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A novel approach on leaching study for removal of toxic elements from thermal power plant-based fly ash using natural bio-surfactant

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A B S T R A C T

A plant extract such as saponin obtained from the fruits of Sapindus laurifolia (S. laurifolia) by both chemical and water-based methods has been introduced as a cheap and inexpensive solvent for the removal of toxic elements from thermal power plants. coal fly ash (FA). An extraction study of elements including Cr, As, Ni, Pb, Zn and Cu from FA particles was conducted and reported systematically. The role of critical factors such as saponin concentration, time, temperature and pH of liXiviant was investigated. Extraction results of sapoin separated by aqueous and chemical extraction were compared and presented. The change in FA phase obtained by SEM analysis, such as the appearance of surface roughness of the normal phases of FA after dissolution, was well explained by the dissolution of metals from FA. Based on the hydrophobic and hydrophilic character, the interaction mechanism resulting from the adsorbed saponin with the FA surface phase during the leaching of these metals was deduced and proposed based on the dissolution results.

1. Introduction

In the present scenario, the management of solid waste like fly ash (FA) and its beneficiation is a greater concern owing to its larger rate of generation rate out from the industries and various incineration pro- cesses [1]. In a country like India, there is extensive usage of coal is noticed exclusively in thermal power plant sectors for electric energy production leading to which the generation of FA from the thermal power plant is projected to be multifold over other sectors. Nonetheless, there is a growing demand for use of coal in power plant sectors day by day as the country's 70% of power generation is exploited from the thermal power plants [2]. As per the literature survey, the electricity demand of India is expected to rise to 950,000 MW by 2030 and that would substantially produce a huge quantity of FA. The production of FA will increase by approximately 442 MT/year by the end of 2035 [3]. The majority of the Fly ash liberated out of the industries and/or processes are disposed of off as it is for landfilling purposes. Thereby, the serious issues are accounted due to FA for causing environmental pollution upon contaminating with soil, water, and air level. The contamination of groundwater level by FA is mostly caused by the content of the heavy metal(s)/metalloid(s) such as Pb, Cd, Cr, Fe, and As in it [4]. These el- ements in the water level cause several acute and carcinogenic diseases to animal and plant lives [3]. Therefore, keeping in view of the greater level of the liberated amount of FA and issues of environment caused by FA [4] it becomes essential to develop a suitable processing technology for the removal of toxic elements from FA prior to its disposal to the environment and that could certainly prevent the risk of causing acute health threats up to greater extent [5,6].

The hydrometallurgical leaching methodology is commonly prac- ticed by researchers to leach the metals from the fly ash phases using mineral acids, alkalis, and other reagents [7]. In connection with the

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Abbreviations

AAS	Atomic absorption spectroscopy
CMC	Critical micellar concentration
S	laurifolia Sapindus laurifolia
SLS	Sodium lauryl sulphate
FA	Fly ash
SEM	Scanning electron microscope

cost beneficiation, process economy, and environmentally friendly perspective, the use of the low-cost green reagents in the leaching pro- cess is often preferred over the above expensive reagents. The natural surfactants [8] containing saponin acts as a promising extracting agent for leaching heavy metals over the common acids (HCl, H_2SO_4, HNO_3), alkalis (NaOH), and chelating agents (EDTA). Though the use of acid- s/alkali is successful in extracting metals from FA, the adoption of high-cost reagents for leaching a very content metal from FA is not economical. In contrast, the extraction by chelating agents namely EDTA and DTPA are least preferred owing to the difficulties in recovering the metals from leached solution bearing metal-chelate complex resulting out of the process [9]. The studies in the context of the leaching of heavy metals from fly ash, bottom ash, dumping site ash, cement, and brick samples, and the mixture of thermal power plant-based fly ash were summarized. From these investigations, leaching of metals such as Zn, Ni, Cu, Fe, Pb, Mn, Mg, and Cd was carried out by applying batch leach test and toxicity characteristic leaching procedure (TCLP) to check the possibility of groundwater contamination. The leaching yield was reportedly high for the metals such as Mg, Mn, and Fe, moderate for Zn, Cu, and Pb, and low for dissolution of from the FA. It was noticed that during batch leaching operation Cd was not leached while employing the above reagents [3,5,10]. As of now, limited studies are accom- plishing on leaching study of toxic heavy metals using the green natural surfactants [8,11,12]. As can be seen in the reported works, the leaching mechanism through the Micellar Enhanced ultra-filtration (MEUF) route with the adoption of saponin extract is a unique and effective approach unlike the common leaching method [13]. In MEUF, the surfactants are usually added to wastewater with concentrations higher than their critical micelle concentration (CMC), and surfactant monomers aggre- gate to form micelles. In this way, the micelles could be able to solubilize organic solutes or bind metal ions on the surface of the oppositely charged micelle via electrostatic interactions. This led to attaining a promising heavy metal leaching yield from the FA phase. The MEUF based metal leaching is efficient and in which the factors such as pH of

metals in FA phases(maximum recovery (%) of copper, zinc, lead, and cadmium from fly ash reached up to 88.34%, 50.33%, 77.46%, and 85.23%, respectively. In another study Mukhopadhyay et al., 2013 re- ported the utility of *Sapindus mukorissi* for removal of As metalloid from soil in comparison with the commercial-grade surfactant i.e., sodium dodecyl sulphate (SDS) [30]. However, there exists no critical study on evaluation of the leaching ability of *Sapindus laurifolia* (*S. laurifolia*) for the removal of toxic metals from any sources. The leaching of various metals from fly ash using numerous reagents has been reviewed and summarized as given in Table 1.

Thus, after evaluating the details of reported works and keeping in view of the scope of the natural surfactant for its economical impor- tance, efficient adoption and futuristic demand on leaching study, this investigation attempted to adopt natural surfactant saponin extracted out of the *S. laurifolia* (fruit portion) having active sites of both hydro- philic and hydrophobic units. *S. laurifolia* is a soapberry plant abun- dantly obtainable in South Asia. The extraction process of saponin has been carried out from *S. laurifolia*, which is a complex admixture of saccharin derivatives. The saponin consists of a variety of naturally producing nonionic surfactant molecules. The hydrophilic segment of this molecule is named glycon. This glycon portion comprises saccha- rides micromolecules like glucose, galactose, rhamnose, xylose, pentose, etc. Furthermore, the hydrophobic segment is aglycone, which has formed of steroids or triterpene. The steroidal arrangement has origi- nated with a C27 spirostane arrangement of a 6 ring design. On the other hand, the triterpenoid has constructed a C30 formation of a pentacyclic orientation [31]. The oxygen molecule has associated with the hemi- ketal or hemiacetal carbon group of the saccharide residual at the hy- drophobic position of this molecule. Furthermore, it is associated with other saccharide residuals within oxygen linkages. Due to its amphi- philic character, it has the ability to dissolvable the organic molecules in water [32,33]. The universal arrangement of saponin is presented in

Fig. 1 agree with the process for removal study of the toxic elements and

other trace metals like Cr [34], As, Ni, Pb, Zn, and Cu from the FA using saponin as a suitable organic reagent (extracted in both aqueous and chemical extraction manners) was systematically investigated. Both extraction processes including the aqueous and chemical route showed different leaching behavior for either of the heavy metal from FA was compared and presented. To ensure the successful removal of the heavy metals/metalloids and the surface modification, the scanning electron microscopy (SEM) analysis of the FA samples (before and after leaching) was examined.

Table 1

Leaching study of Metals from FA by using of different processes.

lixiviant, surfactant concentration, liquid to solid ratio, temperature, feed flow velocity, and retention time plays equally effective unlike
Sl.
No.
Metals Processes References
other commercial reagents [14]. The surfactant namely Saponin is a
01 Cu, Zn, Pb, Cd
Mixed surfactant [8]
variety of natural nonionic bio-surfactant [15,16] that has to be gener- ated by numerous plants [17] and microorganisms. They have the
02 As, Se, Cr, and Al Batch water leaching tests (WLTs) and column leaching tests (CLTs)
[19]
benefits of biodegradable ability, less toxicity for nature, spontaneous
03 Cr, Se, Zn, As Pond [20]
generation ability, and the feasibility of repeated usage [11,18].
04 Se, Ag, Cr, Cd Batch water leaching tests (WLTs)[21]

There are limited works have been reported comparing of the usages of biosurfactants on heavy metal leaching from the municipal waste based flyash. Xu and Chen (2015) have used mixed system of strong

05 Mo, As And Se
06 Mn, Fe, Cr, Zn, Cu,
Ni, Co, Pb and Cd
and column leaching tests (CLTs) Batch test
Cascade method

[22]
[23]
chelating reagents like chelator [S, S]-ethylene diamine disuccinic acid,
07 Zn, Pb, Fe, Cu, Ni Organic acid precipitation [24]
citric acid, along with biosurfactant saponin for removal of metals from
08 Zn, Pb, Cd and Cu Electro-kinetic remediation device [25]
municipality solid waste fly ash [8]. As can be noticed the role of either organic acid like citric acid and or chelating group have strong affinity towards removal of transition metal(copper, zinc, lead, and cadmium)

09 Pb, Zn, Cr, and Cu
10 Ba, B,Cu, Zn
(cylindrical chamber) Batch leaching
Batch water leach tests, column leach tests

[26]
[27]

from the FA phase as they form strong complex in aqueous phase and the

11 Cd, Cr, Se, and Ag. Batch water leaching tests (WLTs)

[28]

role of saponin is insignificant. The synergistic mixture of saponin and ethylene diamine disuccinic acid and citric acid exhibits a solubilisation effect on leaching from fly ash as stated by them. Overall study have very less metal leaching yield even extracting the low concentration of these

12 Cr, Ni and Hg

13 Cu, Zn, Pb,Cr, Ni & As

and column leaching tests (CLTs) Single batch leaching test and column leaching test

Batch leaching using natural surfactant

[29]

Present Study

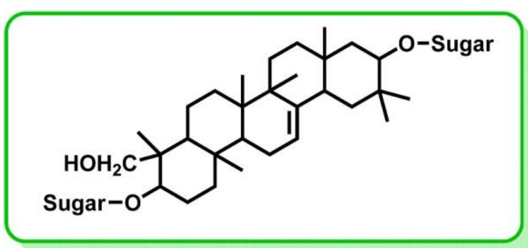

Fig. 1. Structure of saponin.

2. Materials and methods

Fly ash

Fly ash (FA) used in this study was procured from a local power plant (NTPC, PVT LTD.) located at Talcher, Odisha (East zone of India). As shown in Table 2, the results of X-ray fluorescence spectroscopy (Zen- tium, Malvern Pananalytical) were summarized. Furthermore, to ensure the complete elemental profile for analysis trace elements present in FA it was further digested followed by subjected to analysis by anatomic absorption spectroscopy (AAS), and results are given in Table 3. A scanning electron microscope [JEOI, JSM-7100F] was used to examine the surface morphology and chemical constitution (elemental) of the FA sample, as shown in Fig. 2. The presence of micro-spheres in the FA may be seen by SEM, which supports previous morphological investigations undertaken by various studies [35].

Sapindus Laurifolia and its extraction process

The *Sapindus laurifolia* (*S. laurifolia*) is a large tree that can reach a height of 25 m and it is found in the majority of south Asian countries. The fruits of this tree are small-spherical in shape with leathery-skinned pericarp with 1–2 cm in diameter, and the fruit pericarp is rich is saponin. Therefore, the fruits can be a natural source to extract saponin that can be a potential substitute to commercial surfactants (SDS) and can be used as a leaching agent for heavy metal removal [36].

The fruits of *S. laurifolia* were collected from India's southern forest zone. The saponin from the fruit of *S. laurifolia* was extracted in two different methods such as aqueous and chemical extraction. This investigation explores both of the isolation routes of saponin to study the leaching of heavy metals using saponin from FA of a power plant.

Aqueous extraction process

Dry fruits (10 g) of *S. laurifolia* were weighed, and the pericarp was chopped, dried, and pulverized to obtain the desired size. Thereafter the powdered form of the pericarp of *S. laurifolia* was soaked with distilled

Table 2
Chemical composition of FA determined by XRF analysis.

Table 3
Concentration of elements in FA phase and their maximum permissible limits of leaching by USEPA.

Sl. No.	Name of the trace element	Concentration (mg/L)	Permissible limits as Per USEPA [39](mg/L)
01	Chromium (Cr)	72	0.1
02	Arsenic (As)	13	0.01
03	Nickel (Ni)	70	0.02
04	Lead (Pb)	48	0.05
05	Copper (Cu)	87	1.3

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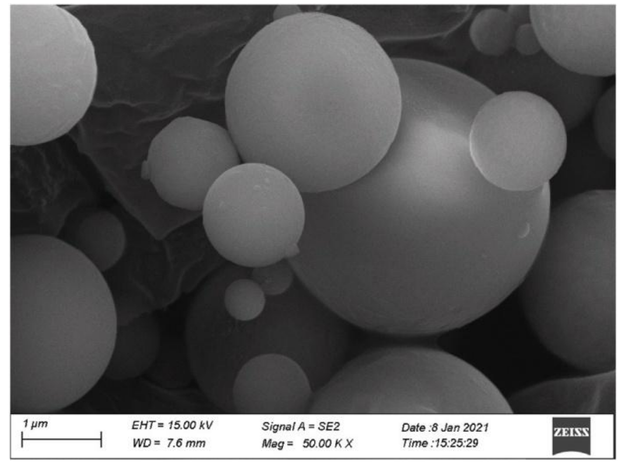

Fig. 2. Morphological results of Fly Ash by SEM.

water (100 mL) and then stirred for a period of 3 h with the help of a magnetic stirrer. The supernatant solution obtained was centrifuged at 10000 rpm (centrifuge, Eppendorf, Pvt. Ltd.) containing an active component as saponin was taken to use for leaching study.

Chemical extraction process

The pericarps of the *S. laurifolia* fruits were chopped into little pieces, then extracted four times with distilled water at room temperature and then with hot distilled water (90-95 °C). The solid-liquid ratio was kept at 1:3 during the extraction process, and the volume of water was reduced using a climbing film. The addition of ammonium sulphate resulted in the solid mass that begins to float fluid surface. The water content was removed from the floating mass, followed by recrystalli- zation from n-butanol to generate saponin, a bushy thread-like mass.

Calculation of critical micellar concentration of S. laurifolia

A surface tension-meter (Kyowa-350, Japan) was used to test the surface activity of saponin extracted from the above aqueous extraction. While the surfactant concentration reaches 0.017 g per cc, the surface tension of pure water was 72 mN/m, while the surface tension of an aqueous extract of *S. laurifolia* solution was 38 mN/m (1.9 wt) [33]. This

Oxides	Weight (%)
SiO_2	60.342
Al_2O_3	30.834
CaO	0.801
MgO	0.548
Fe_2O_3	3.346
K_2O	1.268
Na_2O	0.082
P_2O_5	0.522
TiO_2	1.878
Cr_2O_3	0.026

CuO	0.011
ZnO	0.014
PbO	0.005
NiO	0.010

surfactant concentration could be the dispersant's CMC. There is no significant change in surface tension value above this concentration of *S. laurifolia*. The critical micellar concentration of saponin extracted by chemical extraction was found to be 8 g/L which is in agreement with our previous study [32].

Analysis of trace elements and leaching study

Hansen and Fisher's technique [37] was used to determine the concentration of heavy metals in the taken FA sample. The weighed amount (2 g) of accurately measured FA was digested in 20 mL of concentrated HF for 2 hours in a Teflon beaker with a Teflon lid before being evaporated completely. The residue was leached further for 2 hours with 10 mL of 6 M HCl. Then the dissolved material was collected in distilled water with a volume makeup of 100 mL. The digested so- lution bearing metal/metalloid ions such as Cr, As, Ni, Pb, Zn, and Cu were analyzed by AAS (PinAAcle 500, PerkinElmer). A magnetic stirrer having the provision of temperature control was used in the leaching investigation of FA. The leaching experiment was conducted by taking saponin isolated by both the aqueous and chemical extraction process. Moreover, the leaching characteristics of FA were examined in detail with a variation of surfactant concentration, time, temperature, pH, and solid to liquid ratio. The concentrations of heavy metal ions (Cr, As, Ni, Pb, Zn, and Cu) in the obtained leachate for all of the experimental sets were analyzed by AAS.

3. Results and discussion

The content of metals in FA and effect of the concentration of saponin (S. laurifolia extract) on leaching of metals

As can be seen from the results of Table .3, it showed that Cr, Ni, and Cu are existed up to a greater concentration level (ranging from 70 to 87 mg/L) over other metals. On the other hand, As and Pb are found to be least i.e., in the range of 12–42 mg/L. The high concentration of ele- ments in the FA like Cr, Ni, Zn, and Cu can be attributed to the fact that elements with lesser atomic masses (Cr, Ni, Zn, and Cu) can be carried away with the FA during the burning of coal, whereas elements with high atomic mass (Pb and As) does settle down immediately inside the electrostatic precipitator with the residual mass, i.e., bottom ash [38].

Since the metal/metalloid(s) ions associated with the FA phase are not tightly bound, hence all of the heavy metals detected in this analysis are susceptible to leaching out of FA to varying degrees. The leaching of FA depends upon several factors such as leaching time, temperature, pH of the medium, solid to liquid ratio, and also the source of the FA [37]. The leaching results for metal/metalloid(s) ions were examined while studying varying surfactant concentrations using saponin derived by aqueous and chemical from *S. laurifolia* is shown in Fig. 3a and b. During this leaching study, all other parameters such as temperature (30 °C), leaching duration (2hrs.), pH (6.8), and liquid to solid ratio (1:10) were kept constant. It was evident from Fig. 3a that with varying the saponin concentration from 0.013 to 27 g/L using the aqueous extraction method, the leaching results

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corresponding to the varying saponin concentration values were elucidated. It can be inferred that with the increase in the concentration of saponin, the leaching yield of all the metals was increased out of the FA surface and that may be due to the effective leaching behavior of saponin above the CMC value [40]. On further analysis, it was found that the rate of leaching in all the metals was high in the initial treatment phase as the metal leaching increased significantly with the change in concentration of saponin viz. the leaching value of Cr increased from 0.0029 to 0.0053 mg/L while saponin concentration was increased from 13 to 15 g/L. However, in the latter part, the rate of leaching was drastically slowed down, although, the leaching values were increased. Hence, with a constant increase in the saponin concentration, the difference in the corresponding metal leaching values lowered and a sort of saturation in the leaching was obtained in most of the metals like Zn, Pb, and Cu leaching values did not vary much when the saponin concentration was varied from 25 to 27 g/L except Cr, Ni and As. Therefore, in the case of saponin treatment using the aqueous extraction method optimum values were obtained at 25 g/L of saponin concentration.

The leaching of metals (Cu, Cr, Pb, Zn, As and Ni) at varying higher concentrations from 2 to 16 g/L of saponin (chemical extraction method) concentration was shown in Fig. 3b. The leaching results ob- tained were observed to be promising with adopted saponin as compared to the aqueous extraction method. Initially, the extent of metal ions leached was higher from the FA surface which showed a decreasing trend with the increase in the concentration of the saponin.

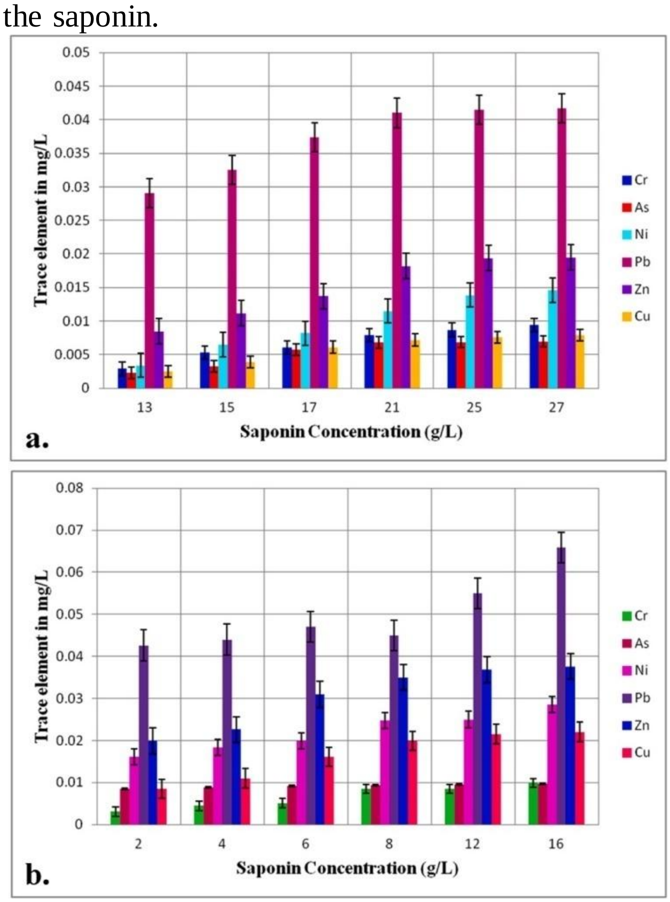

Fig. 3. Metal ion leaching with a variation of saponin concentration **a.** Aqueous extraction **b.**

Chemical extraction.

Thus, metal ion leaching rate behavior was similar to the aqueous leaching extraction method and a plateau value level was attained. From this study, 12 g/L of saponin was chosen to be the optimum concen- tration for leaching of metal ions using the chemical extraction method.

Effect of time

The influence of time is one of the critical factors in leaching of metals as it is mostly dependant on the nature of the source phase. In present study the source phase namely fly ash gets readily undergoes dissolution of metals such as Cu, Cr, Ni, Pb, Zn and As while interacting with saponin of *S. laurifolia* and to investigate the extent of leaching time was varied from at 1–6 hours. As shown in Fig. 4a, most of the metal values were leached in the first 3 h while using the saponin extracted by aqueous extraction method. The leaching values of metals ion from the FA surface increased with time. However, the rate of leaching was initially increased till 3 hours and then remains steady up to 5 hours of leaching this may be due the fact on the attainment of optimum leaching yield in 5 hrs. Since no such significant change in the leaching concen- tration of metal values from the FA surface were observed after 5 hours of treatment time, hence 5 hours kept fixed for substantial leaching investigation for attaining, maximum leaching yield and effective con- dition for leaching under the studied saponin dose obtained by aqueous extraction method.

In similar to above, the time variation leaching was conducted using saponin obtained out of the chemical extraction method. As can be seen from the results of Fig. 4b, the initial extent of leaching obtained was higher as when compared with the aqueous extraction method due to the corresponding higher optimum concentration of the saponin used. However, the releasing behavior of the leached metal ions from the FA

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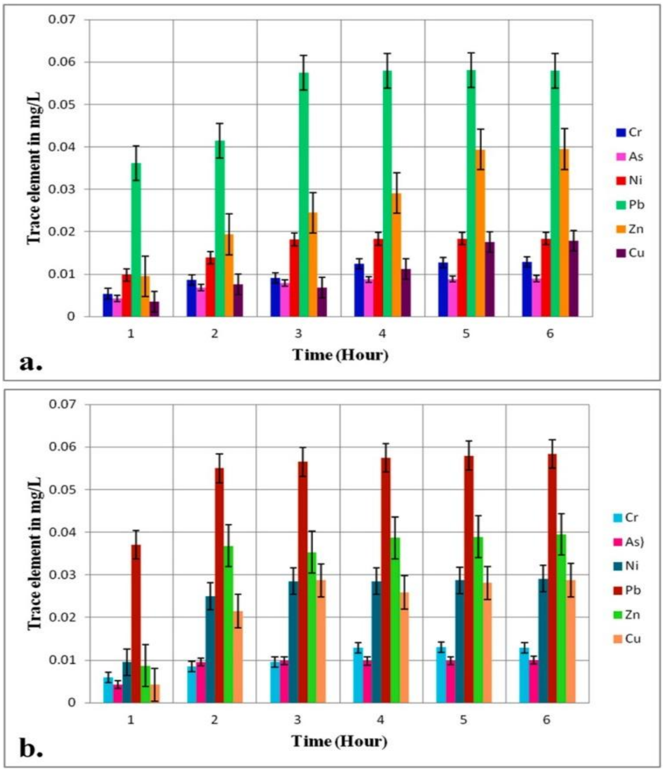

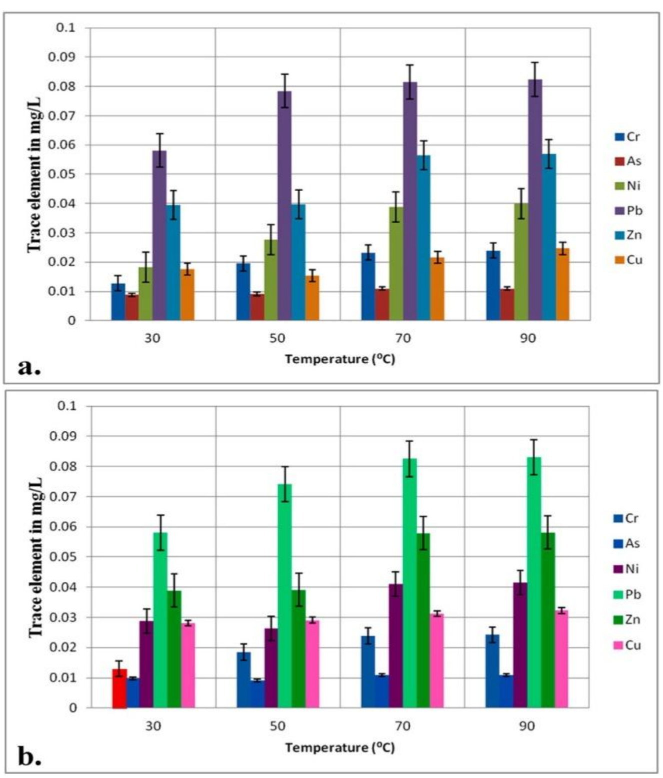

Fig. 4. Metal ion leaching with a variation of time with optimum surfactant concentration **a.**

Aqueous extraction **b.** Chemical extraction.

was found to be similar to that of the aqueous extraction method. Furthermore, the leaching of metal values from the FA surface after the 4 hours did not vary much in most of the metal values. Keeping in the view of the consistent leaching performances 5 hours time was assumed to be the optimum time under both the chemical and aqueous extraction method for the removal the metal ions from FA surface and hence maintained for further experimental studies. Unlike other commercial reagents and or mineral acids usages the leaching of fly ash, the leaching time is comparatively more while using the natural surfactants and mild organic acids due to the content of lower acidity [30]. However, the use of the natural surfactant is significantly beneficial for the lower of the cost and equally efficient with the chelating reagents/mineral acids for leaching out of the trace elements from the Fly ash phase [8,38].

Effect of temperature

The temperature variation study was conducted under optimum conditions using saponin derived by aqueous extraction method for
leaching of metal ions from fly ash. As shown in Fig. 5a, the leaching of metals resulted at the temperature of 50 °C were found to be significant and at the 70 °C the values were considerably higher i.e., 0.0233 mg/L in Cr, 10.99 mg/L in As, 0.0389 mg/L in Ni, 0.0815 mg/L in Pb, 0.0564 mg/L in Zn and 0.0216 mg/L in Cu obtained in AAS. The increment in heavy metal removal with the increase in temperature could be due to
the increase in rate of the interaction of metals of the Flya ash phase by the saponin on the surface of FA [41]. It was noticed that beyond the temperature of 70 °C the metal ion leaching values reached to plateau in most of the metals excepting Cu. Therefore, to attain an efficient metal leaching, the temperature of 70 °C was found to be suitable and hence maintained for subsequent studies. For the temperature variation study, the experiments were conducted at the optimum surfactant

Fig. 5. Metal/metalloid ion leaching with a variation of temperature with optimum surfactant concentration and optimum leaching time 5 hrs. **a.** Aqueous extraction **b.** Chemical extraction.

concentration using the saponin (obtained by chemical extraction method) and from the results, Fig. 5b, significant leaching of the metal ions was obtained just after attaining the 50 °C temperature. However, all the metal ions leached from the FA surface at corresponding temperatures were found to be high in all the cases as compared to the aqueous extraction method.

The optimum leaching for this case was also obtained at 70 °C as the
leaching values of most of the metal ions were initially increased fol- lowed a steady rise till 70 °C due to the attainment of saturation over the FA surface. Hence 70 °C of temperature was obtained to be suitable for achieving enhanced leaching using the saponin derived by the chemical extraction method.

Effect of pH

The pH variation study was performed to study the release behavior of metal ions under different pH environments taking the optimum conditions (L/S ratio, temperature, and surfactant

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concentration) in both aqueous and chemical extraction methods. From Fig. 6a., it is evident that the leaching investigated at different pH, the leaching of metal values increased to maximum i.e., 0.0241 mg/L of Cr, 0.042 mg/L of Ni, 0.085 mg/L of Pb, 0.024 mg/L of Cu, and 0.059 mg/L of Zn is leached under highly acidic conditions i.e., under lower pH of around
3.7. The higher leaching was obtained towards acidic (lower pH), but a highly acidic environment is not preferred as at lower pH may result in the breaking of the saponin molecule thereby diminishing the surface activity of saponin [42,43]. Thus the lower pH is unsuitable as it hinders the reaction occurring between the leaching agents and heavy metals and thus may deactivate the saponin responsible for the metal ion leaching [8]. In addition, It was also observed that the leaching of metal

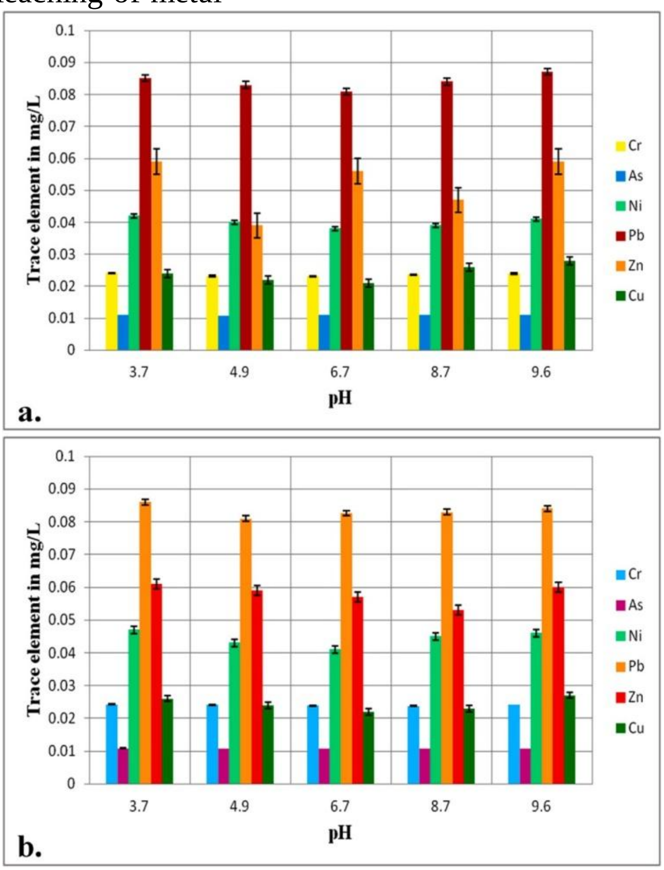

Fig. 6. Metal/metalloid ion leaching at varied pH with optimum temperature and surfactant concentration and optimum leaching time 5 hrs. **a.** Aqueous extraction **b.** Chemical extraction.

values decreases slightly as the pH increases towards the neutral but the metal ions leached values increased again when the pH was increased to highly basic which can be described due to the effect of base responsible
for the leaching. The nature of variation of the leaching values with variation in the pH in the chemical extraction method shown in Fig. 6b., was found to be similar to that of the aqueous extraction method. However, the extent of leaching in chemical extraction methods was found to be considerably higher than the aqueous extraction method at the same pH values. Thus, it can be elucidated that leaching of metal values because of pH variation do not get affected very much

but rather a pH around 6–7 is suitable and best for the saponin to carry out the effective leaching.

Interaction mechanism of saponin with FA during leaching

A hydrophobic carbon unit is one of the surfactant's components, whereas a hydrophilic carbohydrate unit is the other. A multi-step process is involved in the adsorption and desorption of saponin on the FA surface. The first two processes include introducing surfactant mol- ecules to the FA surface, followed by sorption of the surfactant molecule to metal ions attached to the FA surface via its hydrophobic carbon unit [11,30]. In the next two phases, the desorption of coupled metal ions with surfactant molecules proceeded by the entrapment of metal ions in the micellar core of surfactant molecules. Based on the stated mecha- nism, the approach of heavy metal removal employing a natural sur- factant system is clear in this work (as shown in Fig. 7).

In addition the change in surface morphology of the fly ash particles is attributed by the mass transfer due to the leaching of metals by saponin as can be inferred from Figs. 1 and 8. It was also well evident from the SEM results that the surface regular morphology of untreated FA particle (Fig. 1) has been changed to the appearance of roughness at the fly ash surface particle after leaching treatment as shown in Fig. 8. This observation was in well agreement with the change in surface behavior of fly ash surface due to the leaching of metals in reported works while following to the above proposed mechanism [19,32].

Characterization study of FA sample

Process optimization study for removal of toxic elements using saponin was established based on the parameters effect study. To ascertain the mass transfer of the metals from the FA phase to the leachate was further interpreted by characterizing the FA before and

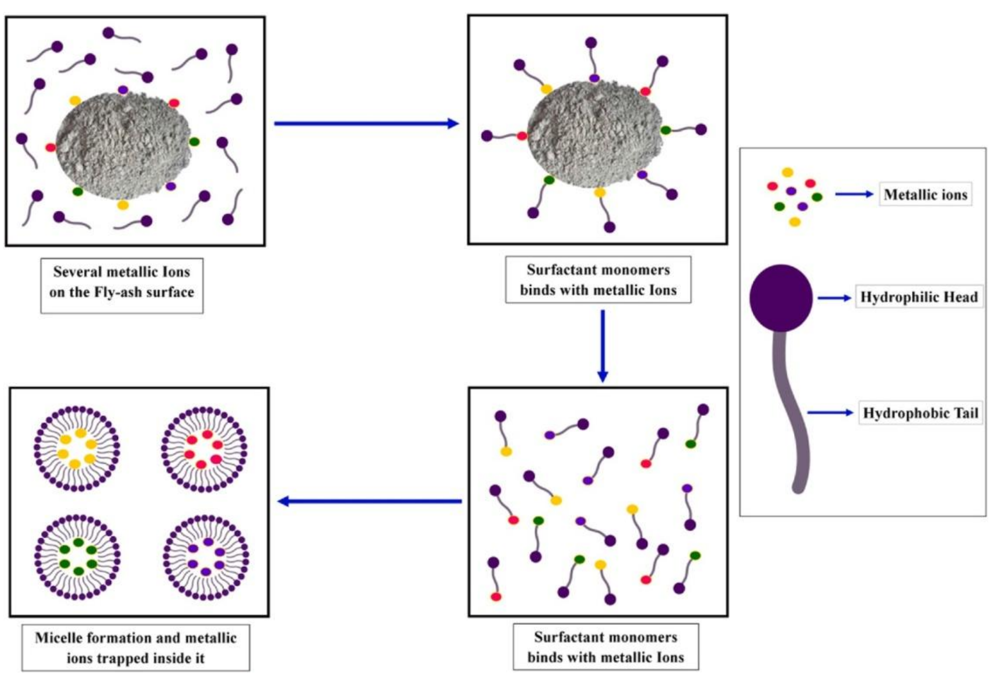

Fig. 7. Mechanism of saponin with FA during leaching.

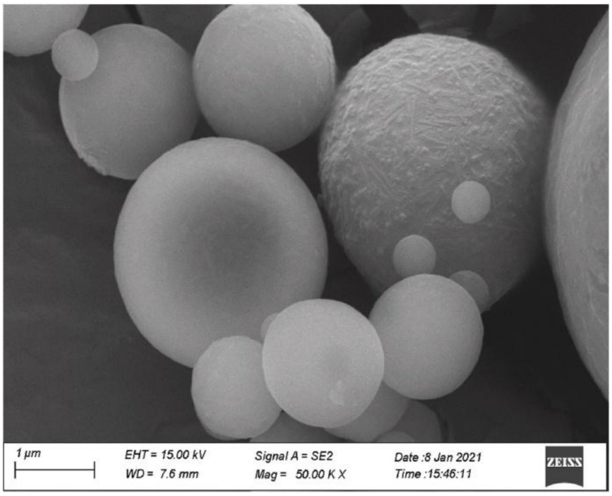

Fig. 8. Modified surface of FA by *S. laurifolia*.

after leaching by SEM. The surface phase analysis of the original FA surface was shown in Fig. 3 and whereas Fig. 8 represents the SEM re- sults of the resulting leached residue after leaching at the optimum leaching condition. The change surface modification accomplishing the development of surface roughness at the leached residue sample (shown in Fig. 8) over the regular surface of the initial FA (before leaching) due to the mass transfer of the toxic elements from the FA surface was ascertained from the SEM analysis results and this result is quite well agreement with the results of an earlier reported study [44].

4. Conclusions

The usages of *S. laurifolia* consisting of saponin showed promising and environmentally friendly leaching for quantitative removal of heavy metal ions and metalloid from the FA surface. Leaching yield of heavy metals is maximized up to the saturation point, which is above the CMC of the saponin isolated by both the method. In case of aqueous extraction the optimum concentration saponin was of 25 g/L, whereas in chemical
extraction it was of 12 g/L. The maximum metal leaching yield was resulted in the leaching time duration of 5 h at 70 °C at either of the saponin isolated approach. The influence of pH of the lixiviant appears to be less significant in enhancing the toxic element leaching yield. The highly acidic condition (low pH) of the solution for the saponin-bearing lixiviant during leaching was avoided to ensure alteration of the prop- erty of saponin. The utilization of *S. laurifolia* extracted by chemical or physical methods showed promising and consistent at the studied parametric variation condition. The change in morphological behavior comprising on the appearance of surface roughness over the surface of the fly ash phase in the residue sample as observed by SEM analysis ascertains and supports about substantial leaching of the metals from the FA phase with saponin.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] M. Basu, M. Pande, P.B.S. Bhadoria, S.C. Mahapatra, Potential fly-ash utilization in agriculture: a global review, Prog. Nat. Sci. 19 (2009) 1173–1186, https://doi.org/10.1016/j.pnsc.2008.12.006.

[2] D. Das, P. Kar, B.R. Das, R.K. Mohapatra, S.N. Das, P.K. Parhi, U. Behera, Natural dispersant in coal water slurry stabilization, in: Clean Coal Technol., Springer International Publishing, Cham, 2021, pp. 39–57, https://doi.org/10.1007/978-3-030-68502-7_2.

[3] H.P. Jambhulkar, S.M.S. Shaikh, M.S. Kumar, Fly ash toxicity, emerging issues and possible implications for its exploitation in agriculture; Indian scenario: a review, Chemosphere 213 (2018) 333–344, https://doi.org/10.1016/j.chemosphere.2018.09.045.

[4] A.K. Dan, D. Bhattacharjee, S. Ghosh, S.S. Behera, B.K. Bindhani, D. Das, P.K. Parhi, Prospective utilization of coal fly ash for making advanced materials, in: R. K. Jyothi, P.K. Parhi (Eds.), Clean Coal Technol., first ed., Springer, Cham, 2021, pp. 511–531, https://doi.org/10.1007/978-3-030-68502-7_20.

[5] D.B. Sarode, R.N. Jadhav, V.A. Khatik, S.T. Ingle, S.B. Attarde, Extraction and leaching of heavy metals from thermal power plant fly ash and its admixtures, Pol. J. Environ. Stud. 19 (2010) 1325–1330.

[6] M.H. Fulekar, Disposal of fly ash—an environmental problem, Int. J. Environ. Stud. 26 (1986) 191–215, https://doi.org/10.1080/00207238608710257.

[7] Z. Ma, X. Zhang, Y. Guo, F. Cheng, Extraction of valuable metals and preparation of mesoporous materials from circulating fluidized bed-derived fly ash via an acid-alkali-based alternate method, ACS Omega 5 (2020) 31295–31305, https://doi.org/10.1021/acsomega.0c04737.

[8] Y. Xu, Y. Chen, Leaching heavy metals in municipal solid waste incinerator fly ash with chelator/biosurfactant mixed solution, Waste Manag. Res. 33 (2015) 652–661, https://doi.org/10.1177/0734242X15592276.

[9] J. Xue, W. Wang, Q. Wang, S. Liu, J. Yang, T. Wui, Removal of heavy metals from municipal solid waste incineration (MSWI) fly ash by traditional and microwave acid extraction, J. Chem. Technol. Biotechnol. 85 (2010) 1268–1277, https://doi. org/10.1002/jctb.2426.

[10] R. Pöykiö, M. Mäkelä, G. Watkins, H. Nurmesniemi, O. Dahl, Heavy metals leaching in bottom ash and fly ash fractions from industrial-scale BFB-boiler for environmental risks assessment, Trans. Nonferrous Met. Soc. China (English Ed. 26 (2016) 256–264, https://doi.org/10.1016/S1003-6326(16)64112-2.

[11] M. Kuczajowska-Zadrozna, U. Filipkowska, T. Jóźwiak, Application of biosurfactants for heavy netals leaching from immobilized activated sludge, Arch. Environ. Protect. 41 (2015) 43–52, https://doi.org/10.1515/aep-2015-0006.

[12] D. Das, A.K. Sarangi, R.K. Mohapatra, P.K. Parhi, A. Mahal, R. Sahu, M. Kudrat-

E- Zahan, Aqueous extract of Shikakai; a green solvent for deoximation reaction: mechanistic approach from experimental to theoretical, J. Mol. Liq. 309 (2020) 113133, https://doi.org/10.1016/j.molliq.2020.113133.
[13] M. Schwarze, M. Groß, M. Moritz, G. Buchner, L. Kapitzki, L. Chiappisi, M. Gradzielski, Micellar enhanced ultrafiltration (MEUF) of metal cations with oleylethoxycarboxylate, J. Membr. Sci. 478 (2015) 140–147, https://doi.org/ 10.1016/j.memsci.2015.01.010.
[14] J. Huang, F. Yuan, G. Zeng, X. Li, Y. Gu, L. Shi, W. Liu, Y. Shi, Influence of pH on heavy metal speciation and removal from wastewater using micellar-enhanced ultrafiltration, Chemosphere 173 (2017) 199–206, https://doi.org/10.1016/j. chemosphere.2016.12.137.
[15] A. Routray, P.K. Senapati, M. Padhy, D. Das, Effect of mixture of natural and synthetic surfactant and particle size distribution for stabilized high-concentrated coal water slurry, Int. J. Coal Prep. Util. (2019) 1–16, https://doi.org/10.1080/ 19392699.2019.1592166, 0.
[16] A. Routray, P.K. Senapati, M. Padhy, D. Das, R.K. Mohapatra, Effect of mixture of a non-ionic and a cationic surfactant for preparation of stabilized high concentration coal water slurry, Int. J. Coal Prep. Util. (2019) 1–16, https://doi.org/10.1080/ 19392699.2019.1674843, 00.
[17] U. Behera, S.K. Das, D.P. Mishra, P.K. Parhi, D. Das, Sustainable transportation, leaching, stabilization, and disposal of fly ash using a mixture of natural surfactant and sodium silicate, ACS Omega (2021), https://doi.org/10.1021/ acsomega.1c03241.
[18] K.J. Hong, S. Tokunaga, T. Kajiuchi, Extraction of heavy metals from MSW incinerator fly ashes by chelating agents, J. Hazard Mater. 75 (2000) 57–73, https://doi.org/10.1016/S0304-3894(00)00171-0.
[19] D.L. Morar, A.H. Aydilek, E.A. Seagren, M.M. Demirkan, Leaching of metals from fly ash–amended permeable reactive barriers, J. Environ. Eng. 138 (2012) 815–825, https://doi.org/10.1061/(asce)ee.1943-7870.0000531.
[20] L. B, A.K. Dikshit, Behaviour of metals in coal fly ash ponds, APCBEE Procedia 1 (2012) 34–39, https://doi.org/10.1016/j.apcbee.2012.03.007.
[21] J.J. Sauer, C.H. Benson, A.H. Aydilek, T.B. Edil, Trace elements leaching from organic soils stabilized with high carbon fly ash, J. Geotech. Geoenviron. Eng. 138 (2012) 968–980, https://doi.org/10.1061/(asce)gt.1943-5606.0000653.
[22] C.R. Ward, D. French, L. Stephenson, K. Riley, Z. Li, Testing of interactions between coal ash leachates and rock materials for mine backfill evaluations, Coal Combust. Gasif. Prod. 2 (2010) 15–27, https://doi.org/10.4177/ccgp-d-09-00019.1.
[23] B. Prasad, K.K. Mondal, Heavy metals leaching in Indian fly ash, J. Environ. Sci. Eng. 50 (2008) 127–132.
[24] H. Elomaa, S. Seisko, J. Lehtola, M. Lundström, A study on selective leaching of heavy metals vs. iron from fly ash, J. Mater. Cycles Waste Manag. (2019), https:// doi.org/10.1007/s10163-019-00858-w, 0, 0.
[25] H. Ji, W. Huang, Z. Xing, J. Zuo, Z. Wang, K. Yang, Experimental study on removing heavy metals from the municipal solid waste incineration fly ash with the modified electrokinetic remediation device, Sci. Rep. 9 (2019) 1–9, https://doi.

org/10.1038/s41598-019-43844-w.
[26] F. Liu, J. Liu, Q. Yu, Y. Jin, Y. Nie, Leaching characteristics of heavy metals in municipal solid waste incinerator fly ash, J. Environ. Sci. Heal. - Part A Toxic/ Hazardous Subst. Environ. Eng. 40 (2005) 1975–1985, https://doi.org/10.1080/ 10934520500184707.
[27] B. Cetin, A.H. Aydilek, L. Li, Experimental and numerical analysis of metal leaching from fly ash-amended highway bases, Waste Manag. 32 (2012) 965–978, https:// doi.org/10.1016/j.wasman.2011.12.012.
[28] S. Bin-Shafique, C.H. Benson, T.B. Edil, K. Hwang, Leachate concentrations from water leach and column leach tests on fly ash-stabilized soils, Environ. Eng. Sci. 23 (2006) 53–67, https://doi.org/10.1089/ees.2006.23.53.
[29] R.K. Goswami, C. Mahanta, Leaching characteristics of residual lateritic soils stabilised with fly ash and lime for geotechnical applications, Waste Manag. 27 (2007) 466–481, https://doi.org/10.1016/j.wasman.2006.07.006.
[30] S. Mukhopadhyay, M.A. Hashim, J.N. Sahu, I. Yusoff, B. Sen Gupta, Comparison of a plant based natural surfactant with SDS for washing of As(V) from Fe rich soil, J. Environ. Sci. (China) 25 (2013) 2247–2256, https://doi.org/10.1016/S1001-0742(12)60295-2.
[31] D. Das, R.K. Mohapatra, P.K. Parhi, A.K. Sarangi, R. Sahu, S.R. Barik, Sustainable and efficient route for the regeneration of carbonyl compounds from oximes using aqueous extract of Sapindus laurifolia under microwave radiation, ACS Omega 5 (2020) 7716–7721, https://doi.org/10.1021/acsomega.0c00774.
[32] D. Das, S. Pattanaik, P.K. Parhi, R.K. Mohapatra, R.K. Jyothi, J.Y. Lee, H.I. Kim, Stabilization and rheological behavior of fly ash-water slurry using a natural dispersant in pipeline transportation, ACS Omega 4 (2019) 21604–21611, https:// doi.org/10.1021/acsomega.9b03477.
[33] A. Routray, D. Das, P.K. Parhi, M.K. Padhy, Characterization, stabilization, and study of mechanism of coal-water slurry using Sapindous Mukorossi as an additive, Energy Sources, Part A Recover, Util. Environ. Eff. 40 (2018) 2502–2509, https:// doi.org/10.1080/15567036.2018.1503755.
[34] R. Acharya, A. Lenka, K. Parida, Magnetite modified amino group based polymer nanocomposites towards efficient adsorptive detoxification of aqueous Cr (VI): a review, J. Mol. Liq. 337 (2021) 116487, https://doi.org/10.1016/j. molliq.2021.116487.
[35] S.K. Das, S. Mishra, D. Das, S.M. Mustakim, C.R. Kaze, P.K. Parhi, Characterization and utilization of coal ash for synthesis of building materials, in: R.K. Jyothi, P.
K. Parhi (Eds.), Clean Coal Technol., first ed., Springer, Cham, 2021, pp. 487–509, https://doi.org/10.1007/978-3-030-68502-7_19.
[36] Y. Zhang, B. Zhang, S. Yang, Z. Zhong, H. Zhou, X. Luo, Enhancing the leaching effect of an ion-absorbed rare earth ore by ameliorating the seepage effect with sodium dodecyl sulfate surfactant, Int. J. Min. Sci. Technol. (2021), https://doi. org/10.1016/j.ijmst.2021.06.002.
[37] L.D. Hansen, G.L. Fisher, Elemental distribution in coal fly ash particles, Environ.

Sci. Technol. 14 (1980) 1111–1117, https://doi.org/10.1021/es60169a015.

[38] P.K. Senapati, R. Mohapatra, G.K. Pani, B.K. Mishra, Studies on rheological and leaching characteristics of heavy metals through selective additive in high concentration ash slurry, J. Hazard Mater. 229–230 (2012) 390–397, https://doi.org/10.1016/j.jhazmat.2012.06.022.

[39] D. Pradhan, L.B. Sukla, M. Sawyer, P.K.S.M. Rahman, Recent bioreduction of hexavalent chromium in wastewater treatment: a review, J. Ind. Eng. Chem. 55 (2017) 1–20, https://doi.org/10.1016/j.jiec.2017.06.040.

[40] J. Tang, J. He, T. Liu, X. Xin, Removal of heavy metals with sequential sludge washing techniques using saponin: optimization conditions, kinetics, removal effectiveness, binding intensity, mobility and mechanism, RSC Adv. 7 (2017) 33385–33401, https://doi.org/10.1039/c7ra04284a.

[41] G.M. Al-Senani, F.F. Al-Fawzan, Adsorption study of heavy metal ions from aqueous solution by nanoparticle of wild herbs, Egypt, J. Aquat. Res. 44 (2018) 187–194, https://doi.org/10.1016/j.ejar.2018.07.006.

[42] D. Das, S. Panigrahi, P.K. Misra, A. Nayak, Effect of organized assemblies. Part 4. Formulation of highly concentrated coal-water slurry using a natural surfactant, Energy Fuels 22 (2008) 1865–1872, https://doi.org/10.1021/ef7006563.

[43] S. Mitra, S.R. Dungan, Micellar properties of quillaja saponin. 1. Effects of temperature, salt, and pH on solution properties, J. Agric. Food Chem. 45 (1997) 1587–1595, https://doi.org/10.1021/jf960349z.

[44] E.M. van der Merwe, C.L. Mathebula, L.C. Prinsloo, Characterization of the surface and physical properties of South African coal fly ash modified by sodium lauryl sulphate (SLS) for applications in PVC composites, Powder Technol. 266 (2014) 70–78, https://doi.org/10.1016/j.powtec.2014.06.008.