CHAPTER-2

MATERIALS AND METHODOLOGY

2.1 Materials

To enhance the mechanical and hydraulic characteristics of bauxite residue and coal mine overburden waste, biopolymer treatment at different concentration and curing period, were used and have been discussed in subsequent subsections.

2.1.1 Bauxite residue

Bauxite residue (Red mud tailing) is an industrial by-product from aluminium industries which is produced during the extraction of alumina from the bauxite ore. About 120 million tons of red mud is discharged globally every year. Around 25–45% of the processed bauxite ore is disposed of in the form of slurry in storage pond consisting of 70 to 90% mud and rest as sand, or as a stack of dry mud near industrial plants, or directly disposed into a nearby sea which raises several environmental and safety concerns [52-53]. In the present study, bauxite residue was collected from an impoundment at Hindalco Industries Ltd., Renukoot, India. The engineering properties were evaluated following American Society for Testing and Materials (ASTM) standards and are presented in Table 2.1. According to the Unified Soil Classification System, bauxite residue, reddish in color, is classified as clayey silts of low plasticity. The chemical composition is shown in Table 2.2.

Table 2.1. Engineering properties of Bauxite residue

Parameters	Bauxite residue
Sand size particles (%)	32.9
Silt size particles (%)	51.6
Clay size particles (%)	15.5
Uniformity coefficient, c_u	50
Coefficient of curvature, c_c	0.53
Average particle size, D_{50}	0.038
Liquid Limit (%)	34.2
Plastic Limit (%)	42.8
Minimum void ratio, e_{min}	0.54
Unified Soil Classification System (USCS)	ML
Maximum dry density, MDD (Mg/m^3)	1.755
Optimum moisture content, OMC (%)	26.75
Specific Gravity	2.72

Table 2.2. Chemical composition of Bauxite residue

Chemical Composition	Bauxite residue (%)
Al_2O_3	31.11
SiO_2	25.78
Fe_2O_3	24.96

TiO_2	7.31
Na_2O	6.41
CaO	0.39
MgO	0.10
K_2O	0.06
P_2O_5	0.34
SO_3	0.23

2.1.2 Coal mine overburden waste (CMO)

Most of the coal production in India comes from open cast mines contributing over 81% of the total production. A large number of open cast mines of over 10 million tons per annum capacity are in operation. Mining activities, particularly opencast mining in huge forest areas, result in loss of biodiversity, nutrient qualities, and microbial activities of the soil system. Opencast mining releases considerable mining wastes to the upper part of the land surface as overburden dump materials [54]. Coal mine overburden waste (CMO) was collected from the mining power plant of Hindalco Industries, Renusagar, Uttar Pradesh, India. The grain-size distribution of the CMO dump showed the presence of 83-96% sand, 12-8% silt, and 3-6% clay-sized particles. The engineering and chemical properties of CMO have been summarized in Table 2.3. According to the Unified Soil Classification System (USCS), it is classified as SM (sand with silt).

Table 2.3. Physical and Chemical properties of Coal mine overburden waste

Parameters	Values	Chemical composition	Values (%)
Sand size particles (%)	83.96	SiO_2	60.23
Silt size particles (%)	12.8	Al_2O_3	18.92
Clay size particles (%)	3.6	Fe_2O_3	2.51
Uniformity coefficient, c_u	41.11	MnO	0.04
Coefficient of curvature, c_c	14.53	MgO	1.96
Average particle size, D_{50} (mm)	0.331	CaO	3.24
Liquid Limit (%)	-	Na_2O	1.70
Plastic Limit (%)	-	K_2O	1.07
Minimum void ratio, e_{min}	0.31	TiO_2	0.73
Unified Soil Classification System (USCS)	SM	P_2O_5	0.12
Maximum dry density, MDD (Mg/m^3)	1.909	Others	1.98
Optimum moisture content, OMC (%)	26.75		
Specific Gravity	2.72		

2.1.3 Biopolymer

The two microbial biopolymers (natural, anionic polysaccharide) employed in the current study are xanthan gum ($C_{35}H_{49}O_{29}$) and guar gum ($C_{10}H_{14}N_5Na_2O_{12}P_3$), bought locally in Varanasi (India). The physical properties of biopolymer are shown in Table 2.4.

2.1.3.1 Xanthan gum

Xanthan gum ($C_{35}H_{49}O_{29}$) is a polysaccharide produced by aerobic fermentation of sugar of the bacterial species *Xanthomonas campestris*, comprising two glucose, two mannoses, and one glucuronic acid unit that primarily forms helical structures (Figure 2.1). Xanthan gum solution structure is either a helix or random coil shape, depending on dissolution temperature and salt level [55, 56]. It is considered widely in civil engineering because of its high stability in a wide range of temperatures, pH, and electrolyte concentrations. Xanthan gum has been regularly utilized in the food industry due to its temperature stability, compatibility with food ingredients, and pseudoplastic rheological characteristics. Moreover, xanthan gum is also practiced as a gelling and suspending agent (flocculant) for viscosity control in the oil industry [57].
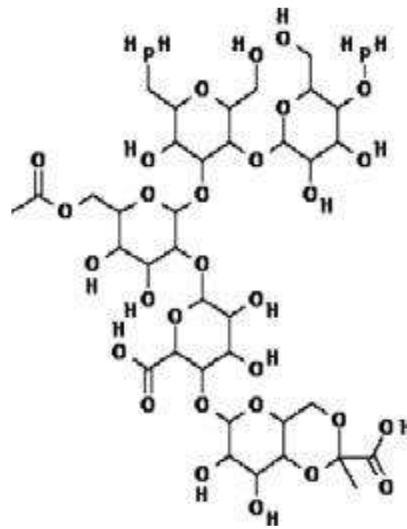

Figure 2.1 Structure of Xanthan gum ($C_{35}H_{49}O_{29}$) [58]

2.1.3.2 Guar gum

Guar gum ($C_{10}H_{14}N_5Na_2O_{12}P_3$) is a neutrally charged polysaccharide extracted from the plant's seeds, called Guar or Cluster bean (Cyamopsis tetragonolobus or C. psoraloides). Its structure consists of a 1,4-linked β-D-mannopyranose backbone with random branch points of α-D-

galactose units (Figure 2.2). Guar shows high stability with temperature variations, yielding highly viscous solutions even at low concentrations. They show the ability to hydrate rapidly in a cold water system and produces highly viscous solution even at low concentration. Guar gum has been widely used in food products as a stabilizer, emulsifier, or thickener [59, 60]. It is used in an amount smaller than 1% of the food weight as a food additive. In industrial applications, guar gum is used as a flocculant, foam stabilizer, filtration aid, water treatment agent, and additive for pharmaceutical drugs [61].
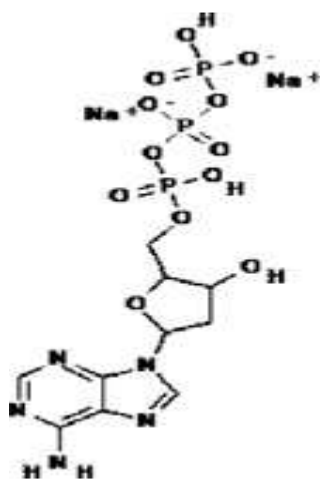

Figure 2.2 Structure of Guar gum [58]

Table 2.4 Physical properties of biopolymer

Biopolymer type	Physical state	Charge	Color	pH	Ash content (%)	Viscosity (cps)
Xanthan gum	Powder form	anionic	Creamish white	7.04	8.5	6550
Guar gum	Powder form	Non-ionic	Yellow white	6.4	0.6	1605

2.2 Testing Methodology

A number of laboratory experiments have been performed to study strength (Triaxial compression test and Unconfined compressive test), permeability (Falling head permeability test, colorimeter analysis), durability (Freezing and thawing analysis), Mineralogical and morphological (X-ray diffraction and Scanning electron microscopy) on bauxite residue and coal mine overburden waste stabilized with xanthan and guar gum following different procedures. Bauxite residue and CMO were collected from the site, dried in an oven for 24 h at 10 5°C, and cylindrical samples were prepared for the unconsolidated-undrained triaxial test (UU) (ASTM D 2850, 2015) and unconfined compression test (ASTM D2166-06, 2006). Firstly, the compaction test was conducted following ASTM D698 (2012) standard at a varying concentration of each biopolymer (m_b / m_w = 0, 0.25, 0.5, 1, and 1.5%) to evaluate their compaction characteristics (MDD and OMC). Then, several identical cylindrical samples were prepared by compacting at OMC to achieve the targeted MDD. For this, the biopolymer solution was prepared by blending the required amount of powder with water at different (m_b / m_w) ratios. For example, to make a biopolymer solution at a ratio of m_b /m_w = 1%, m_b = 1 g of biopolymer powder was

mixed in m_w = 100 g of water. Then, the biopolymer solution at varying concentrations was blended with oven-dried bauxite residue or CMO.

2.3 Detailed description of Testing Methodologies

All the laboratory test were performed as per testing methods described in the relevant ASTM standards. The standards adopted for testing are mentioned in Table 2.5.

Table 2.5 Relevant Standard for Laboratory Testing

Test conducted	Standard adopted
Particle size distribution (Sieve analysis)	ASTM D6913-04 [62]
Particle size distribution (Hydrometer analysis)	ASTM D422-63 [63]
Consistency limits	ASTM D4318-10 [64]
Soil classification	ASTM D2487-11 [65]
Specific gravity	ASTM D854-10 [66]
Compaction	ASTM D698-12 [67]
Falling head permeability	ASTM D5084-03 [68]
Triaxial Compression test	ASTM D2850-03 [69]
Unconfined Compressive strength	ASTM D2166-13 [70]
Freezing and thawing	ASTM D560M-15 [71]

2.3.1 Specific Gravity

The specific gravity of bauxite residue and coal mine overburden waste was evaluated with the help of a density bottle of 50 ml capacity provided with a stopper having a capillary hole.

Firstly, the weight of the empty density bottle with stopper (W_1) is recorded. About 20 g of oven-dried sample is cooled and transferred to the density bottle, and the weight of bottle along with sample and stopper is measured as W_2. Then the density bottle having the sample inside it is filled with water, and the sample is weighed (W_3). Then the bottle is emptied and cleaned, and filled with water to find weight W_4. The process is repeated 2 to 3 times to measure the average reading of it. Specific gravity is calculated by the formula:

$$G = \frac{W_2 - W_1}{(W_2 - W_1) - (W_3 - W_4)}$$

Where,

W_1= Weight of density bottle in g;

W_2= Weight of density bottle + dry soil in g;

W_3= Weight of bottle + dry soil + water in g;

W_4= Weight of bottle + water in g.

The specific gravity values should be reported at 27 °C. If the room temperature is different than 27 °C, then the corrected specific gravity at 27 °C = K (Specific gravity at room temperature).

$$G' = KG$$

Where G' = Corrected specific gravity at 27 °C

2.3.2 Grain size distribution

2.3.2.1 Sieve analysis

The test is carried out with the utilization of a set of sieves with different mesh sizes. Each sieve has square-shaped openings of a specific size. The sieve separates larger from smaller particles, distributing the soil sample in 2 quantities. The grains with diameters larger than the size of the openings are retained by the sieve, while smaller diameter grains pass through the sieve. The test is conducted by placing a series of sieves with progressively smaller mesh sizes on top of each other and passing the soil sample through the stacked sieve "tower". Therefore, the material particles are distributed as they are retained by the different sieves. A pan is also used to collect those particles that pass through the last sieve (No. 200). Finally, the particle size distribution curve with percentage finer as the ordinate and the particle diameter as the abscissa is being plotted.

Table 2.6 Sieves utilized in the Grain Size Analysis test

Sieve #	Opening Diameter (mm)
4	4.75
10	2
20	0.85
40	0.425
60	0.25
100	0.15
140	0.105
200	0.075

2.3.2.2 Hydrometer analysis

Hydrometer analysis is a measurement method carried out to determine the grain size of the sample because the significant amount of particle sizes of both wastes are less than approximately 0.75 mm in diameter. A hydrometer is placed in a container filled with a water and material mixture, and measurements are taken over time to perform the test. When performing a hydrometer analysis, the first step is to take the sample and mix it into a slurry with the dispersing agent. Then, the slurry is placed into a graduated cylinder, and water is added until the combination reaches a specified volume. Next, a hydrometer is placed into the graduated cylinder to measure and compute the particle size and percentage finer to get the particle size distribution.

2.3.3 Consistency limit

Soil consistency is the strength with which soil materials are held together or the resistance of soils to deformation and rupture. Consistency limits, namely liquid limit and plastic limit were determined following ASTM D4318-10 standards.

2.3.3.1 Liquid limit

The liquid limit is the moisture content at which the groove, formed by a standard tool, designed by Casagrande, into the sample of material taken in the standard cup, closes for 10 mm on being given 25 blows in a standard manner. The bauxite sample finer than 425µ sieve was thoroughly blended with distilled water to form a homogenous paste on a flat glass plate. The paste is placed in the brass cup of Casagrande apparatus, and a groove is cut with a standard grooving tool. The rotation rate of the handle is kept constant, i.e., about two revolution per second and the number

of blows are counted until the bottom of the groove cut meet along a 12 mm length due to flow not by slide. About 10 g of bauxite residue from near the closed groove is taken for water content determination. This process is repeated at different water content. After taking measurements, the flow curve is drawn on a semi-logarithmic graph representing water content on the arithmetical scale and the number of drops on the logarithmic scale. The flow curve is a straight line drawn as nearly as possible through the four or more plotted points. The moisture content corresponding to 25 drops as read from the flow curve and reported as the liquid limit of the soil.

2.3.3.2 Plastic limit

The plastic limit of a material is the moisture content, expressed as a percentage of the weight of the oven-dried material, at the boundary between the plastic and semi-solid states of consistency. It is the moisture content at which a material will just begin to crumble when rolled into a thread ⅛ inch (3 mm) in diameter using a ground glass plate or other acceptable surface. The plastic limit of a bauxite residue was determined by taking 20 g of thoroughly mixed portion of the material passing through 425 micron sieve. Mix it with distilled water till the bauxite residue mass becomes plastic enough to be easily molded with fingers. Take about 8 g of this plastic soil mass and roll it between fingers and glass plate with just sufficient pressure to roll the mass into a thread of uniform diameter up to 3 mm throughout its length. This process continues until the thread crumbles when the diameter is 3 mm. The crumbled thread are kept in air tight container for moisture content determination. The test is repeated to at least 3 times and the average of the results are calculated to determine plastic limit.

2.3.4 Compaction

Compaction is the process of densification of soil/waste by reducing air voids. The degree of compaction of a given material is measured in terms of its dry density. The dry density is maximum at the optimum water content. Firstly, oven-dried sample, approximately 5 kg in the given pan is thoroughly mixed with sufficient water to dampen it with approximate water content of 4-6 %. Afterward, blend is compacted in the Proctor mold and compacted it in 3 layers giving 25 blows per layer with the 2.5 kg rammer falling through. After compaction, the sample is removed from the mold, and its bulk unit weight is recorded, moisture content determined and resultant dry unit weight is calculated.

2.3.5 Permeability Test

Following ASTM D5084-03, the coefficient of permeability of bauxite residue and coal mine overburden waste was determined by falling head and constant head permeability, respectively. Firstly, the material was compacted at its OMC and MDD in three layers in the standard mold for falling head permeability. Afterward, the compacted material was kept for saturation, and then a standpipe of the standard cross-sectional area is fixed over the permeameter, and water is permitted to run down. The bottom outlet shall be opened, and the time interval required for the water level to fall from a known initial head to a known final head as measured above the center of the outlet shall be recorded. The stand-pipe shall be refilled with water, and the test repeated till three successive observations give nearly the same time interval.

$$K = \frac{2.303aL}{At} \ (\log\frac{h_1}{h_2})$$

Where,

a= cross-sectional area of standpipe

L= length of sample column

A= area of the sample column

T= time required for head drop

h_1= initial head; and

h_2= final head

Constant Head Method: According to Darcy's law, the total quantity of flow Q in time t can be stated as:

$$Q = qt = k\, i\, A\, t$$

Where A is the area of the specimen cross section. The hydraulic gradient is equal to h/L (L is the length of the specimen), and therefore:

$$K = \frac{Ql}{hAt}$$

2.3.6 Strength study

The strength characteristics, namely triaxial compressive strength and unconfined compressive strength, were performed on bauxite residue and coal mine overburden waste samples as per ASTM D2850-03 and ASTM D2166-13 respectively.

2.3.6.1 Triaxial compressive test

The triaxial test is used to determine the shear strength of soil/waste under drained or undrained conditions. In this test, a material specimen approximately 3.8 cm in diameter and

7.6 cm in length is enclosed in a thin rubber membrane and placed inside a cylindrical plastic chamber filled with water or air and is subjected to a confining pressure σ_3 by application of pressure to the water. The porous stone is connected to the lower and upper cap for the drainage system, which allows the sample to saturate or drain. The specimen in the chamber is then subjected to a confining pressure σ_3 by applying pressure to the fluid (air). Axial stress $\sigma 1$ is applied through a vertical ram. The difference between σ_1 and σ_3 is termed as deviatoric stress $\Delta\sigma$.

2.3.6.2 Unconfined compressive strength

The unconfined compressive strength (σ_u) is the maximum load per unit average cross-sectional area at which the cylindrical specimen of materials falls in compression. The UCS test was performed on biopolymer stabilized bauxite residue and coal mine overburden waste following relevant standards. The samples were prepared in a mold with an aspect ratio of 2, i.e., 38 mm in diameter and 76 mm in height, with a strain rate of 1.25 mm/min for testing.

2.3.6.3 Sample preparation for the strength test

Bauxite residue and coal mine overburden waste was oven-dried and cylindrical samples were prepared for the unconsolidated-undrained triaxial test ((UU)) (ASTM D 2850, 2015) and unconfined compression test (ASTM D2166-06, 2006). Firstly, the compaction test was conducted, following ASTM D698 (2012) standards, at a varying concentration of each biopolymer ($m_b/m_w = 0$, 0.25, 0.5, 1, and 1.5%), to evaluate their compaction characteristics (MDD and OMC). Then, several identical cylindrical samples were prepared by compacting the blend in three layers in the cylindrical mold at OMC to achieve the targeted MDD. For

this, the biopolymer solution was prepared by blending the required amount of powder with water at different (m_b/m_w) ratios. For example, to make a biopolymer solution at a ratio of m_b/m_w = 1%, m_b = 1 g of biopolymer powder was mixed in m_w = 100 g of water. Then, the biopolymer solution at varying concentrations was blended with oven-dried materials. The prepared samples of bauxite residue were stored in a sealed plastic bag (to minimize moisture loss from evaporation) and cured in a desiccator for 7, 14, and 28 days for the triaxial test (UU). The standard deviation in the strength of three individual samples, molded at the same moisture content, would not vary by more than 10% from their mean strength, which is considered as a test result.

2.3.7 Durability study

This study investigates the durability and degree of hardness of biopolymer stabilized bauxite residue by performing a freezing and thawing (F-T) test.

2.3.7.1 Freezing-thawing (F-T)

The freezing and thawing cycles have been performed in closed-system freezing. The closed system is referred to as a freezing process, where there is no water source during the freezing phase except which is initially present in the pores [72]. This freezing system relates to soil conditions where no significant changes are expected in the in situ moisture content between winters and summer periods [73].

Following the ASTM D560M-15 standard, the F-T resistance of the untreated and stabilized biopolymer bauxite residue samples were tested. The cured samples were frozen in a deep freezer (Figure 2.3) at -20 °C for 24 h to achieve a complete frost penetration and then

allowed to thaw at room temperature (25 ± 5 ℃) for another 24 h (Figure 2.4). The previous studies suggest that the temperature range close to 0 ℃ can cause partial freezing or no freezing in specimens because of incomplete frost penetrations (74-76). Thus, these temperature ranges were mainly selected to obtain complete frost dispersion (i.e., at -20 ℃) and complete thaw weakening (i.e., at 25 ℃). All the cured specimens were subjected to 0, 1, 3, 5, 8, and 10 F-T cycles before testing for compression strength.

Figure 2.3 Deep freezer for durability study (F-T cycles)

(a)   (b)

Figure 2.4 Biopolymer stabilized bauxite residue samples after curing for 28 days: (a) Without F-T cycles, and (b) after F-T cycles for thawing

2.3.8 Mineralogical and morphological analysis

The mineralogical and morphological changes of the biopolymer stabilized bauxite residue were examined using X-ray diffraction (XRD) test and scanning electron microscope (SEM).

2.3.8.1 X-Ray diffraction

X-Ray diffraction analysis is the identification of materials based on their diffraction pattern. As well as phase identification, XRD also yields information on how the actual structure deviates from the ideal one, owing to internal stresses and defects. In the present study, X-ray diffraction (XRD) on bauxite residue samples was performed on the MiniFlex X-ray diffractometer from Rigaku.

Figure 2.5 A photograph of high resolution X-Ray diffractometer (Rigaku Miniflex 600, Germany)

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda = 2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each

mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

2.3.8.2 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a test process that scans a sample with an electron beam to produce a magnified image for analysis. The method is also known as SEM analysis and is used very effectively in microanalysis and failure analysis of solid inorganic materials. Electron microscopy is performed at high magnifications, generates high-resolution images, and precisely measures microscopic features and objects. The sample collected after performing strength test were used for SEM analysis. The imaging was performed using a ZEISS EVO 18 SEM from ZEISS Microscopy at different magnifications.

Figure 2.6 A photograph of high-resolution scanning electron microscope (SUPRA 40, Zeiss 4.0)