Sustainable Transportation, Leaching, Stabilization, and Disposal of Fly Ash Using a Mixture of Natural Surfactant and Sodium Silicate

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ABSTRACT: The present study evaluates the transportation, leaching, and stabilization ability of novel saponin extracted from the fruits of *Acacia auriculiformis*. To enhance the dispersing behavior of the fly ash slurry (FAS) at a lower dosage of sodium silicate, *A. auriculiformis* was incorporated in FAS. In addition to the rheological study, an attempt has been made to remove heavy metals through leaching for the safe disposal of FAS. Critical factors such as the fly ash (FA) concentration, saponin dosage, surface tension, ζ potential, temperature, and combination of saponin and sodium silicate, affecting the rheology of FAS, were extensively studied. The addition of a nonionic natural surfactant saponin has been proved to enhance the wettability of FA particles by decreasing the surface tension of FAS. The obtained rheology results were compared with the stabilization yield of the previously reported commercial surfactant cetyltrimethylammonium bromide. The incorporation of sodium silicate in the FAS system was found to be phenomenal in the settling and stabilization of FAS, thereby developing reaction products like sodium aluminum silicate (N-A-S). This facilitates the sustainable disposal of FA preventing air pollution after dewatering. The formation of N-A-S was further supported by scanning electron microscopy (SEM) and X-ray diffraction (XRD) studies.
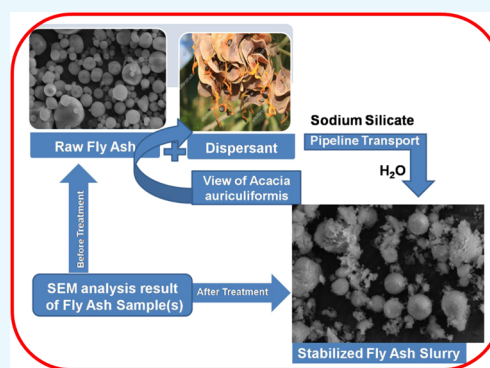
1. INTRODUCTION

The amount of coal ash generation due to the burning of coal is increasing year by year considering its requirement in thermal power sectors and so there is a constant need of handling the huge amount of fly ash (FA) generated.[1] As per the reports,[2] total electricity demand in a country like India is projected to be up to 950 000 MW by the year 2030. Thermal power plants are completely dependent on coal and the current contribution of the power sector is about 70%. Considering the continuous increase in energy demand, it is presumed that there will be a huge generation of FA in the next 3 to 4 years. Therefore, it will be a challenging task to handle such a huge amount of FA for its prospective utilization. The generation of a large quantity of FA not only requires a large area of precious land for its disposal but also has become one of the sources of environmental pollution of both air and water.[3] The need for new and innovative methods is urged for reducing the impact on the environment due to the above issues of FA. The existing classical approach for the disposal of FA into the FA pond accomplishes the transportation of FA in the form of a slurry. Generally, FA is disposed to ash landfills or ash ponds by pipeline transportation.[4] The standard method of FA management includes landfilling and making composite materials such as building bricks, cement, and geopolymers.[5−8] Furthermore, the FA-derived particles can be used as a potential drug delivery system[9] and antibiofouling system;[10] however, only a small amount of FA can be managed by the above methods.

Hence, methods and strategies should be developed to focus on the mass disposal of FA. The former process creates environmental pollution due to the presence of toxic heavy metals and other components, whereas the latter approach converts waste to value-added materials. As most of the disposed FA is located around the industrial site, which causes several environmental issues including groundwater and air pollution; therefore, essential steps must be adopted for preventing the above concern. The proposed work accomplishes the pipeline transport of the aqueous fly ash slurry (FAS), which is an attempt to address the issues of mine subsidence with hydraulic stowing of FAS in underground mines.[3] Therefore, the work addresses both sustainable utilization of FA and economical mine backfilling. The efficient disposal of FA mostly depends on its transportation through slurry pipelines.[11] In the pipeline transportation study, slurry pipelines are used to transport solid particulate materials using carrier fluids such as water or any other fluid, which reduces the energy consumption remarkably as well as water
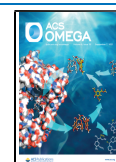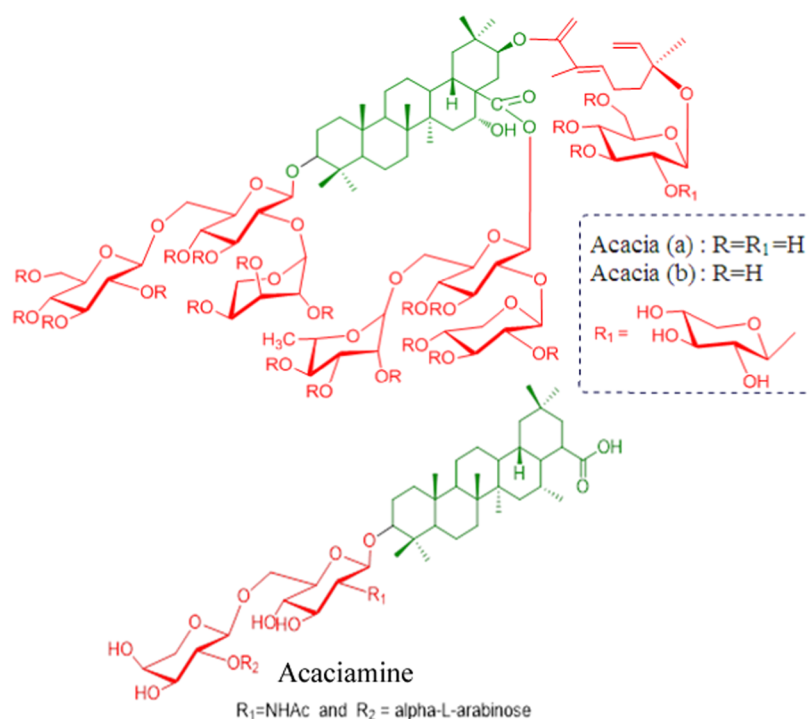
Figure 1. Structure of Acaciasides A, Acaciasides B, and Acaciamine[26] (Reprinted (Adapted or Reprinted in part) with permission from ref [26]). Copyright @2020 [Elsevier].

consumption in the high-concentration slurry, which improves pipe economy.[12] The key issue encountered by FA transportation is the agglomeration of fine FA particles in the slurry phase. Thus, the prime objective would be to keep the FA particles in the dispersed state, leading to an ease in transportation behavior. Accordingly, rheological investigation plays a critical role in stabilizing the FAS.[13] In the rheology of the slurry, the surfactant acts as a dispersing reagent, and upon its use, the wettability of FA particles increases, which leads to the reduction of the surface tension of the slurry.

To date, several refresh works[14−18] have been devoted in the context of the study on FAS stabilization, factors affecting the stabilization of FA, and the subsequent pipeline transportation. Yang et al.[14] studied the effect of FA microspheres on the rheology and microstructure of alkali-activated fly ash paste. The rheological characteristics of the FA paste were improved using sodium silicate. The influence of henko detergent and sodium carbonate on the pressure drop and flow characteristics of highly concentrated FA dispersion was investigated by Chandel et al.[15] In this study, the rheological properties of ash slurry, as well as the pressure drop due to the addition of additives, were determined at a concentration of $Cw = 60\%$ (by weight). The additives such as Rhamsan gums, xanthan gum, and carboxymethyl cellulose were also considered for use in the pipeline transportation of dense FAS, and it was noticed that the additives helped to attain the stable settling of FA particles.[16] The effect of the mixture of two commercial surfactants sodium silicate and ghadi detergent for stabilization of FAS was studied, and it was reported that a slurry concentration in the range of 50−60% exhibits a non-Newtonian behavior with significant reduction of viscosity and yield stress.[17] Three different types of surfactants, namely, cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and Triton X-100, have been employed for the investigation of rheological characteristics of FAS. The slurry

was characterized by variation of the surfactant concentration, temperature, and pH.[18] Kolǎr et al.[19] experimented using novel additives such as Tusimice Separan AP-302 (drag reducing polymer) in an ash-slag hydro transport pipeline at an 18 km range of pipeline of length having a pipe diameter of 60 mm. Significant reduction of the viscosity of the slurry was obtained using a mixture of the surfactant (hydroxypropyl guar gum and xanthan gum) and the stabilizing agent (SDS).[20,21] In addition to viscosity, the yield stress of the FAS was also dropped to 50% using a low dose of the stabilizing agent (0.2−0.6%) without the incorporation of the surfactant, as reported by Naik et al.[22] Besides the flow behavior of the slurry, leaching of heavy metals such as Cu, Ni, and Cd was achieved up to 85.5, 89.3, and 89.2%, respectively.[23]

Though commercial additives showed potential applicability in FAS stabilization, the negative impact due to their chemical effect on the ecosystem and carbon footprints during production could not be avoided. In contrast, the use of natural additives could be a suitable alternative in FAS stabilization considering both the economy and environment. For example, saponin isolated from the plant of *Sapindus laurifolia* showed excellent stabilization and transportation behavior of FAS. Moreover, the wettability of FA particles is significantly improved by adding an aqueous extract of *S. laurifolia*, which is confirmed by the decrease of the surface tension value (72 mN m^{-1}) and becomes saturated at 40 mN m^{-1}.[24] The mechanism of stabilization is due to a steric factor that is shown to decrease the ζ potential value.[24,25] Thus, it is essential to explore innovative green additives having wide structural differences for their potential stabilizing ability.

The present investigation is an attempt to evaluate the stabilizing ability of noble saponin extracted from *Acacia auriculiformis* with the supplement of lower doses of sodium silicate. The advantage of using *A. auriculiformis* in this study is with respect to its geographical location and natural

abundance. The saponin extracted was characterized to ensure its structure.[26,27] The critical factor affecting the rheology of FAS accomplishing the concentration of FA is *A. auriculiformis*, which decreases the yield stress of FAS. Other parameters like temperature and pH of FAS were investigated and reported. The results were comprehensively discussed by presenting the ζ potential and also comparing the overall stabilization yield with the previously reported commercial surfactant CTAB. The stabilization interaction mechanism was also proposed. In addition to the rheology, the attempt to remove toxic and other trace metals by the leaching method was also investigated to address the safe disposal of FA for mine backfilling application.

2. RESULTS AND DISCUSSION

2.1. Optimization of Surfactant Concentration for Stabilization of the Fly Ash Slurry.
It was found that the surfactant on mixing with water stabilizes the slurry system by increasing the wettability of the solid particles. Thus, the wettability of solid particles increases in the aqueous solution of the surfactant in comparison to water alone. As a result, the dispersion of particles present inside the liquid increases due to the coating of the surfactant over the solid particles (Figure 1).[25,28]

A coherent relation exists between the amount of the surfactant and the stability of FAS, which can be explained on the basis of repulsive or attractive forces (van der Waals force). The more the attractive force among the FA particles, the lesser the stability and solid concentration in the slurry. Depending on the critical micelle concentration (CMC) of the dispersant (saponin) isolated by two different processes (see Section 4), different concentration ranges were fixed to study the dispersing action of saponin in FAS stabilization. The 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, the concentration range was 0.001−0.016 g cm^{-3} at a fixed concentration of FA of 55%. It is observed from Figure 2 that a sharp decrease in viscosity from 994 to 387 mPa·s occurs by increasing the saponin concentration by 0.01−0.020 g cm^{-3}, and thereafter, a plateau value is obtained. Similarly, when saponin is extracted by the chemical extraction method, the plateau value is around 0.010 g cm^{-3}. A decreasing
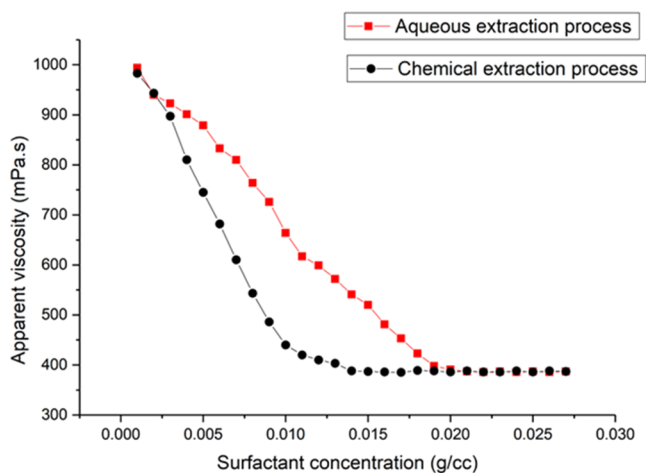
trend of viscosity may be due to the increasing rate of adsorption of saponin molecules on the FA surface, which created a greater number of effective barriers around each FA particle. This prevents the close approach of the various layers of FA particles.[24,25] Beyond the concentration of 0.020 g cm^{-3}, the apparent viscosity is leveled up due to the formation of the CMC of saponin. Since saponin adsorbs at the interface as a monomer only, the decrease in apparent viscosity is leveled up after the formation of CMC.[24,29]

2.2. Optimization of Sodium Silicate at a Fixed Concentration of *A. auriculiformis*.
Sodium silicate (Na_2SiO_3) is an ionic compound having detergent activity and has been employed as a suitable dispersant for FAS stabilization and transportation.[23,30] Besides stabilization and transportation, it can effectively bind FA particles so that after the disposal of the slurry to the ash pond, it can settle in the ash pond, thus minimizing environmental pollution. Our main objective is to use the maximum amount of the natural extract with the minimum amount of sodium silicate to form a stable slurry within an acceptable range of viscosity. Therefore, optimization of sodium silicate concentration is essential with respect to apparent viscosity. Figure 3 represents the variation
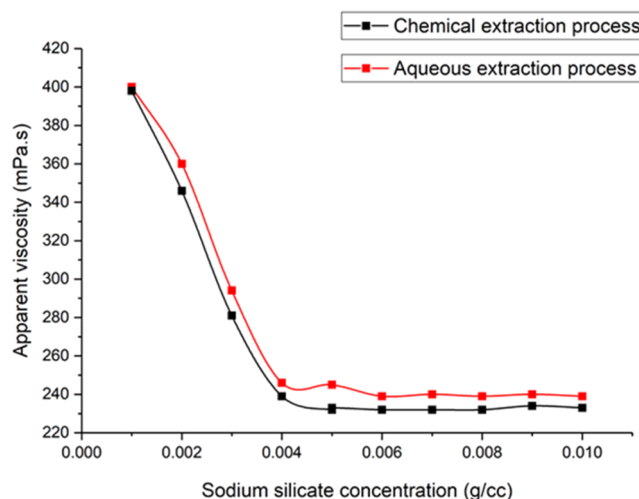

Figure 3. Effect of sodium silicate concentration on the apparent viscosity of FAS.

of sodium silicate concentration with the apparent viscosity of FAS at a fixed concentration of the dispersant, *A. auriculiformis* (0.020 and 0.010 g cm^{-3}). From the figure, it is observed that the apparent viscosity of FAS decreases with an increase in the concentration of sodium silicate from 0.001 to 0.004 g cm^{-3}.[23,30] Beyond this concentration, viscosity remains approximately constant. Also, it is clear from Figure 3 that different isolation processes have no significant impact on stabilizing and viscosity reducing tendency of sodium silicate.

2.3. Effect of Fly Ash Concentration on the Apparent Viscosity.
Pipeline transportation of a highly concentrated slurry involves a linear relationship between the solid concentration and the viscosity of the slurry. Because of the van der Waals force of attraction operating between FA particles, at a high solid concentration, the particle agglomeration takes place. This results in the increase of the viscosity of the slurry. A low viscous slurry easily settles down under gravity and a high viscous slurry requires more energy for pipeline transportation. Thus, for the economic trans-

Figure 2. Effect of *A. auriculiformis* concentration versus apparent viscosity of FAS.

portation of a slurry, FA concentration should be as high as possible with an acceptable range of viscosity.[16,24,25,31] In the present work, we vary the FA concentration in the range of 45−64% while keeping the surfactant concentration fixed, i.e., at the optimized concentrations of *A. auriculiformis* (0.010 and 0.021 g cm^{-3}) and CTAB (0.5 × 10^{-3} g cm^{-3}, around CMC). The viscosity of FAS at different concentrations was measured at a shear rate of 90 s^{-1} at room temperature. From the figure, it is observed that the viscosity of FAS increases with an increase in FA concentration.

In our present investigation, the apparent viscosity of FAS was measured at a shear rate of 90 s^{-1} with 0.020 g cm^{-3} saponin at CMC by varying the FA concentration in the range of 50−64%, as shown in Figure 4. The apparent viscosity was
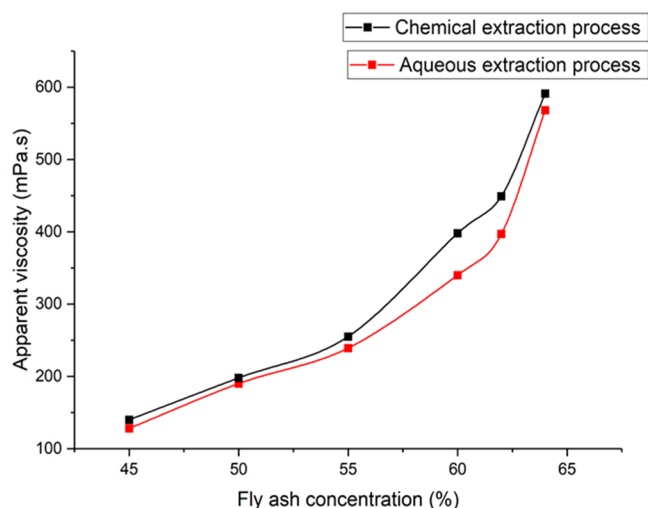

Figure 4. Effect of FA concentration on the apparent viscosity.

found to increase with the FA concentration in the slurry. With the addition of FA, the water volume fraction in the slurry network decreases and the number of direct particle−particle contacts increases, resulting in an increase in the apparent viscosity of FAS. Thus, *A. auriculiformis* along with sodium silicate can be a suitable substitute for the commercial dispersant CTAB.

2.4. Effect of Shear Rate on Apparent Viscosity and Shear Stress. The flow characteristics of the slurry in motion are generally described by a relationship between the shear stress and the rate of shear strain, which is called the flow curve or rheogram. Newton's law of viscosity is the common rheological model that correlates the shear stress to the shear rate by means of proportionality constant. A slurry that does not obey Newton's law of viscosity is referred to as a non-Newtonian slurry. In slurry rheology, the minimum shear stress required for slurry deformation and flow to occur is known as yield stress. For a nonlinear flow curve, a shear-thinning or shear-thickening response may be observed in a material under flow conditions. The former is when the viscosity decreases with the increasing shear rate and the latter exhibits an opposite trend. The variation of the shear rate with the apparent viscosity of FAS at two different FA concentrations is represented in Figure 5 at the optimized concentrations of *A. auriculiformis* (0.010 and 0.021 g cm^{-3}) and sodium silicate (0.004 g cm^{-3}). The figure represents a shear-thinning behavior, i.e., apparent viscosity decreases with an increase in shear rate. It has also been observed that the commercial
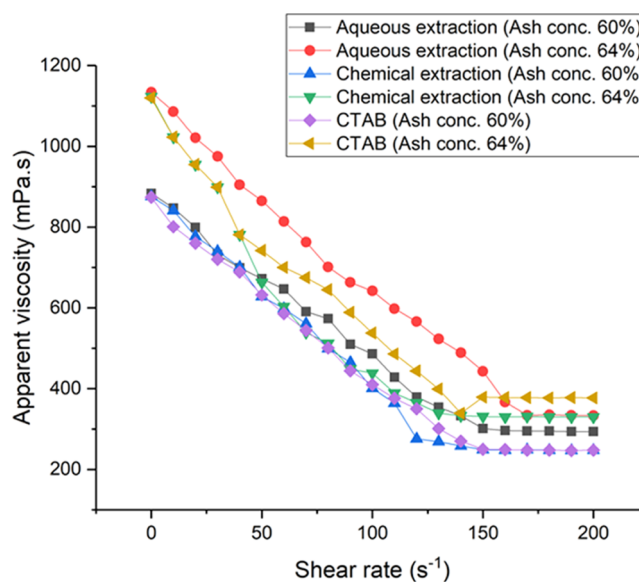

Figure 5. Effect of the shear rate on the apparent viscosity of FAS.

dispersant CTAB and the natural dispersant *A. auriculiformis* exhibit similar types of shear rate−apparent viscosity plots in the same range of FA concentration.
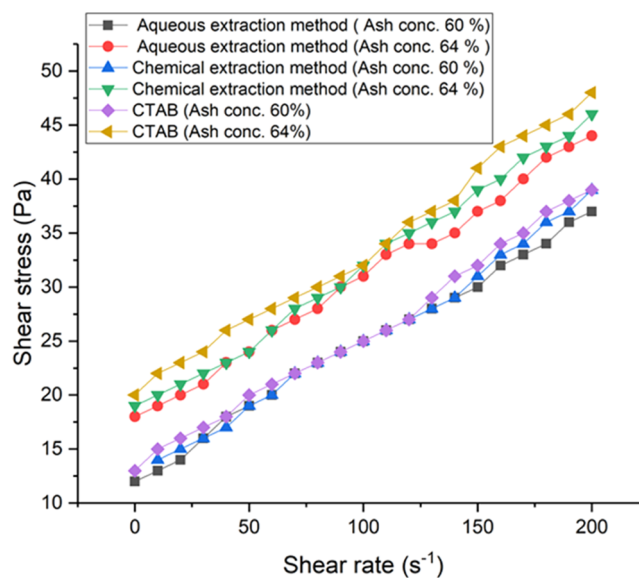

Figure 6. Shear rate versus shear stress at different FA concentrations.

Figure 6 represents the plot of shear stress versus shear rate with an initial threshold, indicating that FAS acting as a non-Newtonian Bingham plastic fluid[32,33] obeys eq 1

$$\tau = \tau_0 + \eta\gamma \tag{1}$$

where τ and γ are the shear stress and applied shear rate, respectively, τ_0 represents the yield stress, and η is the coefficient of rigidity. The intercept of these linear plots gives the yield stress of the slurry and yield stress increases with an increase in the percentage of FA concentration in the slurry. For the achievement of the yield stress around the same range in the present set of dispersants in comparison to that reported earlier, various researchers[24,25] suggest that the present set of

additives also can be effective both as adsorbents and dispersants for FAS stabilization.

2.5. Effect of Temperature on Apparent Viscosity. Particle activities in the slurry increase with an increase in temperature and cause the breakdown of aggregation in the slurry. This leads to an increase in the momentum of particles with the increase in temperature. From Figure 7, it can be
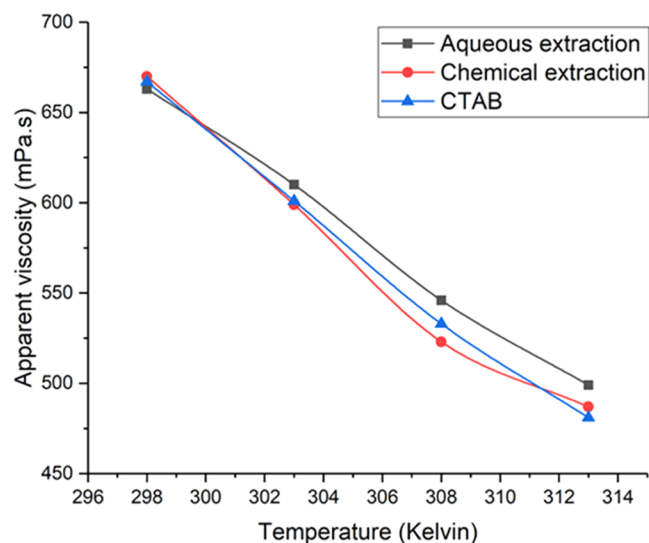

Figure 7. Effect of temperature on the apparent viscosity of FAS.

noted the apparent viscosity of FAS was found to be reduced exponentially with an increase of temperature according to the Arrhenius expression.[27] It can be represented in the form of eqs 2 and 3.

$$\eta = A \exp^{E/RT} \tag{2}$$

$$\ln(\eta) = \ln(A) + E/RT \tag{3}$$

where, "η" is the viscosity at a particular shear rate, "E" is the fluid flow activation energy, "T" is the temperature in Kelvin, "A" is the fitting parameter, and "R" is the universal gas constant. The experiment represented in Figure 7 was carried out at a FA concentration of 64% and at optimized concentrations of the surfactant and sodium silicate. With an increase in the kinetic energy, there is a decrease in cohesive force among the FA particles, thus resulting in the decrease of slurry viscosity.[24,25,34]

2.6. Surface Tension of the Fly Ash Slurry. Surfactants are wetting agents that decrease the surface tension of water when dissolved in it.[35,36] This decreased surface tension allows easier spreading of water molecules over FA. Thus, the wettability of FA particles increases and the FAS preparation becomes easier. The decrease of the surface tension value depends on the replacement of solvent (water) molecules at the air−water interface by the surfactant (*A. auriculiformis*). The more the surfactant molecules at the air−water interface, the more the reduction of the surface tension value.[37,38] Thus, the decrease of the surface tension value is directly proportional to the concentration of *A. auriculiformis* in the solution. In the present work, we have studied the stabilizing effect of saponin isolated by two different processes from *A. auriculiformis* on the surface tension value of FAS at a FA concentration of 20% and a sodium silicate concentration of 0.004 g cm^{-3}. Figure 8 shows that with increasing *A.*
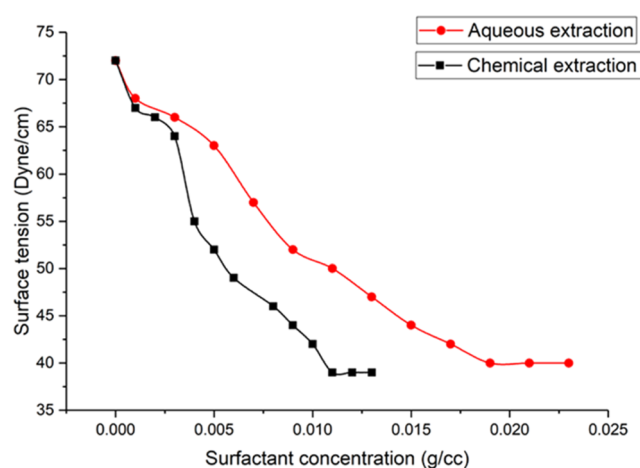

Figure 8. Effect of *A. auriculiformis* on the surface tension value.

auriculiformis, there is a gradual decrease in the surface tension value from 72 mN m^{-1} and remains approximately constant at around 40 mN m^{-1}. At this saturation level, the concentration of saponin is around its CMC (0.021 and 0.010 g cm^{-3}, respectively). Therefore, irrespective of the isolation route of saponin, the decrease of the surface tension value of FAS lies approximately in the same range.

2.7. ζ Potential Analysis of the Fly Ash Water Slurry. ζ potential is the strength of the magnitude of electrostatic repulsion among the charged particles in a colloidal system and determines the stability of the colloidal suspension. To keep the particles in the suspension, electrostatic repulsion should be greater than the van der Waals force of attraction. The strong electrostatic repulsion among the solid colloidal particles prevents aggregation or coagulation among the particles, thus keeping the solid particles in a well-dispersed state.[39] The variation of the *A. auriculiformis* concentration with ζ is shown in Figure 9. It is observed from the figure that
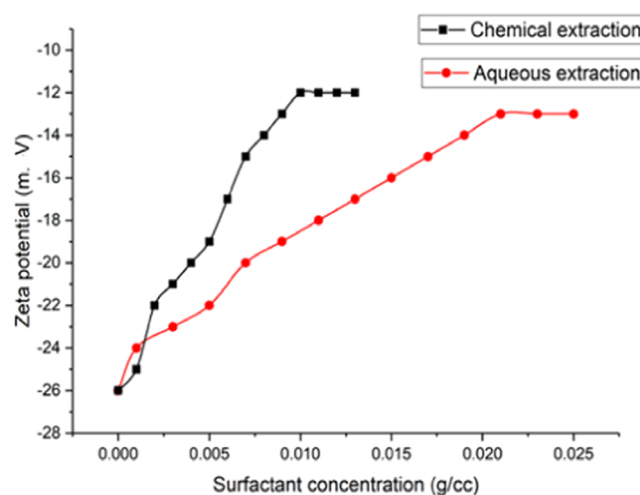

Figure 9. Effect of *A. auriculiformis* concentration on the ζ potential.

without *A. auriculiformis*, the ζ of the FA suspension is −26 mV. But with a gradual increase in the dispersant concentration, the ζ value decreases to −11 mV. Since saponin is a nonionic surfactant, its adsorption on the FA surface decreases the exposed surface charges of FA particles, resulting in a decrease in the surface charges. Other reasons for the

decrease in surface charges on FA particles may be due to mechanical dislocation of the original shear plane by the overhanging hydrophilic sugar string. Similar types of decreasing trends of the surface charge at the solid−liquid interface were reported earlier by different studies.[40−42]

2.8. Trace Element Detection Analysis and Leachability of *A. auriculiformis* and Sodium Silicate.
From Table 1, it is seen that Cr, Ni, Zn, and Cu are the most

Table 1. Metal Ion Concentration of FA by AAS in ppm

sl. no.	name of the trace element	concentration (in ppm)
01	chromium (Cr)	78
02	arsenic (As)	12
03	nickel (Ni)	73
04	lead (Pb)	42
05	zinc (Zn)	152
06	cupper (Cu)	90

abundantly present elements, while As and Pb are the least abundantly present elements, with concentrations ranging from 12 to 42 ppm. The presence of high concentrations of elements like Cr, Ni, Zn, and Cu can be justified by the fact that due to their lower atomic masses (Cr, Ni, Zn, and Cu), they can be transported with FA during coal combustion, while elements with higher masses (Pb and As) can settle quickly after combustion with bottom ash in electrostatic precipitators.[23]

Elements present in FA are not strongly bound to the particles, and therefore, all of the trace elements quantified in this experimental investigation are capable of leaching out from FA up to various extents. The leaching of FA depends on several factors such as leaching time, temperature, pH of the medium, solid-to-liquid ratio, and also the source of FA.[43]

The leaching results for metal ions with variation of time and temperature at the optimized surfactant concentration of *A. auriculiformis* and sodium silicate are presented in Table 2. The selection of the optimized concentration of *A. auriculiformis* (0.020 g cm^{-3}) and sodium silicate (0.004 g cm^{-3}) is based on the performance regarding its ability to stabilize and reduce the viscosity of FAS for improved rheological behavior.

It is observed that at a leaching duration of 8 h, most of the heavy metals get leached out from the FA surface. Moreover, it is also encouraging to see that at an elevated temperature (80 °C), the leaching rate increases by twice and saturation of leaching occurs at a leaching duration of around 8 h. Therefore, before hydraulic stowing of FAS in underground mines, an elevated temperature can be induced to accelerate

the leachability for the safe disposal of FAS. Furthermore, the leachate from the underground mine can be recirculated for reuse in FAS to avoid groundwater contamination, thus promoting sustainable utilization of FA.

2.8.1. Mechanism of Metal Removal. A saponin surfactant consists of two parts, one is a hydrophobic triterpenoid ring and the other is a hydrophilic sugar unit. The adsorption and desorption of surfactants on the FA surface follow a four-step process. In the first two steps, the introduction of surfactant molecules on the FA surface takes place followed by sorption of surfactant molecules through its hydrophobic carbon chain to metal ions attached to the FA surface by means of physical forces.[44,45] In the next two steps, the desorption of the attached metal ions with surfactant molecules occurs followed by the encapsulation of metal ions into the micellar core of the surfactant molecules. The mechanism of the heavy metal removal process by the mixed surfactant system is presented in Figure 10.
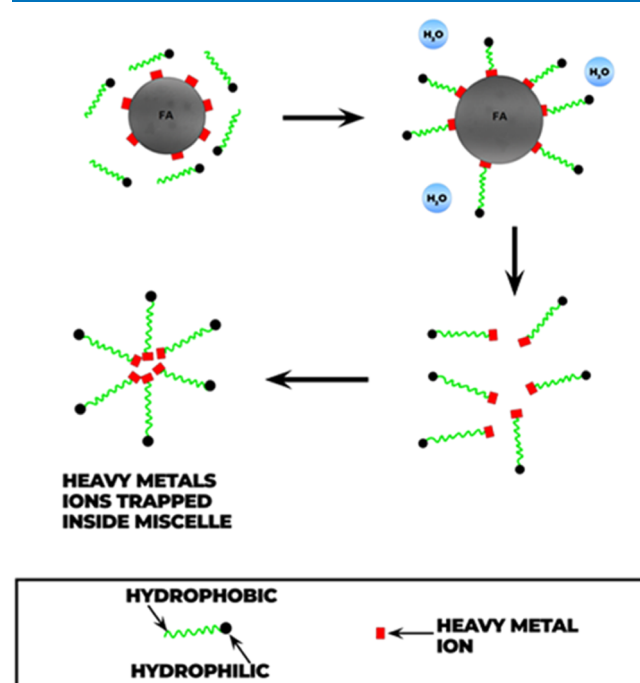

Figure 10. Mechanism of removal of metal ions from the FA surface.

2.9. Mechanism of Stabilization of the Fly Ash Slurry.
From X-ray fluorescence (XRF) analysis (Table 3), it can be observed that the major components of FA are silica (SiO$_2$)

Table 2. Leaching Test Results for Metal Ions with Variation of Time and Temperature at the Optimized Surfactant Concentration of *A. auriculiformis* (0.020 g cm^{-3}) and Sodium Silicate (0.004 g cm^{-3})^a

	trace elements (in ppm)											
	Cr		As* (in ppb)		Ni		Pb		Zn		Cu	
time (in h)	AT	ET	AT	ET	AT	ET	AT	ET	AT	ET	AT	ET
1	0.0081	0.0171	7.73	8.94	0.0151	0.0260	0.0402	0.0721	0.0171	0.0398	0.0059	0.0145
2	0.0097	0.0203	8.11	9.67	0.0167	0.0296	0.0421	0.0771	0.0201	0.0489	0.0084	0.0177
4	0.0106	0.0242	8.54	9.99	0.0215	0.0322	0.0477	0.0853	0.0273	0.0534	0.0144	0.0201
8	0.0121	0.0263	8.99	11.98	0.0264	0.0361	0.0537	0.0946	0.0333	0.0577	0.0186	0.0255
12	0.0129	0.0274	9.11	11.90	0.0269	0.0368	0.0547	0.0957	0.0346	0.0589	0.0198	0.0271
16	0.0132	0.0281	9.15	12.03	0.0271	0.0377	0.0553	0.0971	0.0354	0.0599	0.0201	0.0275

^{a}N.B: A—ambient temperature, E—elevated temperature (80 °C).

Table 3. Chemical Component Analysis of FA (XRF)

oxides	weight (%)
SiO_2	60.40
Al_2O_3	30.85
CaO	0.81
MgO	0.55
Fe_2O_3	3.35
K_2O	1.27
Na_2O	0.09
P_2O_5	0.53
TiO_2	1.88
Cr_2O_3	0.03

and alumina (Al_2O_3) with percentages of contribution up to 60.40 and 30.85%, respectively. Therefore, the mechanism of stabilization primarily depends on the stabilization of silica and alumina compounds. Our objective is not only to pack the maximum amount of FA but also to stabilize, bind, and settle the slurry in the ash pond to such an extent that it should be stable and not easily dispersed to create dust explosion after water drainage. The vital condition behind the stabilization mechanism of the slurry during transportation is to increase the net interparticle repulsion, which may be due to electrostatic repulsion or steric repulsion. Stability can be explained on the basis of electrostatic repulsion theory if there is an increase in the magnitude of the ζ potential value. In the present study, stabilization is due to the steric effect because of the decreased surface charge of FA particles (−29 to −10 mV). The hydrocarbon part of saponin (Figure 1) molecules has affinity toward the FA surface because of the hydrophobic−hydrophobic attraction, and hydrophilic sugar entities are oriented toward the aqueous part (Figure 11). Thus a
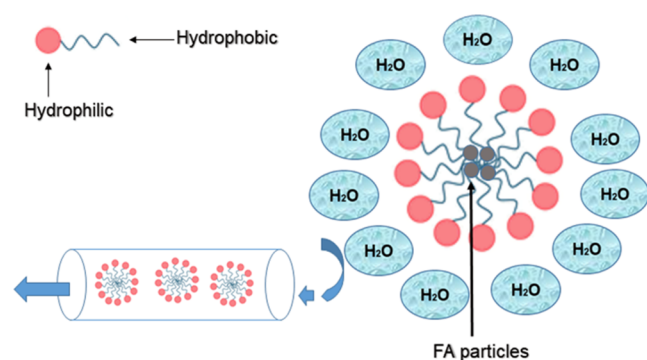

Figure 11. Stabilization and transportation of FA particles in the micellar core of *A. auriculiformis*.

mechanical barrier appeared on each FA particle hindering a close approach between them.[24,25,46,47] The binding ability of *A. auriculiformis* and sodium silicate to FA can be examined from the SEM image (Figure 12). The obtained SEM micrograph clearly shows almost complete agglomeration and dissolution of FA particles with *A. auriculiformis* and sodium silicate; henceforth, the spherical shape of the FA particles has been converted to a gel like matrix.[48] Moreover, the addition of sodium silicate in FAS helped in settling and stabilization of FA, developing reaction products like sodium aluminum silicate (N-A-S, PDF#01-089-6428) in between 27 and 30° (2θ value) as obtained from the X-ray diffraction (XRD), which justifies the scanning electron microscopy (SEM)

observations (Figure 13). The formulation of N-A-S-like compounds is generally found in alkali-activated materials,[49] taking FA in the presence of sodium-based activators.[6] The formation of the N-A-S gel helps the FA particles to stabilize and settle after disposal and dewatering, which prevents air pollution caused by FA particles. Thus, combination of *A. auriculiformis* and sodium silicate can be a suitable dispersant as well as a stabilizing agent for the sustainable disposal of FAS.

3. CONCLUSIONS

The natural surfactant *A. auriculiformis* is of biodegradable and non-hazardous nature, which appears to be promising in improving the dispersing ability toward stabilization of FAS over the commercial dispersant CTAB. The addition of low dosages (0.004 g cm^{-3}) of sodium silicate in the slurry could reduce the viscosity, resulting in the increase of the stabilizing ability of FA particles was increased. The amount of the surfactants required for the maximum stabilization of FAS was expressed in terms of CMC values obtained, which were 0.021 g cm^{-3} and 0.010 g cm^{-3} for aqueous and chemical extraction methods, respectively. The overall slurry wettability was observed to be significantly increased due to the addition of *A. auriculiformis* as supported by the results of the decreasing tendency of surface tension. The steric stabilization mechanism was further confirmed by ζ potential analysis. The SEM and XRD study of the slurry examined after transportation indicates the complete settling and agglomeration of FA particles. The formation of sodium aluminum silicate (N-A-S) at the dewatering stage was confirmed by XRD-SEM studies by which the stabilization behavior of FAS was effectively improved. The finding of the present investigation confirms the successful implementation of the rheology study for transportation of numerous FAS particles as well as the stabilization processes using noble surfactants.

4. MATERIALS AND METHODS

4.1. Fly Ash Sample. The FA sample was procured from Jindal Steel, Angul, India. The chemical composition of FA was analyzed by XRF (Zentium, Malvern Pananalytical) and is presented in Table 3. The particle size distribution (PSD) of the FA sample was measured using a laser scattering particle size analyzer (LA-960, HORIBA), as shown in Figure 14. The mineral characteristics of FA were studied by X-ray diffraction analysis (XRD) using a diffractometer (Ultima IV, Rigaku), and its peak pattern is presented in Figure 15. The XRD results indicated the presence of quartz (SiO_2, PDF#01-085-0798) and mullite ($Al(Al_{1.272}Si_{0.728}O_{4.864})$, PDF#01-083-1881) in the FA phase. As shown in Figure 16, the surface morphology of the FA sample ensured the presence of the particles in the spherical order as observed from SEM analysis (JEOI, JSM-7100F) similar to other FA cases.[50]

4.2. Preparation of the Aqueous Extract of *A. auriculiformis*. The dispersant *A. auriculiformis* is readily available across India. To prepare an aqueous extract of the above material, 10 g of the fruit was dried and converted into the powdered form. The powdered form of *A. auriculiformis* was dissolved in 100 mL of water, followed by stirring for 3 h using a magnetic stirrer.[26] Thereafter, the resulting supernatant solution was centrifuged (Centrifuge-Ependrop, Pvt., Ltd.) and filtered to extract the active component as saponin into the aqueous medium. This extract was utilized as a dispersant in the preparation of FAS.
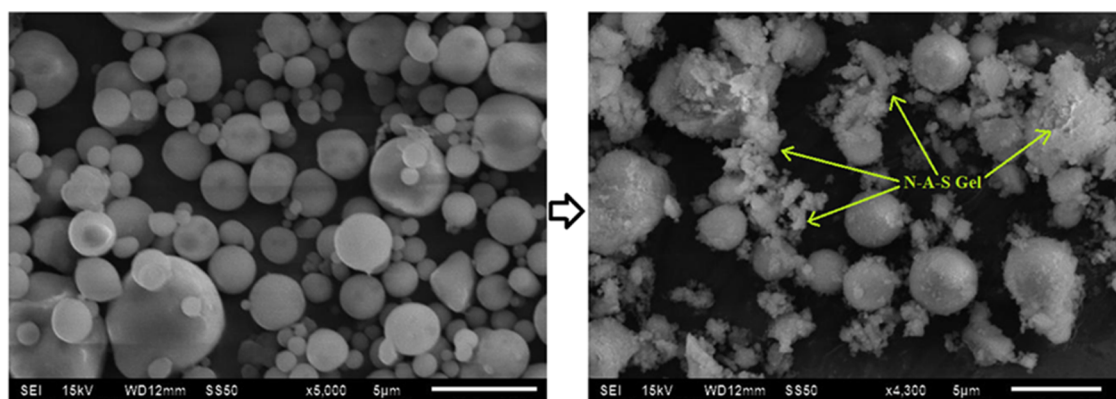
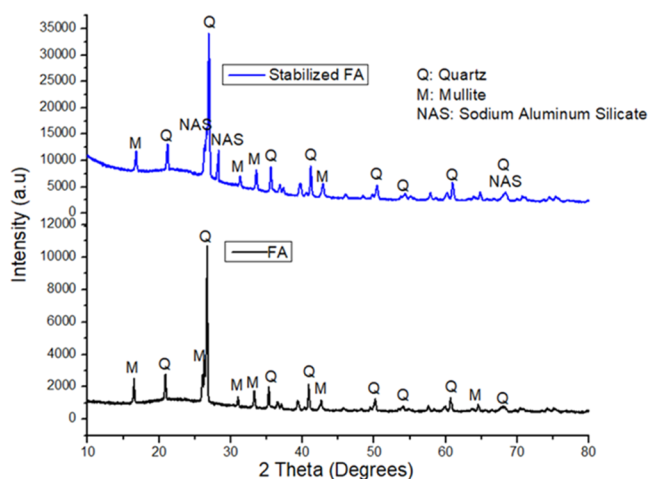**Figure 12.** SEM micrograph of stabilization of FA.

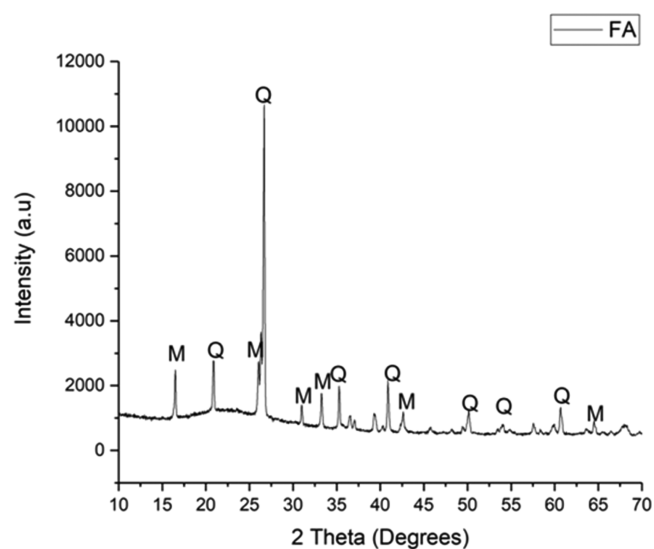**Figure 13.** SEM micrograph of stabilization of FA.

Figure 15. XRD curve of FA.
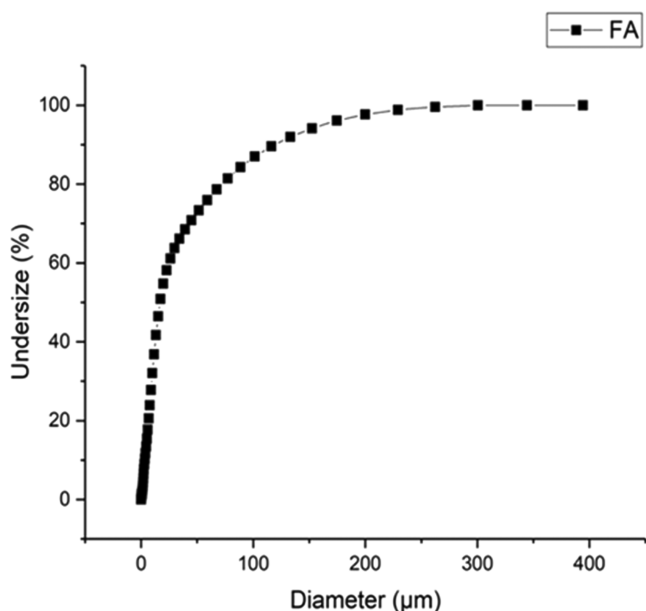

Figure 14. PSD curve of FA.

Figure 16. SEM image of untreated FA.

4.3. Surface Activity of the Aqueous Extract of *A. auriculiformis*.

The surface activity of the aqueous extract from *A. auriculiformis* was examined using a surface tensiometer (Kyowa-350, Japan). It was noticed that while increasing th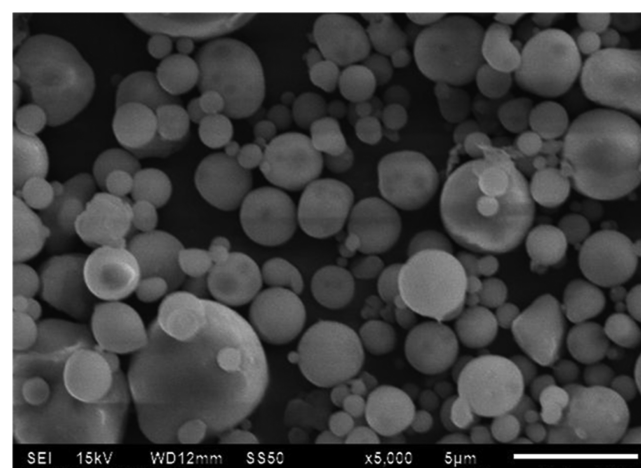e surfactant concentration, there was a quick drop in the surface tension value of *A. auriculiformis*.[26] Thus, the CMC of saponin isolated by the aqueous extraction process was found to be 0.021 g cm^{-3} (2.1 wt %). Similarly, other studies illustrated saponin isolation by the chemical method and found the point of saturation at 0.010 g cm^{-3} (CMC value).[26] Saponin isolated by the above two processes was employed for the stabilization study of FAS.

4.4. Commercial Surfactant. The commercial surfactant cetyltrimethylammonium bromide (CTAB) and sodium silicate were procured from Merck India Ltd. and used as is.

4.5. Measurement of the Surface Charge on Fly Ash Particles. An instrument ζ probe 24V (52–60 Hz) T3A attached to a microprocessor was used for measuring the ζ potential of the FAS sample. Ten grams of FA was added into 100 mL of deionized water and subjected to stirring at 500 rpm for 30 min at a temperature of 25 °C. The subsequent 1 mL of the resulting sample was taken for the ζ potential study. Most of the experiments were investigated in the triplicate mode and the mean values were considered and reported.

4.6. Measurement of Rheological Behavior. Rheological measurements of the FAS were examined using a HAAKE RheoStress 1 (Thermo Scientific, rheometer). The slurry required for testing was prepared by the slow addition of FA with weight concentrations ranging from 45 to 64% to a beaker containing an aqueous solution of *A. auriculiformis* maintained under constant stirring for 10–15 min. Around 30 mL of the slurry sample was introduced in a cleaned rheology cup, and the temperature was maintained up to 30 °C.

4.7. Analysis of Trace Elements and Leaching Study. The analysis results of the trace elements present in the FA sample are shown in Table 3 and Section 2. The concentrations of trace elements present in the FA sample were calculated using Hansen and Fisher's method.[43] In a Teflon beaker with a Teflon cover, about 2 g of the precisely weighed FA sample was digested in 20 mL of concentrated HF (49 and 28.9 M) for 2 h before being evaporated to dryness. The residue was leached for another 2 h in 10 mL of HCl with a molarity of 6 M before being evaporated. Then, in a total volume of 100 mL, the dissolved content was collected in acidified water. At last, the solution was tested for metal ions such as Cr, As, Ni, Pb, Zn, and Cu using an atomic absorption spectrophotometer (AAS) of PerkinElmer with model name PinAAcle 500.

The leaching experimental setup was done with a temperature-controlled magnetic stirrer. The optimum dosage of the leaching reagent was taken for the leaching study, i.e., 0.020 g cm^{-3} of *A. auriculiformis* and 0.004 g cm^{-3} of the sodium silicate solution. The solid-to-liquid ratio was maintained as 0.1, i.e., FA/surfactant solution is 1:10 during the experiment. The magnetic stirring rate was fixed at 300 rpm and the leachate was collected at time intervals of 1, 2, 4, and 8 h. Also, the effect of the elevated temperature on the leaching behavior was studied taking three different temperatures, i.e., 40, 60, and 80 °C. The collected leachate was then analyzed using the AAS for quantification of heavy metal (Cr, As, Ni, Pb, Zn, and Cu) concentrations.

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■ ABBREVIATIONS

CMC	critical micellar concentration
A. auriculiformis	Acacia auriculiformis
H	dynamic viscosity
τ_0	yield stress
γ	applied shear rate
ζ	zeta potential
τ	shear stress

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