rated or complete formation of a monolayer, residual surfactant mole- cules go in to bulk and forms a cluster like structure called micelle. Thus above CMC there is no further reduction in liquid-air surface ten- sion [10]. To obtain a suitable CWS, use of an appropriate type and

amount of dispersant is necessary. Rheological behavior of CWS can be improved by adjusting the molecular weight, molecular structure, length of the side chain, ratio of hydrophobic to hydrophilic groups of dispersant [11,12]. SDS and CTAB were adsorbed on the coal surface through its hydrophobic group while hydrophilic group is oriented to- wards the aqueous phase [12]. Dynaflow and NSF both have hydropho- bic naphthalene ring in its molecular structure and is highly affinited with coal surface that have polycyclic aromatic property. Therefore it is expected to flatly adsorb on the coal surface and exposing its hydro- philic group towards water medium [13]. Similar type of stabilization mechanism occurs through using different additives such as electrolyte, polyelectrolyte, surfactant and polymer [14–19] which are very impor- tant for preparation and stabilization of high concentration slurry.

In addition to viscosity reduction additive also has significant effect on burnout rate of slurry. Petrochemical can also act as an additive in the formulation of CWS, which is known as Coal water slurry petro- chemical. In this type of slurry burnout rates don't depend on the drop- lets of coal water slurry where as in coal water slurry containing petrochemicals the burnout rates varies with variation of temperature, droplet size, properties of concentration of the main components. Oil addition breaks the droplet which leads to decrease the ignition delay and increase the burnout rates [20]. Similarly, coal particle size can af- fect limiting ignition temperature and ignition delay times of organic coal water fuel droplets than coal water fuel [21–23].

A detailed analysis of the literature survey reveals that the work on the stabilization of the slurry with the biodegradable and eco-friendly compounds and their mixtures as additive is flimsy. We have reported

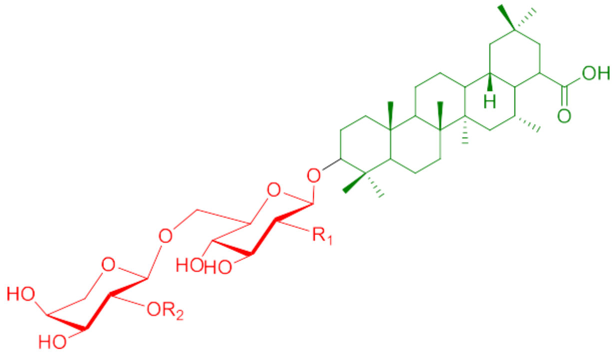
[24–26] the use of saponin, a surface active material extracted from *S. laurifolia* and *A. conicina* plant in stabilizing the CWS formed from a high ash–noncoking coal available in Odisha, India and we could achieve a concentrated CWS containing around 65% of coal. With the continuing interest in developing novel plant based additive for the pro- duction of low cost, and biodegradable CWS, the present work is an an- other successful attempt in which we have used a natural dispersant derived from the drupes of an indigenous plant, *A. auriculiformis*. The fruits of *A. auriculiformis* give copious froth when shaken with water in powder form, indicating the presence of saponin. It contains five tri terpenoid saponin [27,28] Proacaciaside-I, Proacaciaside-II, Acaciamine, Acaciasides A and Acaciasides B (Fig. 1a). Out of five saponin isolated from *A. auriculiformis*, Acaciamine is the nitrogeneous saponin (Fig. 1b). Acaciasides A and Acaciasides B have three point of attach- ment of hydrophilic sugar unit to the hydrophobic hedragenin part (Fig. 1a). Therefore, it is an advantage in comparison to other saponin which has two attachment hydrophilic sugar unit to the hydrophobic hedragenin part [24,25]. Thus more steric repulsion can be created by adsorbing *Acacia auriculiformis* extract on coal surface.

1. Experimental section

Isolation of solid saponin from A. auriculiformis by chemical method

100 g defatted fruit pericarps were soaked in methanol for 12 h. The methanol extract obtained after separating the undissolved fruit was partitioned between water and n-butanol. The butanol soluble fraction

(a)



R₁=NHAc and R₂ = alpha-L-arabinose

(b)

Fig. 1. (a). Structure of Acaciasides A and Acaciasides B. (b). Structure of Acaciamine.

was adsorbed in silica gel and washed successively with ethyl acetate, - acetone and chloroform - methanol mixture (80:20). The ethyl acetate and acetone fractions were evaporated and the solid mass obtained (20 g) was subjected to column chromatography. On chromatographic resolution, the acaciaside and three triterpenoid saponins namely Proacaciaside-A and Proacaciaside B and Acaciamine were obtained [28]. Solid saponin isolated by the above process was found to be 8 g.

Isolation of aqueous saponin solution using magnetic stirrer and centrifusion machine

100 g of dry fruit pericarp *A. auriculiformis* was converted in to pow- dered form and dissolved in 1000 mL of water. The mixture was then subjected to stirring for 3 h using a magnetic stirrer at high speed. After this the Supernatant solution was centrifuged for about 45 min using centrifugation machine. The liquid solution was filtered and col- lected which is known as aqueous extract because no chemical is used for the above process.

Carboxymethylcellulose (Merck), 98% purity

Carboxy methyl cellulose was procured from Merck India Ltd. having 98% purity and used as such.

Calculation of CMC by surface tension measurement

The surface activity of aqueous extract *A. auriculiformis* was studied by surface tensiometer (Kyowa-350, Japan). The decrease in the surface tension value of the aqueous solution as a function of *A. auriculiformis* concentration is plotted in Fig. 2(a) and (b). It can be seen that with in- crease in *A. auriculiformis* concentration surface tension value of solu- tion decreases rapidly. For pure water surface tension it is 72 mN/m and when *A. auriculiformis* concentration becomes 0.021 g/cm^3 (2.1 wt %), Surface tension value saturates to 41 mN/m. Thus CMC for the sapo- nin isolated by aqueous extraction process was found to be 0.021 g/cm^3, or 2.1 wt%. Similarly for saponin isolated by chemical method saturates at 0.010 g/cm^3 which is the CMC value.

Preparation of coal sample

Coal samples taken for this study were collected from Talcher coal mines area of Odisha, India. Ball mills of laboratory were used to pulver- ize the samples into fine and coarse sizes. Four different sizes of coarse particles such as 217–295 µm, 97–295 µm, 155–217 µm, and 80–145 µm were mixed with fine particle size of below 37 µm to form Table 1

Proximate analysis of coal sample.

Moisture, %	5.77
Ash, %	37.90
Volatile matter, %	24.21
Fixed carbon, %	32.12

Table 2
Ultimate analysis of coal sample.

Carbon, %	84.25
Hydrogen, %	4.77
Nitrogen, %	1.75
Oxygen, %	8.67
Sulphur, %	0.56

bimodal samples of Sa-1, Sa-2, Sa-3, and Sa-4, respectively. Proximate and ultimate analyses of the samples have been indicated in Tables 1 & 2 respectively. Malvern Particle size analyzer was the measuring instrument for the particle size distribution of the samples. Particle size distribution of the samples have been indicated in Fig. 3 and Table 3, which includes the data values of d10, d50, d90 of the particles.

Rheological measurement

Study of rheology of CWS has been taken up by HAAKE Rotational viscometer (Model RV 30) which contains temperature vessel with circulator, measuring drive unit, sensor system and a data logger. Distilled water was used for preparation of about 100 mL of slurry, the concentration of which was varied from 50 to 67.2% by weight. Best-fit model was fitted to the experimental data to obtain the nature of CWS.

Measurement of static stability

Coal-water slurries containing *A. auriculiformis* and carboxymethyl cellulose were prepared at different weight concentrations ranging from 50 to 67.2%. Then the slurries were kept in cylinders of about 100 mL and the top of the cylinders were sealed, and were stored at room temperature. In rod penetration method a glass rod of fixed weight and diameter was inserted into the beaker containing slurry to observe the type of sedimentation during storage period [29]. If the sedimentation is hard it cannot be easily disintegrated by mild stirring and soft sedimentation can be easily disintegrated which can be transferred to other containers without any difficulty. The static stability was

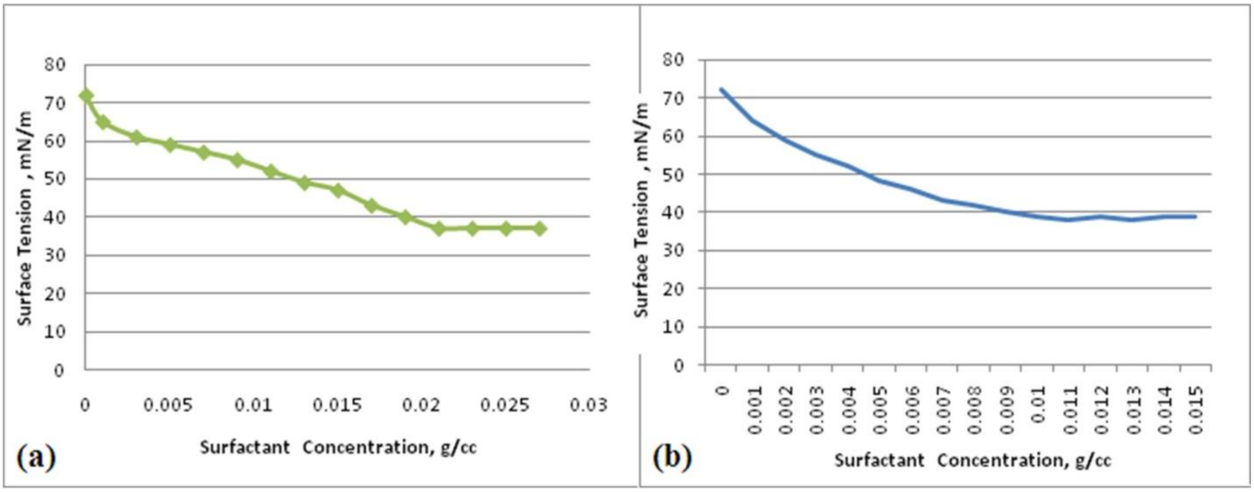
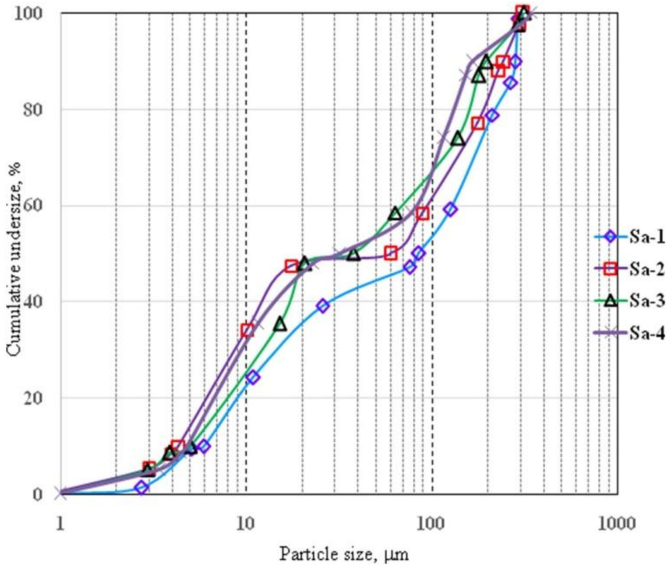


Fig. 2. Calculation of CMC of surfactant ‘*A. auriculiformis*’ (a) aq. extraction method, (b) chemical extraction method.



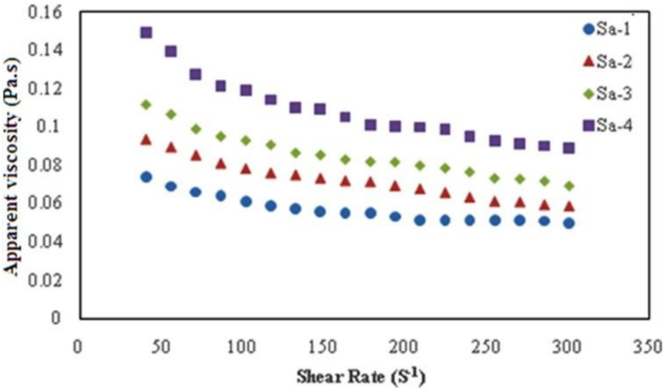


Fig. 3. Particle size distribution of coal sample.

measured by appearance of soft sediment in terms of number of days and the data are given in Table 4.

2. Result and discussion

Measurement of optimum particle size

Particle size plays an important role in the flow behavior of the slurry. So, determination of particle size is a vital factor during rheo- logical measurement. Mineral slurries with finer particle sizes indicate higher apparent viscosity than with only coarse particles [30]. This is because fine particles in the slurry absorb water, as result flu- idity is restricted thereby viscosity enhances. Similarly only coarse particles in the slurry enhance viscosity because more chances of set- tling of particles at the bottom which deters the fluidity. With a view to achieve an equilibrium and attain greater coal loading a mixture of fine and coarse particles at a certain percentage in the slurry has been taken for further study. Fig. 4 explains the variation of shear rate with apparent viscosity at a particular concentration of 62% by weight. It reveals from the graph that increase in shear rate de- creases the viscosity in all samples, out of which Sa-1 sample has lowest viscosity. This is due to the packing of fine and coarse parti- cles in the slurry which enhances fluidity. Hence, Sa-1 sample has been taken as ideal particle size for further study.

Fig. 4. Variation of Shear rate with Apparent viscosity of coal water slurry for a concentration of 62 wt% for samples Sa-1, Sa-2, Sa-3, and Sa-4.

Determination of optimum coarse to fine particle ratio

Fluidity being a criterion of viscosity equilibrium of coarse and fine particle in the slurry is essential. So determination of coarse to fine ratio plays an important role in the slurry. Fig. 5 indicates the variation of shear rate with apparent viscosity for Sa-1 sample at a concentration of 62% by weight with different coarse to fine ratio. Graph reveals that slurry having coarse to fine ratio (C:F) of 60:40 has minimum viscosity than coarse to fine ratio (C:F) of 65:35 and 55:45. Increase in coarse particle in the slurry enhances void, resulting settlement at the bottom. Similarly enhancement of fine particle in the slurry absorbs water which deters the fluidity and increases viscosity. Hence, the ideal ratio of coarse to fine of Sa-1 should be 60:40.

Effect of A. auriculiformis concentration on the viscosity of coal-water slurry

The additive in CWS helps to maintain a suitable interaction between the coal particles and water molecules so that the adhesive force between the coal particle and water is improved over the cohesive force among the coal particles. In order to establish the competence of the additive to keep the viscosity in the acceptable range, the apparent viscosity was measured with increase in percentage of the additive. Depending upon the CMC of dispersant isolated by two different process (as described in materials and methods section), different concentration range above CMC was fixed to investigate the dispersing action of saponin. Dispersant concentration in the aqueous extraction method was varied in the range of 0.01–0.028 g/cm^3 and in the chemical extraction method; concentration range was of 0.001–0.016 g/cm^3. As can be

Table 3
Particle size distribution of coal samples (Sa-1, Sa-2, Sa-3 and Sa-4).

Sample	d10	d50	d90
Sa-1	5.88	84.62	279.73
Sa-2	4.31	59.75	242.43
Sa-3	4.99	37.58	196.49
Sa-4	4.82	31.89	165.45

Table 4
Static stability test.

Coal concentration (%)	Stability (days)
50	7
55	10
60	15
65	20
67.2	26

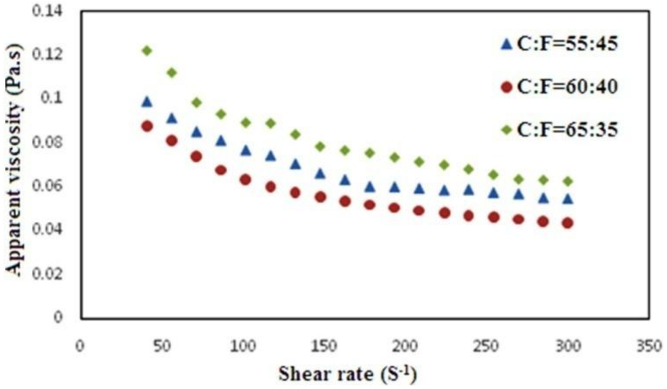


Fig. 5. Variation of Shear rate with Apparent viscosity for a concentration of 62 wt% coal loading for sample Sa-1 at different coarse and fine ratio (C:F) of coal.

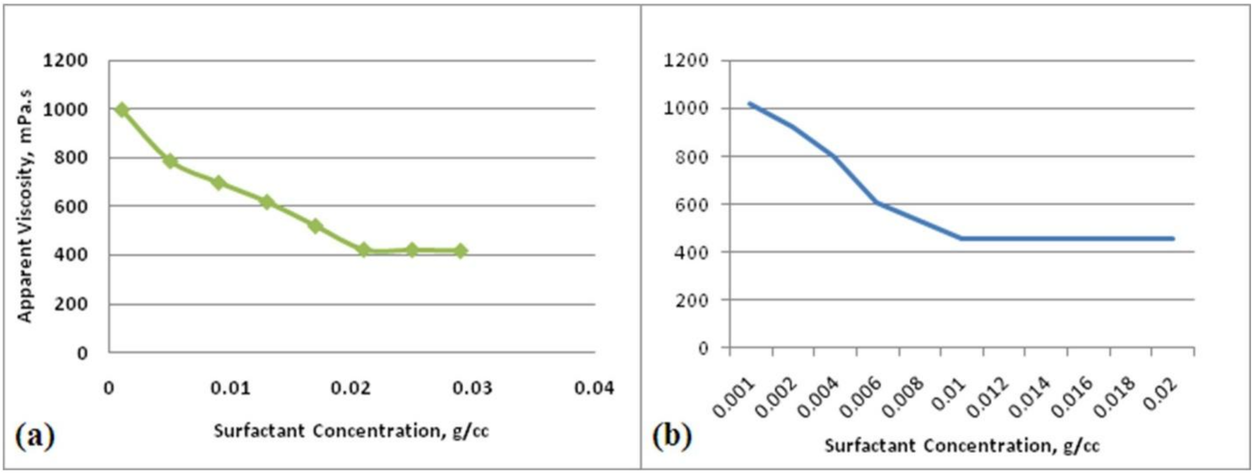


Fig. 6. Effect of Surfactant concentration vs Apparent viscosity,
(a) aq. extraction method, (b) chemical extraction method.

seen from Fig. 6(a) and (b), with increasing dispersant concentration (0.01–0.021 g/cm^3) a sharp decrease in viscosity occurred from 998 to 425 mPa·s and thereafter, a plateau value is obtained. Similar trend was also observed for the saponin isolated by chemical extraction method. Saponin on being adsorbed at the coal-water interface creates steric barriers by its glucosides hydrated head groups protruded towards bulk water [24]. As a result, the viscosity of the CWS decreased steadily with increase of the amount of saponin in the CWS. The viscosity continued to decrease as long as the saponin has the tendency to adsorb to the coal surface. But at higher concentration i.e. beyond 0.021 g/cm^3 of saponin (aqueous extraction method) and 0.010 g/cm^3 of (aqueous extraction method), the CMC of the viscosity attains a minimum flat value which did not change with further addition of saponin [24,25]. It is also known that the surfactant gets adsorbed to the interface as monomer. Beyond the CMC, saponin loses its affinity towards the coal surface and starts aggregating to form the micellar clusters. Since saponin adsorbs at interface as monomer only, the decrease in apparent viscosity is leveled up after the formation of critical micellar concentration [24,31].

Optimization of carboxy methyl cellulose (stabilizer) concentration

Carboxymethyl cellulose is a complex polymeric long chain aliphatic structure and its hydrophilic carboxyl group interacts with hydrophilic

functional group on coal surface to form a three dimensional network structure inhibiting coal –coal agglomeration. But three dimensional network formed can restricts free movement of coal particle which may increase the viscosity of coal water slurry [32]. Therefore optimiza- tion of stabilizer concentration is essential with respect to apparent vis- cosity and coal concentration. Fig. 7(a) & (b) represent the variation of carboxy methyl cellulose concentration on apparent viscosity of coal water slurry at the optimized concentration of dispersant, *Acacia auriculiformis* (0.021 g/cm^3 and 0.008 g/cm^3). From the graph it is found that apparent viscosity decreases with increase in the concentra- tion of carboxy methyl cellulose up to 0.005 g/cm^3 and after this viscos- ity slightly increases. This can causes the limitation in the coal loading. From the above discussion it is clear that optimization value of carboxymethyl cellulose is same in both the experiment that is saponin isolated from both process.

Effect of coal concentration on apparent viscosity

The amount of coal in coal-water slurry is one of the important re- quirements that decide the efficiency of the slurry as a suitable source of energy. In suspension rheology, solid concentrations are expressed as volume fraction. The free flowing tendency of the slurry gradually de- creases with increase of the volume fraction of coal in the slurry [24,33]. Therefore viscosity of CWS increases with increase in coal concentration

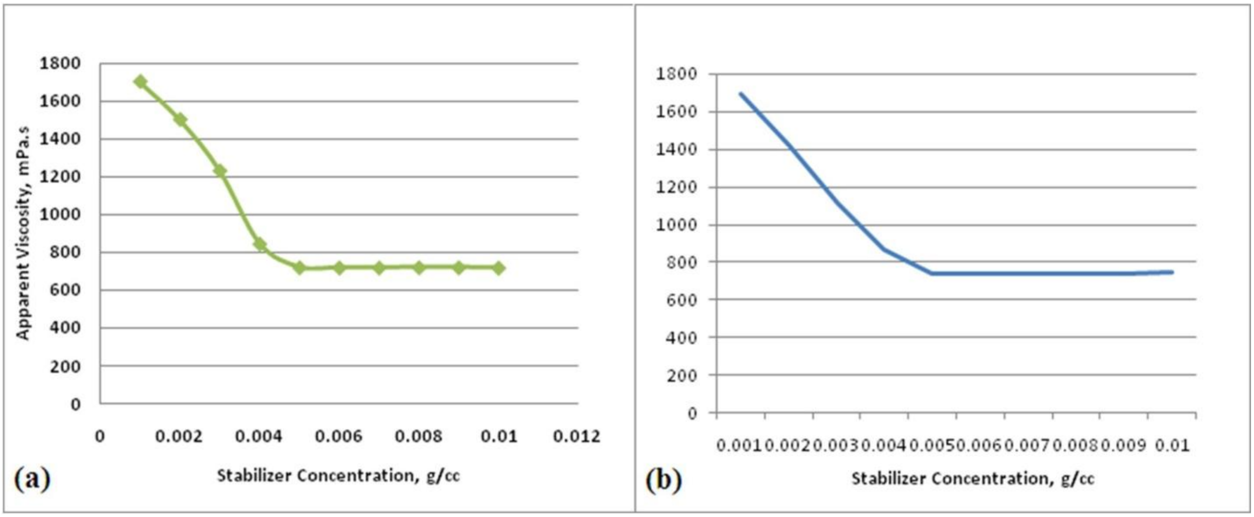


Fig. 7. Optimization of stabilizer concentration (a) aq. extraction method, (b) chemical extraction method.

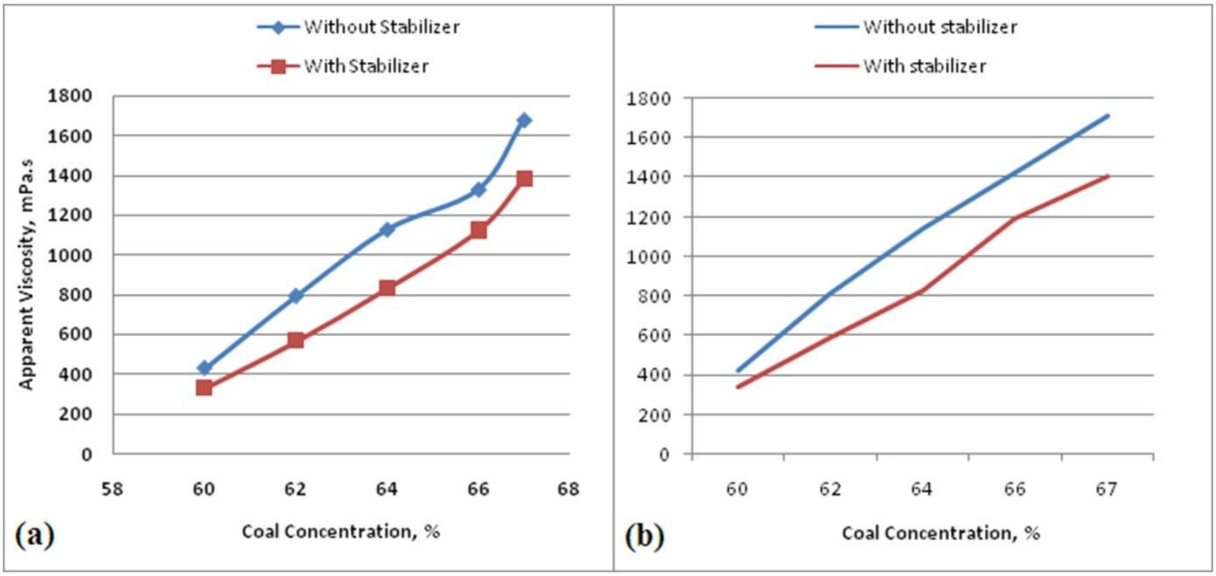


Fig. 8. Variation of coal concentration with Apparent Viscosity
(a) aq. extraction method, (b) chemical extraction method.

in CWS. The combustion efficiency of a CWS depends on the amount of coal concentration in the slurry. Therefore, it is essential to increase the amount of coal, keeping the viscosity in minimum level, so that the CWS can be easily transported through the pipelines. Due to the adsorption of the additives at the coal-water interface, the association of the coal particle is hindered and, hence the coal concentration in the CWS can be increased in presence of the additive. The coal load was increased in the concentration range of 60–67.2% at the optimized dispersant concentration. The viscosity of the CWS was found to be increased (Fig. 8(a) & (b)) with increase in coal concentrations in it indicating that the free flowing characteristics of the slurry gradually decreases with increase of the volume fraction of coal in the slurry [24,25,34,35]. Saponin isolated by two different processes gives similar type result which confirms that whatever may be the isolation process of saponin from *a. auruculiformis* similar types of results are obtained.

Shear rate and shear stress relationship

In order to identify the nature of CWS, the shear stress was measured as a function of shear rate. This is shown in Fig. 9(a) & (b). It is seen that the CWS sustains the shear stress up to certain extent determined by

the Y-intercept in the plot (initial shear-stress threshold value). [24–26,36] This value of shear stress, knows as yield stress is an important parameter during the pipeline transport. When shear will be applied during pumping, the shear rate has to be applied to overcome this yield stress. After this yield stress the fluid is shown to flow linearly with increase of shear rate. The nature of the plot in all case fits to the equ.-1 belonging to the behavior of Bingham plastics fluids.

σ ¼ a · γ þ b ð1Þ

where, a = Dynamic viscosity, b = yield stress, and γ = applied shear rate.

All the experiments were carried out at optimized concentration of dispersant ‘*A. auriculiformis*’ (0.021 g/cm^3) and stabilizer ‘carboxymethyl cellulose’ (0.005 g/cm^3) in studied range of coal concentration 60 to 67.2%. Saponin isolated by using above methods resulted similar type of plots between shear rate and shear stress.

Effect of stabilizer concentration on yield stress value

Yield stress refers to the minimum stress value at which slurry will deform without application of significant load. In other words, yield stress is the minimum stress required to make a material flow and it is a measure of the strength of the material structure. In the prepara- tion of high concentration slurry three important stages are storage, pumping, and pipeline transportations [24,25,37]. Therefore, it is necessary to study the apparent yield stress of this aqueous suspen- sion or their slurry with respect to stabilizer concentration. The yield stress is computed graphically from the plot of shear stress versus shear rate. Fig. 10(a) & (b) represent change of yield stress with carboxymethyl cellulose concentration. It is observed from the graph that

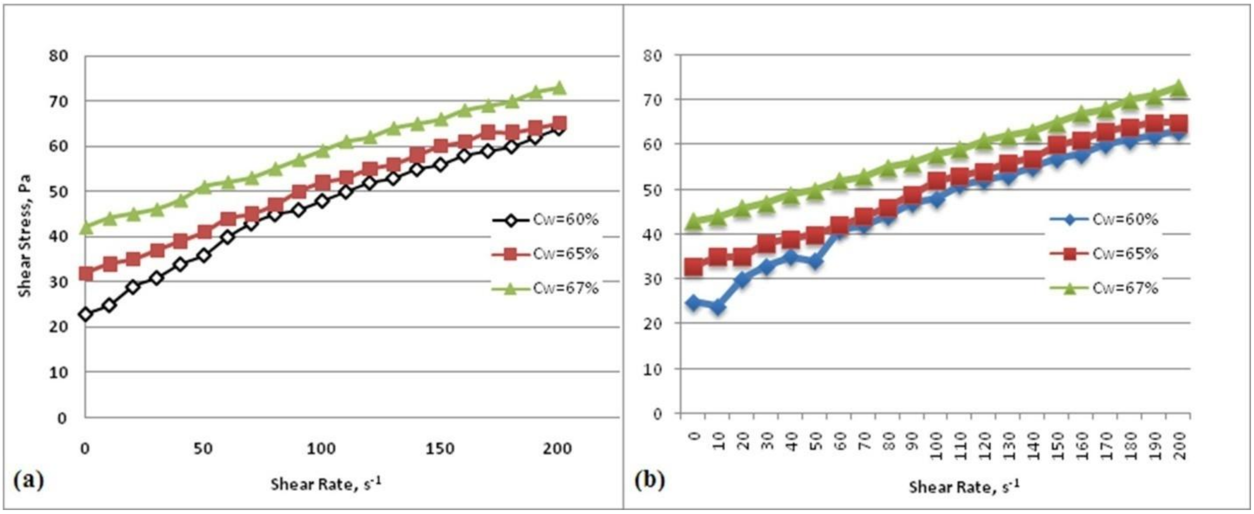


Fig. 9. Yield stress vs stabilizer concentration (a) aq. extraction method, (b) chemical extraction method.

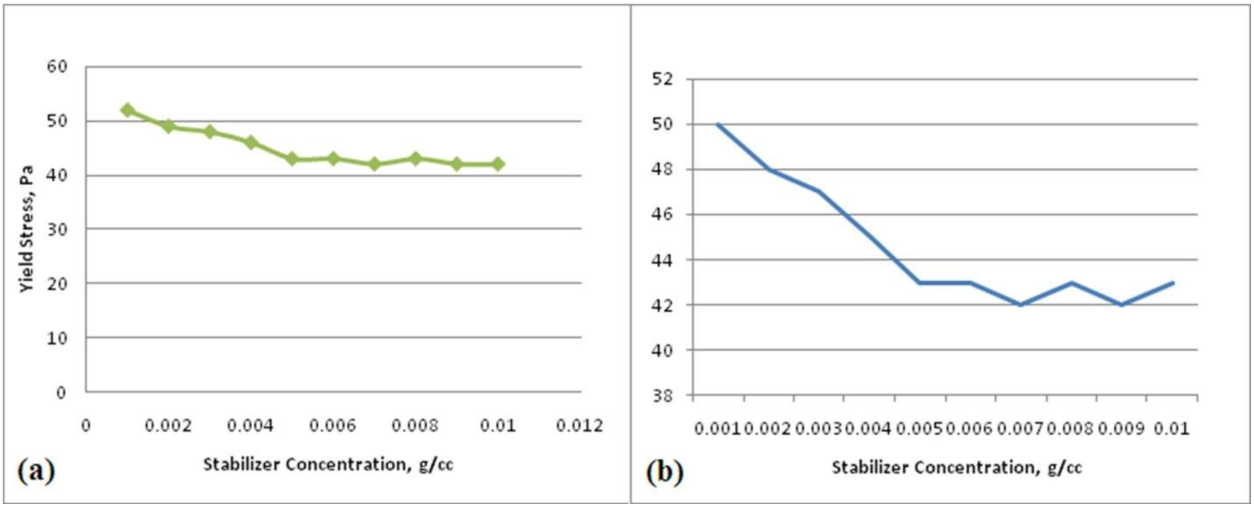


Fig. 10. Shear rate vs shear stress at different coal concentration, (a) aq. extraction method, (b) chemical extraction method.

with increase in the stabilizer concentration yield stress value decreases and is leveled up around 0.005 g/cm^3 concentration. Beyond this concentration yield stress value slightly increases due to the more number of three dimensional network structure in slurry [32]. Saponin obtained from both the isolation processes gave ap- proximately same value of yield stress.

Zeta potential analysis

Zeta potential (ζ) refers to the electrostatic repulsion or attraction

suspension. ζ value of coal water slurry without addition of stabilizer was −65 meV. Fig. 11(a) & (b) showed the variation of ζ of coal slurry with the amount of carboxymethyl cellulose (stabilizer) concentration in the presence of optimized concentration of dispersant concentration. Result indicated that with increase in stabilizer concentration magni- tude of ζ decreases which may be due to the formation of a network structure by carboxymethyl cellulose molecule with coal particle. But the decreasing trend is more after the optimized concentration of stabi- lizer due the increasing number of three dimensional network struc- tures [32]. Stability of slurry is not affected by reduction in ζ value because at the optimized concentration of stabilizer (carboxymethyl cellulose) magnitude of ζ is around −45 meV.

Modeling the rheological behavior of CWS

The empirical rheological models

Casson model. Rheological behavior of concentrated slurry with pseudo plastic behavior may be explained by Casson model. [39].

between the charged particle present in the emulsion or slurry. It is 1 1
measured by calculating the electrophoretic mobility of charged parti-
cle. Magnitude of ζ can be used to optimize the formulations of suspen- sions and emulsions [38]. Thus knowledge of the ζ can optimize the amount of dispersed phase and dispersion medium in the colloidal σ2 ¼ aðγÞ2 þ b ð2Þ

where, a^2 = Dynamic viscosity; b^2 = yield stress; γ = shear rate, and σ = shear stress.

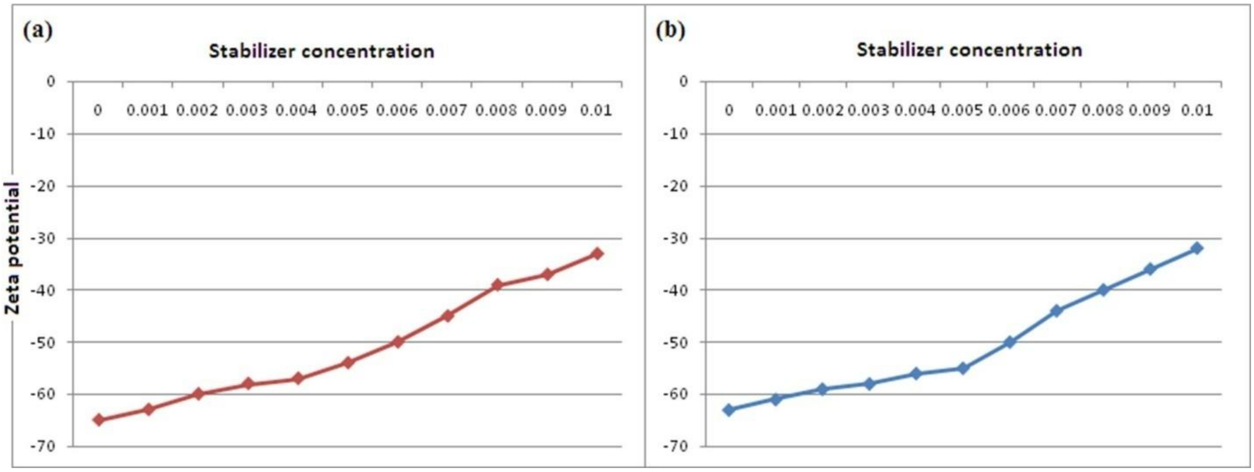


Fig. 11. Variation of zeta potential (a) aq. saponin, (b) chemical saponin.

Bingham model. Rheological characteristics of slurry with linear rheological profiles having a yield stress can be explained by Bingham model [40].

σ ¼ a · γ þ b ð3Þ

where, a = Dynamic viscosity; and b = yield stress.

Ostwald-Power Law model. Rheological behavior of slurry having dilatants profile or a pseudo plastic without yield can be explained by Ostwald model [41].

$\sigma = a \cdot \gamma^n$ (4)where, *a* = coherence parameter, and n = behavior index of the flow.

Herschel-Buckley model. The Herschel-Buckley model presents a generalization of all the rheological models that have been cited [42–45].

σ ¼ a · γ^p þ b ð5Þ

where, a = dynamic viscosity related to Herschel-Buckley model, b = yield stress, and p = exponent.

The various rheological data obtained from experiment (Section 3.6) can be fitted to Bingham, Herschel Buckley, Otswald-power law, and Casson models to identify the best fitted rheological model that describes the experimental data at each concentration index.

Four models fitting

This section describes application of four above models mentioned to the experimental data obtained. A best fit model is obtained which can describe the rheological behavior of the coal water slurry at each index of concentration. Therefore, it is necessary to establish the parameters of optimal regressions of each model so as to have a trend curve which perfectly describes the curve obtained experimentally. We have observed from Section 3.3 to 3.8 that *A. auriculiformis* gives similar type of result whether it involves aqueous extraction process or chemical extraction process. Since aqueous extraction of saponin is an economic and ecofriendly process, in our theoretical study we have taken the experimental rheological result of *A. auriculiformis* of aqueous extraction process. Best fit model can describe the rheological behavior of the Coal slurry and in the mathematical sense R^2 value should be close to one. It is essential that best fit model generates values of viscosity and yield stress in the ranges design or close to these ranges. (Figs. 12, 13 & 14).

Calculation of rheological parameters

The regression parameters resulting from the modeling of the rheological behavior of the Coal Slurry through the four models for each concentration index are grouped together in Tables 5 & 6. The parameters *a* and *b* are successively dynamic viscosity and yield stress related to each model, and the parameters n and p are the exponents of the models Ostwald and Herschel-Buckley.

Mathematically, the Herschel Buckley model is a model with an R^2 close to 1 for various concentrations. It is, therefore, the most suitable model for the description of rheological profile of the

Coal slurry. The Casson and Bingham models have R^2 values varying between 0.96 and 0.99, we can admit them too. For the Power Law model it has R^2 very far from 1. Therefore the Power Law model is not an adequate model for the description of the rheological behavior of Coal slurry.

Best fitting models

The modeling of the rheological profile via four rheological models allows us to identify the dynamic viscosity and the yield stress of coal slurry. This is done through the regression of experimental data (Shear stress vs Shear rate) to the empirical models of Casson, Bingham, Power Law and Herschel Buckley. During this investigation, we sort the most suitable models to describe the rheological behavior of Coal Slurry. We noticed that Herschel Buckley model is a model with an R^2 close to 1 for various concentrations. It is, therefore, the most suitable model for the description of rheological profile of the Coal slurry. The Casson and Bingham models have R^2 values varying between 0.96 and 0.99, we can admit them too. For the Power Law model it has R^2 very far from
1. Therefore, the Power Law model is not an adequate model for the de- scription of the rheological behavior of CWS.

We suggest, therefore, taking into account the experimental data. We can experimentally identify the yield stress. Then, it could be

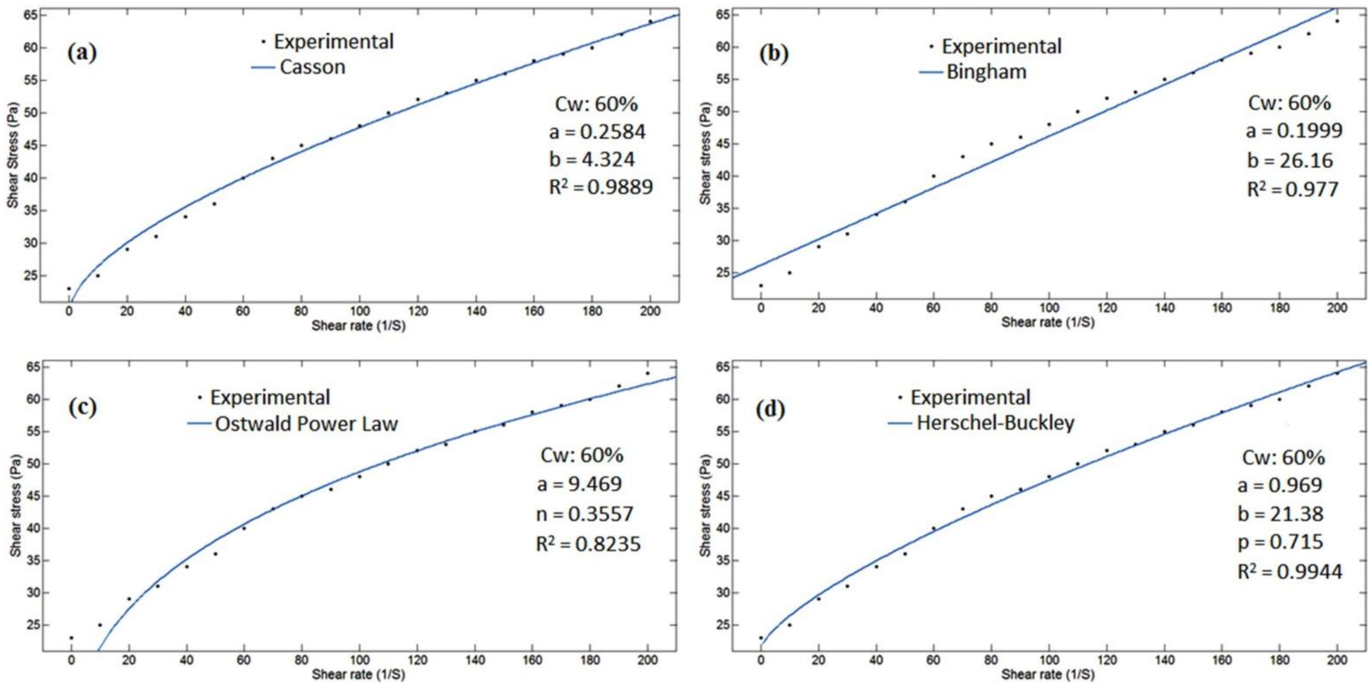


Fig. 12. At coal concentration, Cw = 60%: (a) Casson model, $\sigma^{\frac{1}{2}} = 0.2584\ \gamma^{\frac{1}{2}} + 4.324$, (b) Bingham model, $\sigma = 0.1999\ \gamma + 26.16$, (c) Ostwald model, $\sigma = 9.469 \cdot \gamma^{0.3557}$, (d) Herschel-Buckley, $\sigma = 0.969 \cdot \gamma^{0.715} + 21.38$. 0.281

Fig. 13. At coal concentration, Cw = 65%: (a) Casson model, σ2 = 0:2106 γ2 + 5.084, (b) Bingham model, σ = 0.1742·γ + 32.77, (c) Ostwald model, σ = 14.41 · γ, (d) Herschel-Buckley, $\sigma = 0.4197 \cdot \gamma^{0.8397} + 30.76$.

compared with the yield stress values obtained via the empirical models to find out which is the most reliable model for the coal slurry. Our main aim is to prepare a high concentration CWS. i.e., coal concentration should be maximum with an acceptable range of viscosity. Therefore, we have to consider the best fit model at high concentration (67%). The Bingham and Herschel-Buckley models generate yield stress values closer to the yield stress given experimentally. Consequently, the Bingham and Herschel-Buckley

models are the most suitable models for describing the rheological behavior of CWS at high concentration.

Stabilization mechanism

Saponins are mixture of saccharine derivatives [24–26,46–49] and belongs to a class of natural occurring non-ionic surfactants. Therefore, the hydrophilic part of these molecules (glycon) consisting of

Fig. 14. At coal concentration, Cw = 67%: (a) Casson model, $\sigma^{\frac{1}{2}} = 0{:}1745\ \gamma^{\frac{1}{2}} + 5.97$, (b) Bingham model, σ = 0.1586·γ + 42.33, (c) Ostwald model, $\sigma = 22.74 \cdot \gamma^{0.2126}$; (d) Herschel-Buckley, $\sigma = 0.2551 \cdot \gamma^{0.913} + 41.41$.

Table 5
Rheological parameters of Casson and Bingham models at each concentration.

carboxymethyl cellulose further stabilizes the slurry by forming a three dimensional network structure (Fig. 15).

Concentration Cw%	Casson model			Bingham model		
	^{2} (Pa·s) (viscosity)	b^2 (Pa) (yield stress)	R^2	a (Pa·s) (viscosity)	b (Pa) (yield stress)	R^2
60%	0.0667	18.69	0.9889	0.1999	26.16	0.977
65%	0.0443	25.84	0.9716	0.1742	32.77	0.9882
67%	0.01045	35.64	0.962	0.1586	42.33	0.9953

4. Conclusion

The dispersant isolated is cheap, biodegradable, environmentally safe, and non- hazardous in nature. The present study deals with the preparation and stabilization of a concentrated CWS using a bimodal coal sample, *A. auriculiformis* as dispersant and carboxymethyl cellulose as stabilizer. Out of four types of bimodal coal sample (Sa-1, Sa-2, Sa-3, and Sa-4), sample Sa-1 displayed lowest apparent viscosity. Slurry having coarse to fine ratio (C:F) 60:40 of sample Sa-1 has minimum viscos-

Table 6

Rheological parameters of Ostwald and Herschel-Buckley models at each concentration.

Concentration Cw%	Ostwald-power Law model			Herschel-Buckley model			
	a (Pa·s)	n	R^2	a (Pa·s)	b (Pa)	p	R^2
60%	9.469	0.3557	0.8235	0.969	21.38	0.715944	0.9
65%	14.4181	0.2	0.5332	0.4197	30.76	0.8397 0.993	
67%	22.74126	0.2	0.03765	0.2551	41.41	0.913966	0.9

ity than others ratio. Lowest viscosity of CWS is found at the optimized concentration of dispersant (0.021 g/cm^3 and 0.010 g/cm^3 for aqueous and chemical extraction method respectively). Yield stress value decreased and is leveled up around 0.005 g/cm^3 concentration of stabilizer. The steric repulsions offered by bulky hydrated heads leading to huge hindrance for coal particle association. The stabilizer bridges the coal particles, as a result a three dimensional network is formed which stabilized the slurry by decreasing the viscosity. Aqueous extraction process is economic because it does not involve any chemical for isolation of saponin. Therefore, in our theoretical study, we have taken the

sachharides such as glucose, xylose, galactose, pentose, rhamnose, etc. and hydrophobic part (aglycone) consisting of steroids and triterpene orient themselves in coal water dispersion in such a way that hydrophobic part of saponin adsorbed on to coal surface and hydrophilic part is oriented towards aqueous solution. In the present investigation the dispersant *A. auriculiformis* contains varieties of saponin in which one is nitrogeneous and other two non-nitrogeneous. Saponin of this plant contains three hydrophilic sugar chain attached to hydrophobic hedragenin moiety (Fig. 1a & b). Therefore, this plant has more advantages in comparison to others plant because saponin present in this plant plant can impart more steric stabilization [24–26] due to more number of attached sugar chain to the hydrophobic triterpene (Hedragenin). The aglycone part would lie on the coal surface interacting with it through hydrophobic interactions and its glycon part would be projected towards bulk water medium. (Fig. 15) This orientation will encourage large number of water molecules to interact with the adsorbed saponin through polar-polar interaction as a result of which the steric wettability of coal surface would be increased. Further, the bulky group a will also provide steric shock during the association of coal particle. Due to the presence of saponin, acacia amine (Fig. 1b) its stabilizing power is more in comparison to *Acacia concinna* [25]. The –CONH-group in acaciamine can impart more steric effect due to its bulky nature in comparison to -OH group. Also due to the lesser polarity of amide group in comparison to hydroxyl group, it is less hydrated and due to this more number of water molecules is available in between the coal particle. As a result viscosity is lowered and higher concentration coal-water slurry is achieved. The presence of

rheological result of *A. auriculiformis* in aqueous extraction process. Experimental data obtained are well matched with theoretical simulation analysis. Bingham and Herschel-Buckley models are the most suitable models for describing the rheological behavior of CWS at high concentration. In addition to experimental result numerical simulation has been used to study the characteristics of pipeline transportation and desirable results have also been achieved.

Abbreviations

CMC	critical micellar concentration	CWS	coal water slurry
A. auriculiformis	*Acacia auriculiformis*		
S. laurifolia	*Sapindous laurifolia*		
A. conicina	*Acacia conicina*		
SDS	sodium dodecyl sulfate		
CTAB	cetyl trimethyl ammonium bromide		
a	dynamic viscosity		
b	yield stress		
γ	applied shear rate		
ζ	zeta potential		
R^2	regression factor		

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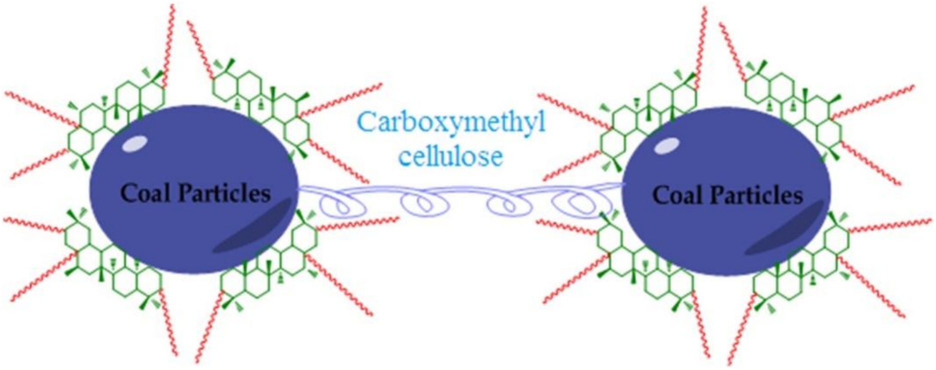

Fig. 15. Mechanism of stabilization.

CRediT authorship contribution statement

Debadutta Das: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing - original draft. Ranjan K. Mohapatra: Methodology, Supervision, Writing - review & editing. Hamza Belbsir: Software, Validation, Data curation. Anupama Routray: Data curation, Formal analysis. Pankaj K. Parhi: Methodology, Re- sources, Supervision. Khalil El-Hami: Data curation, Formal analysis, Writing - original draft.

Declaration of competing interest

There are no conflicts to declare.

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