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Introduction

It is a known fact that coal constitute a considerable portion of the global fossil fuel reserve. A continued demand and supply of this resource generate vast quantities of spoil and low grade waste. Despite the discoveries of many microorganisms capable of lignite, lignin and humic acid breakdown, large scale bioremediation technologies for the bene ciation of low grade coal have unfortunately not yet been realized. Coal bio-solubilization technology has the potential to elevate low rank coal to either as a clean, cost-e ective energy feedstock or a source of complex aromatic compounds for bio-catalytic conversion to value-added products. In recent past, the application of biotechnology in monitoring and removing metal pollution has triggered tremendous interest. An alternative process is bio-sorption, which utilizes various materials of biological origin, such as bacteria, fungi, yeast, algae, etc. ey own metal-sequestering property and can be used to decrease the concentration of heavy metal ions from ppm to ppb level. It can e ectually and quickly sequester dissolved metal ions out of complex molecule and is ideal for the treatment of high volume and low concentration complex industrial waste [1,2]. Living microorganisms have the ability to accumulate on metal elements and is considered from the toxicological point of view. In the present decade, extensive research is being carried out on the bio-sorption phenomena, especially in the removal of metal ions [2-5]. Fungi are large and diverse groups of eukaryotic microorganisms, of which three groups have paramount importance: molds, yeast and mushrooms. Filamentous fungi and yeast are able to bind metallic elements and can a ect fermentation process. Fungi like Penicillium spp and A. niger are widely used for the elimination of heavy metal ions and radio-nuclides from aqueous solutions.A. niger is also ecologically important in biodegradation of toxic chemicals and bioconversion of waste water sludge. As it secretes carboxylic acids, A. niger can be used to bioleach metals from mining ores.

Organic acids may a ect mineral weathering rates by at least 3 mechanisms: by changing the dissolution rate far from equilibrium through decreasing solution pH or through forming complexes with cations at the mineral surface or a ecting the saturation state of the solution with respect to the mineral [5-10]. Under favourable conditions, the microorganism secretes organic acids which have the ability to degrade the coal minerals in an eco-friendly manner [11]. Use of mineral acids in demineralization not only modi es the surface morphology and deteriorates the carbon structure, but also reduces the calori c value. ese acids have strong oxidising power and the safe disposal of the spent liquid is a major environmental concern. For commercial utility of coal bio-demineralization, fungal leaching is an ideal eco-friendly method. But the secretion of carboxylic acid takes longer time with minimal output. In order to overcome such drawbacks, some mild organic leachants are applied directly for de-ashing coal. In this study, e ciency of organic acid such as gluconic acid on solubilizing silicate, aluminates and calcites mineral were discussed.

Materials and Methods

Sub-bituminous coal was air-dried and ground to the particle size <75 µm, of which 50 g was treated by employing carboxylic acids like gluconic acid (40%, 20%,10% and 5%) separately in a 500 ml te on beaker for 24 h at room temperature (27°C). e sample was recovered from the respective organic acid solution by ltration using a poly-propylene funnel. It was washed repeatedly in distilled water to remove the acid contents and nally dried in an oven at 80°C. e quanti cation of minerals in virgin and bioleached coal samples were carried out using a SEM (JEOL model JED-2300). e XRD pattern was recorded by a Bruker AXS D8 Advance X-ray powder di ractometer. Powdered samples were scanned from 4-70° in 2 range with 0.020°step intervals and 2 s/step counter time. e structural parameters are elucidated from the XRD analysis of the sample using the following equations (1-4)

 e aromaticity (fa) of coal (ratio of carbon atoms in aliphatic chain to aromatic rings)

$$f_a=A_{002}/ (A_{002}+A_{¢})$$

where A is the integrated under the respective peak

$$\text{Coal rank}=I_{26}/I_{20} \quad (2)$$

$$\text{Stacking height } L_c=0.89\lambda/B_c\cos\theta_c \quad (3)$$

where is the wavelength of X-ray used and Bc is half width of the (002) peak while θ_c is the scattering angle of (002) peak in radian.

e number of layers and average number carbon atoms per aromatic lamellae can be estimated by the formula

$$N=L_c+d_{002}/d_{002} \text{ and } n=0.32\,N^2 \quad (4)$$

Result and Discussion

e SEM-EDS analysis was performed on the virgin and gluconic acid solubilized products in order to monitor the change in mineral content and surface morphology. e micrographs (Figures 1-6) revealed coal structure is composed of homogeneously distributed network of small mineral crystallites. Many ssures, cleats, cracks and veins were also observed. e luminosity is due to the presence of aluminum, potassium and sodium, while the dark regions indicate chalcophiles [7-10]. Randomly distributed etch pits, layers, islands, hills and valleys could also be noticed,which might have resulted from the calcinations of dolomite and calcites or their assemblages, owing to thermal shock during metamorphism [9-12]. It is evident that, the solubilized coal contains large proportions of silicates, calcium carbonates and dolomite, as well astraces of aluminum and sulphur. e elemental composition quanti ed by EDS (Si-1.18 wt%; Al-0.95 wt% and Ca-0.18 wt%) indicated Si and Al as major minerals in the virgin sub-bituminous coal. e bright particles observed on the micrograph are due to bassanite and kaolinite. e SEM-EDS pro le of the coal sample treated with 40% gluconic acid.

Figure 2 showed that leaching caused changes in the morphology of coal (C=94.61 wt%, N=2.8 wt%, O=1.92 wt% Al=0.37 wt% and Si=0.31 wt%). With gluconic acid treatment, calcium minerals were removed with the formation of calcium gluconate.

$$2\,(C_6H_{12}O_7)\ \ (C_{12}H_{22}O_{14})^{2-} + 2\,H^+$$

$$C_{12}H_{22}O_{14} + Ca^{2+}\ \ C_{22}H_{22}CaO_{14}\text{(Calcium gluconate)}$$

e experiments performed using various concentration of carboxylic acids and the results of SEM-EDS analysis is presented in Table 1.

e content of carbon is increased signi cantly above 93.% in all the cases. e mineral content shows a systematic decrease with increase in concentration. A drastic reduction in the nitrogen and oxygen content with increase in concentration of the leachant was noticed. is implies that there is no oxidation happened to the coal matrix during leaching. e silicate content is changed from 1.10 wt% to 0.30 wt%. whil e the aluminates reduced to 0.27 wt% with leaching.

e gluconic acid treated sample (40%) is further treated with hydro uoric acid (10%) to demineralize the bound minerals. e analysis con rmed total removal of aluminates and silicates with the formation of uro-silicates and aluminates. e oxygen and nitrogen content is totally eliminated along with minerals.

e SEM-EDS analysis of the coal sample treated with gluconic acid and HF is presented in Figure 6. e micrograph shows the morphology of nano-graphene layers. e EDS analysis of the surface indicates only carbon in the form of akes.

e X-ray di ractograms of pure graphite and bioleached samples are depicted in Figures 7-12. e study on X-ray scattering from coal has paramount importance, as it enables quanti cation of low and high temperature ash making mineral. e di raction pro les were recorded using a BRUKER D8 advance powder di ractometer (XRD) with nickel ltered CuK radiation (=1.5406 Å). e patterns were examined over the 2-theta range of 5-90 , with a scan step of 0.02 . e peaks observed at 12.4, 20.5 and 33.3 are assigned to kaolinite ($Al_2Si_2O_5(OH)_4$), while, that at 29.3 is because of the presence of dolomite in the samples [9-15]. Except for the intense sharp spikes corresponding to inorganic components such as kaolinite, pyrite, quartz, crystoballite and mullite, the strong di raction maxima at 25.8 is due to crystalline carbon in coal samples. e weak peak at 43° is ascribed to (101) plane re ection of graphite [9,15]. is is due to the random layer lattice structure of crystallites in coal [12-15]. e pro les exhibited strong di raction peaks, suggesting the crystallinity of Indian coals.

e X-ray di raction pro les for demineralized coal samples (Figures 7-12) exhibited intense background, con rming highly disordered amorphous carbon. e X-ray spectrum is deconvoluted by origin pro 2015 so ware to identify the di erent type of carbon

Figure 1: SEM-EDS analysis of sub-bituminous coal (GX).

Figure 2: SEM-EDS analysis of sub-bituminous coal leached with gluconic acid (40%).

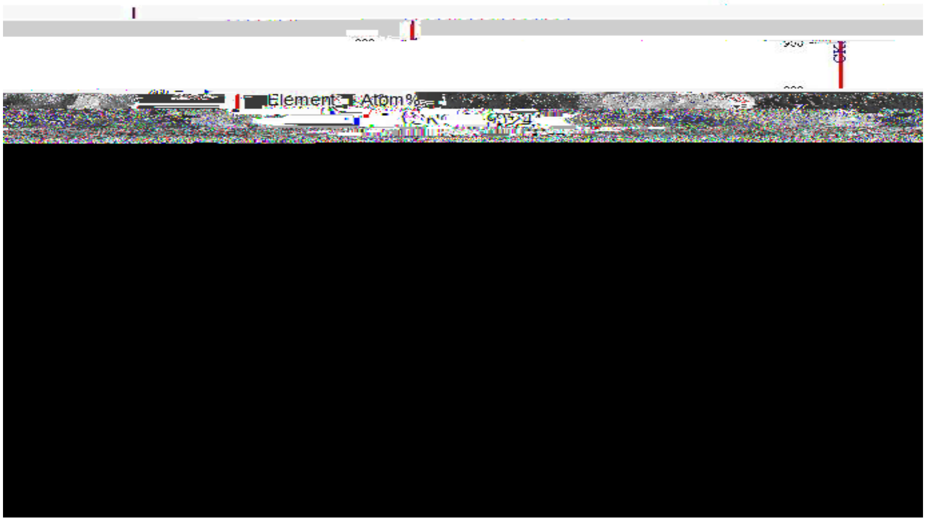

Figure 3: SEM-EDS analysis of sub-bituminous coal leached with gluconic acid (30%).

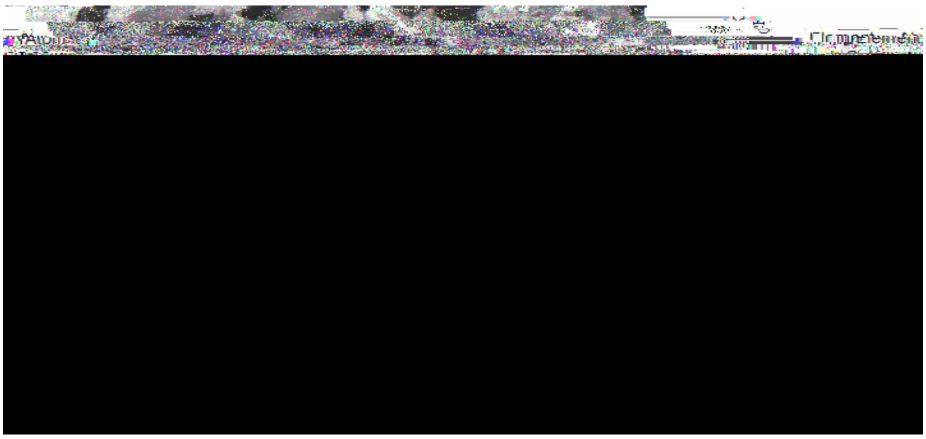

Figure 4: SEM-EDS analysis of sub-bituminous coal leached with gluconic acid (20%).

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aromatic layers and average number of carbon atoms per aromatic lamellae is also found to vary between 6-7 and 11-17 respectively. e values of stacking parameters are in very close agreement to that of HF leached coal sample.

Conclusions

Coal biodegradation is a naturally complex process, which appears to be driven by extracellular enzymes in the presence of various chelators released by di erent fungi. Despite slow conversion rates in the biological breakdown of coal, optimization of the process on a large scale develop the technology for remediation of low rank coals. e calcites mineral content in coal samples was completely removed by leaching with gluconic acid. e intensity ratio (I_{26}/I_{20}), a measure of disorder in amorphous carbon, was found to be 1.80 and 1.82 when leached with gluconic acid of concentration 20% and 40% respectively. e lateral size along the c-axis (L_c) was varied from 2.06 to 1.90 nm as the concentration of gluconic acid varied from 10% to 40%. Gluconic acid (40% and 30%) was able to remove minerals e ciently, than other concentration as is evident from the XRD studies and EDS analysis. e interlayer spacing of sample leached with 10, 20 and 40% gluconic acid leached sample were found to be 0.344 nm, which is near to that of ordered graphite (0.335 nm). It is conclude that with mild leachant like gluconic acid, there is ordering of the stacking parameters of amorphous carbon in coal. ere is a systematic elimination of mineral content in the coal matrix with optimum removal during the combined leaching of mineral acid and gluconic acid.

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