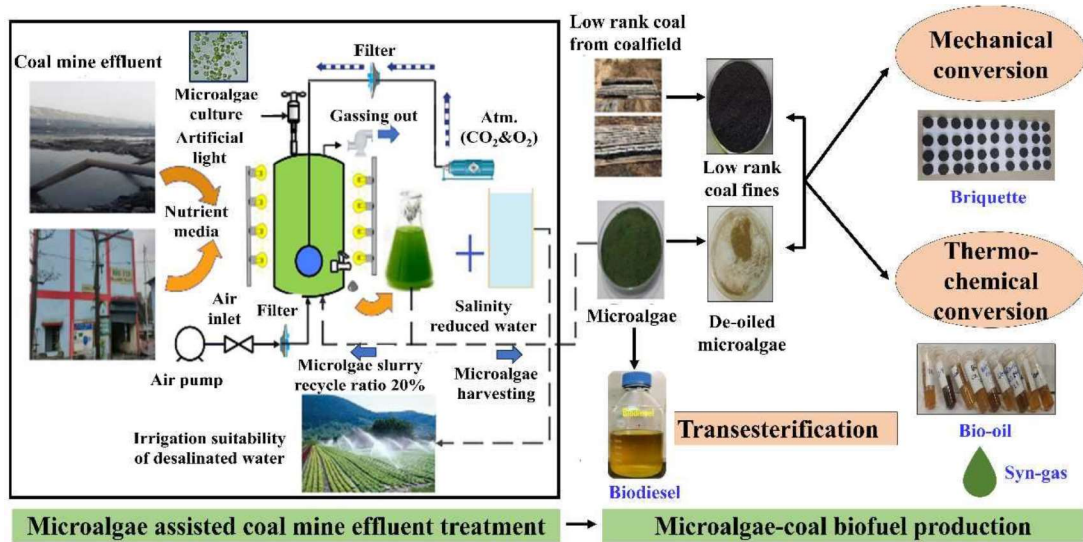


CHAPTER 2

Review of literature on coal mine effluent treatment, resource utilization and fuel production using microalgae platform*



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Abstract

Coal excavation is highly associated with the discharge of substantial amount of mine water contaminated with high levels of metal ions, salt ions, oil and grease, resulting long standing negative environmental impact upon marine ecosystems. Opencast and underground mining activities are interrelated with ecological deterioration and pollution of nearby rivers in coal mine sites. Addressing this issue, present chapter elaborates biological methods, specifically microalgae associated methods to treat coal mine effluent (CME). The perspective of microalgae cultivation in CME along with desalination and heavy metal removal mechanism are discussed in detail. Considering circular water economy approach, coal mine water treatment is further coupled with resource recovery and biofuel production. Further, transesterification is discussed in the direction of biodiesel production from CME cultivated microalgae biomass. Following lipid extraction of microalgae biomass, de-oiled microalgae is highlighted as potential feedstock for biofuel production. In this direction, mechanical and thermochemical conversions are discussed to formulate solid, liquid, and gas fuel using de-oiled microalgae feedstock. Mechanical conversion in the form of densification or agglomeration is discussed, along with different process strategies for formulating different de-oiled microalgae blended coal composites. In thermochemical conversion processes, co-pyrolysis with hydrothermal liquefaction and gasification are considered potential processes for producing bio-oil, biochar, and gas using feedstock of low-rank coal and de-oiled microalgae biomass. At the end, present chapter identifies subsequent research gaps in the area of microalgae assisted CME treatment and biofuel production.

2.1 Background

Coal is considered the most abundant and significant fossil fuel in global energy production. Excessive coal mining activities may be associated positively with the world's economy but possess negative environmental impact associated with discharge of substantial wastewater volumes, resulting in ecological deterioration and pollution that is costly and challenging to manage (Mosai et al., 2024). The metal dispersion by mining activities is responsible for high levels of heavy metals (Cd^{2+} , Pb^{2+} and Cr^{2+}), cations (Na^+ , Mg^{2+} , Ca^{2+} and K^+), anions (HCO_3^- , CO_3^{2-} , Cl^- , F^- and NO_3^-), oil and grease resulting long standing negative environment impact (Mansilha et al., 2021). Coal mining is the major contributor in acid mine drainage (AMD), wherein sulfide rich waste is exposed to the environment and has very low pH due to sulfuric acid formation along with high concentrations of elements (i.e., Al, Fe and Mn) as reported in the literature (Park et al., 2019; Mosai et al., 2024; Wu et al., 2022). Coal excavation is possible through opencast or underground mining and both (more specifically, opencast mining) pollute water bodies with metal contamination in the worst way. Besides active mines, closed mines highly contribute to water pollution due to a series of unmanaged issues, i.e., (i) mine sumps filling with water, (ii) leachate formation, (iii) mine sludge generation interlinked to the surface and groundwater pollution (Mosai et al., 2024; Xia et al., 2023). The global representation of closed/ abandoned mines, including physicochemical characteristics, is given in Table 2.1. Globally, about 20,000 abandoned mines exist, which cause polluted water drainage (Rezaie and Anderson, 2020; Mohan and Chander, 2006). According to the U.S. Energy Information Administration, there has been an 18% decline in existing coal mines annually since 2019 (EIA, 2020). Inactive coal mines still cause ecological deterioration and pollution to nearby rivers, leading to serious health effects (Yang et al., 2019).

Table 2.1 Physicochemical characteristics and heavy metal concentration of water discharged from some representative coal mines in different countries.

Country	Coal mine status	Representative mine	pH	EC (mS cm ⁻¹)	Heavy metal concentration* (mg L ⁻¹)				References
					Cu	Cr	Fe	Pb	
India	Active	Makum, Assam	2.3 – 8.37	6.36	1.38	0.126	255.6	0.42	Equeenuddin et al., 2010
India	Active	Sukinda, Odisha	5.4-7.20	0.009	ND	3.12	1.69	ND	Das et al., 2013
India	Active	North Karanpura,	7.64	ND	0.002	0.002	1.30	ND	Bharat et al., 2024
India	Active	Ib coalfield, Odisha	6.0	ND	0.026	0.009	0.78	0.004	Bharat et al., 2024
Bangladesh	Active	Barapukuria, Northwestern Bangladesh	6.0 – 7.7	0.38	ND	ND	17.2	ND	Bhuiyan et al., 2010
South Korea	Abandoned	Ilwal	2.3 – 3.4	0.83	ND	ND	1.5	ND	Kim, 2009
China	Active	Shendong Daliuta, Shaanxi Province	7.0 – 8.2	1.78	0.020	0.019	3.22	0.019	Zhang et al., 2024
China	Abandoned	Yudong river basin, Kaili, Guizhou Province	< 3.07 – 8.37	ND	0.017	0.098	752.95	ND	Li et al., 2021
China	Abandoned	Xingren, Southwestern China	2.7 – 8.4	4.01	0.315	ND	740	ND	Zhao et al., 2007
Nigeria	Active	Maiganga, Gombe	< 2	ND	1.02	0.03	ND	0.05	Aluwong et al., 2024
Brazil	Active	Laranjinha river, southern Brazil	2.94 – 6.04	4.26	ND	ND	2824.00	ND	Galhardi and Bonotto, 2016
South Africa	Abandoned	Mpumalanga	2.0	0.6	ND	ND	8000	ND	Masindi et al., 2017
South Africa	Active	Navigation	2.0	0.015	0.47	0.23	4219.14	ND	Alegbe et al., 2019
USA	Abandoned	Pittsburgh Coal seam, Uniontown Syncline	6.2	NA	ND	ND	26.3	ND	Lambert et al., 2004

EC: Electric conductivity; ND: Not detected; *Maximum observed value.

2.2 Methods to treat coal mine effluent

Coal mine water treatment is crucial to ensure the availability and sustainable management of safe water for all human beings by 2030. In this direction, conventional strategies such as membrane-based and thermal-based technologies require a continuous supply of energy and chemicals, as well as expensive maintenance, high labor costs, and long-term monitoring (described in previous section 1.1). In comparison, biological treatment techniques are economically viable and more effective in minimizing the negative environmental impacts of water bodies and ecosystem interaction (Chartrand and Bunce, 2003).

2.2.1 Biological methods to treat coal mine effluent

Microorganisms-based bioremediation plays a crucial role in low-cost effluent treatment with minimum environmental impact. Recently, several studies have paid greater attention to the mining water/ metal-contaminated water treatment and remediation (Yu et al., 2021; Li et al., 2023). Potential sulfidogenic bacteria, i.e., *Desulfurobacterium*, *Pyrococcus*, *Ammonifex*, *Desulfurella*, *Pseudomonas* and *Thermosulfurimonas*, are able to grow in water reservoirs with the presence of toxic heavy metal ions, broad pH range (1 to 11) and temperature range (−2 to 110 °C) (Florentino et al., 2020). These sulfidogenic bacteria play critical roles in the bioremediation of metal-contaminated water via their dissimilatory sulfate and/or sulfur reduction metabolism. When sulfate acts as the electron acceptor, sulfate first reduces to sulfite and then converts to sulfide (Zeng et al., 2020). The surface interactions between metal ions and sulfidogenic bacteria include surface adsorption, intracellular absorption, insoluble precipitates formation and extracellular organic complexation (Li et al., 2023). Biological methods are economical, efficient, and environmentally friendly, which are directly affected by the mine's effluent properties and operating parameters. These methods mostly apply to running and abandoned mine water

(Xia et al., 2023). Salinity hazards and heavy metal contamination may be considered two major concerns in CME.

Towards metal bioremediation, *Phragmites australis* and *Typha orientalis* are reported to show the best adsorption performance for Zn and Mn in the Yangquan Mine discharge in Shanxi Province (Wu et al., 2023). Mostly, the heavy metal absorption ability of specific bacteria lies in the range of 1 to 500 mg g⁻¹ (Roy et al., 2024). Few heavy metals induce toxicity at very low concentrations, such as Cr, Se, Cd, Hg, Pb and As (Roy et al., 2024). In the direction of Hg bioremediation, *P. aeruginosa* was reported to absorb 180 mg g⁻¹ mercury ions (Roy et al., 2024). In similar direction, *P. putida* was reported to absorb Hg from marine environment and convert harmful Hg²⁺ to Hg (Tarfeen et al., 2022). During coal mining, arsenopyrite rock oxidation results in As intermixing with CME. Arsenopyrite exposure releases trivalent As³⁺ and pentavalent As⁵⁺ into an aqueous environment (Preetha et al., 2023). Towards As remediation, recombinant *Escherichia coli* strains and engineered *P. putida* have been reported to convert As³⁺ (poisonous) to As⁵⁺ (less toxic). Like As, Cr normally exists in two oxidation states as Cr³⁺ (harmless) and Cr⁶⁺ (more toxic). Bacterial isolates found in the Cr⁶⁺ contaminated mine effluents show specific Cr⁶⁺ resistance. In scientific literature, bacterial genera such as *Bacillus*, *Pseudomonas*, *Klebsiella* and *Microbacterium* have been reported as Cr⁶⁺-resistant genera that have the potential to detoxify Cr⁶⁺ by reducing its oxidation state (Tekerekopoulou et al., 2013).

Medium to high salinity may be considered as another serious environmental issue in CME. In between, strictly limiting reported studies of bacteria-assisted mine effluent desalination, halotolerant ureolytic strain *B. subtilis* LN8B showed the highest removal efficiency of 100% to remove Ca²⁺ in four days and 80% Mg²⁺ removal in six days through the biomineralization in fluidized bed bioreactor (Arias et al., 2020). In this direction, halotolerant bacterial strains belonging to the genera *Pseudomonas*, *Bacillus*, *Shewanella*,

Halomonas and *Rhodococcus* have been reported to show desalination potential (Arias et al., 2019).

2.2.2 Microalgae mediated coal mine effluent treatment

Application of microalgae for advanced treatment and nutrient recovery of municipal, industrial and agricultural wastewater has been considered a promising approach (Wang et al., 2024). According to scientific reports, algae application in wastewater treatment was first studied in California, USA, in 1950 (Li et al., 2022). Microalgae are a diverse group of unicellular microorganisms, typically 3–100 µm long, exhibiting high photosynthetic efficiency, high cultivation rate, high CO₂ fixation rate and significant economic value (Arbour et al., 2024). Microalgae are generally categorized as (i) green algae, (ii) diatoms, (iii) cyanobacteria (blue-green algae) and (iv) golden algae. The potential and sustainable applications of microalgae as biofuel reservoirs are represented in Fig. 2.1.

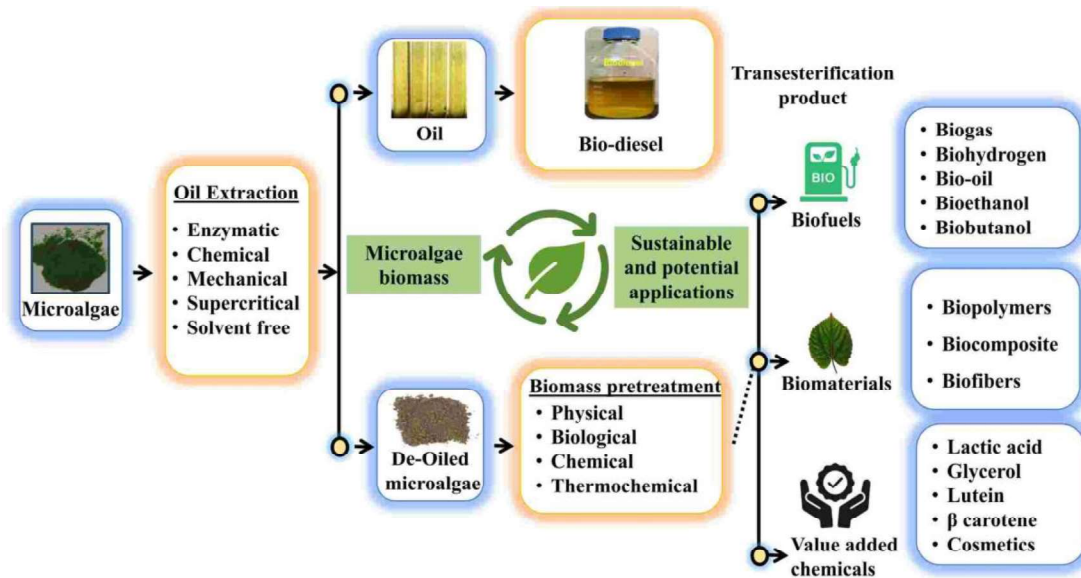


Fig. 2.1 Commercial applications of microalgae as a potential reservoir of bioenergy

The abundance of nutrients containing nitrogen, phosphorus, sulfur, heavy metals and other contaminants in CME makes it an ideal low-cost, sustainable medium for

microalgae cultivation (Lopez et al., 2022). Microalgae-assisted CME treatment may be sustainable long term applicable solution due to: (1) simultaneous removal of multiple pollutants from effluent without requiring additional energy, processing or high costs; (2) utilization of recyclable resources as nutrients for biomass and lipid production; (3) CO₂ fixation and carbon capture, utilization, and storage through photosynthesis; (4) High value-added product formation as biofuel, fertilizer, feed, etc. (Kim et al., 2022). The perspective of microalgae cultivation in coal mine water to treat water for irrigation suitability and biofuel, along with value-added bioproduct formation, is depicted in Fig. 2.2.

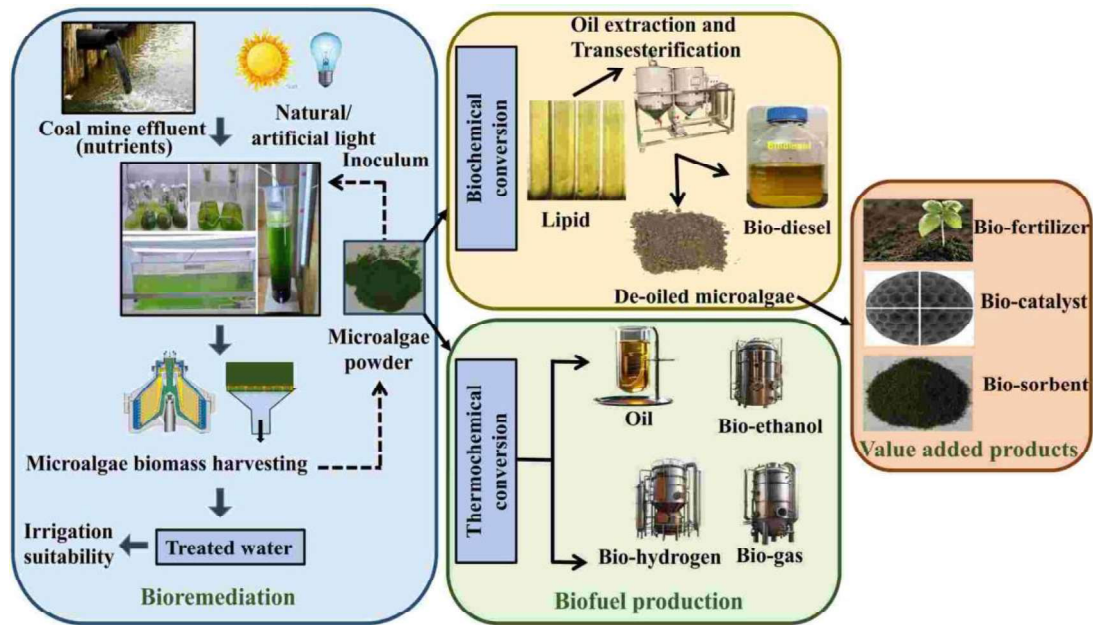


Fig. 2.2 Schematic representation of microalgae culture systems to treat coal mine water and biofuel or other value-added product formation.

Considering the strong adaptability of microalgae to grow in different type of wastewater, a wide range of algal species, i.e., *C. pyrenoidosa*, *C. vulgaris*, *C. emersonii*, *C. sorokiniana*, *C. kessleri* and *C. reinhardtii* has been used for wastewater treatment (Arita et al., 2015). As discussed previously, AMD shows low pH up to 2–4 due to sulfide rich rock interaction with oxygen and water to produce sulfuric acid as co-product. Acidophilic

microalgae sp., i.e., *Chlamydomonas*, *Euglena*, *Klebsormidium* and *Mougeotia* are explored to treat AMD (Chen et al., 2023).

2.2.2.1 Biodesalination process using microalgae platform

Mostly, coal mine discharge faces high salinity issues as seams of the coalfield usually lie in sandstone strata within which the aquifer gradually increases salinity with increasing depth of discharge (Andersson and Andersson, 1999). Conventional desalination (membrane and thermal based) is associated with high process cost, brine discharge issues and high CO₂ emission (Saavedra et al., 2021). To mitigate all these challenges of conventional technologies, CME desalination using a microalgae platform is considered as sustainable and environment friendly approach (Fig. 2.3). The biodesalination efficiency depends upon the type of microalgae species, temperature, light intensity, pH, and saline water nutrients (Esmaeili et al., 2023).

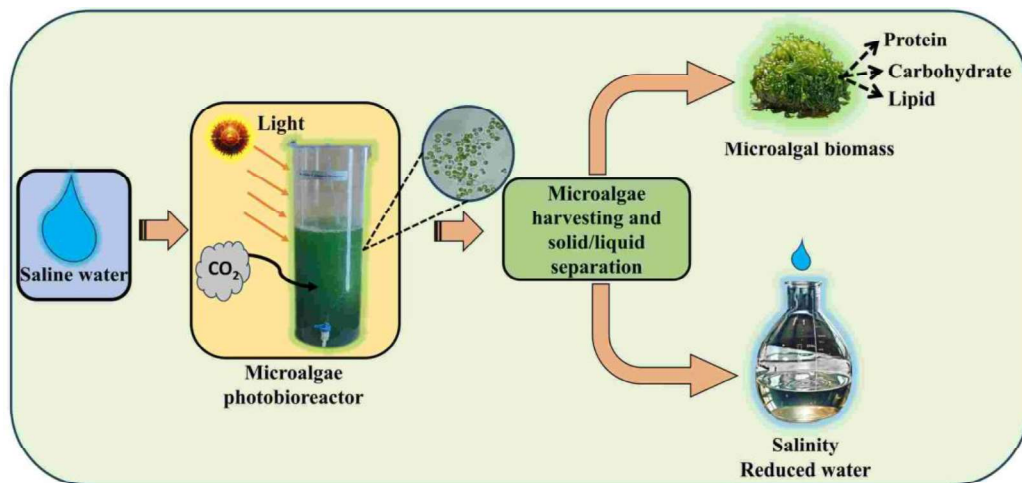


Fig. 2.3 Conceptual representation of coal mine effluent biodesalination using microalgae platform.

In recent years, many halophilic microalgae and freshwater microalgae are explored as salt-tolerant species to treat saline water (Patel et al., 2021). Amongst different potential microalgae, *Scenedesmus* sp. and *C. vulgaris* are reported as salt-tolerant hyper-

accumulators, able to grow in a wide range of salinity from 2–20 g L⁻¹. Both algae species follow a pseudo-first-order kinetic model with a reaction rate constant from 3.58–7.68 d⁻¹ reaching 30 % of salt uptake in a single cycle (Demessie et al., 2019). Towards brackish water desalination, *S. obliquus* was cultivated for 16 days in BG-11 medium of varying salinities (1.2, 2.8, 4.8, 6.8 and 8.8 g L⁻¹ NaCl). It achieved a sedimentation efficiency of almost 77–83% in 60 min except in a hypersaline medium of 8.8 g L⁻¹ (Gan et al., 2016). In natural freshwater species, different *Chlorella* sp. is explored for high salinity content adaptation. In this direction, *C. vulgaris* is reported to sustain a high NaCl concentration of nearly 0.75M (Talebi et al., 2013). Similarly, *C. vulgaris* is reported to sustain NaCl concentrations in the range of 1000 and 5000 ppm maintained in MBG11 medium with an 80 % and 40 % electrical conductivity removal efficiency, respectively (Barahoei et al., 2021). In another study, algae *S. obliquus* was investigated under different TDS concentrations of 2000, 4000, 10,000, 15,000, 20,000, 25,000, 30,000, 35,000, and 40,000 ppm for biodesalination (Nadi et al., 2014). Further, dry and fresh *S. obliquus* was investigated to explore biological desalination mechanisms, finding that adsorption and absorption significantly contribute to NaCl removal. This study found the Langmuir isotherm model more applicable to predicting NaCl adsorption (Wei et al., 2020).

The halotolerant algae from marine sources have been reported to perform successful desalination. In this direction, *D. salina* was reported to sustain wide range of NaCl concentration (0.05 M–5.5 M) by maintain osmotic balance at high salinities via osmoregulatory response (Chen et al., 2009). Further, *D. salina* was reported to absorb salt concentration of 130 mS.cm⁻¹ and showed significant salinity reduction in sodium, bicarbonate and chlorine levels from saline water (Moayedi et al., 2019).

Microalgae cultivation in coal mine water has been successfully explored regarding treatment such as desalination, metal removal, and biomass production. In this aspect,

Scenedesmus sp. is investigated to treat AMD. Further, microalgae harvesting was assessed via coagulation/flocculation and dissolved air flotation (Vandamme et al., 2011). A group of specific acidophilic and non-acidophilic microalgae synergistically interact with bacteria to provide algal biomass derived metabolites for bacterial growth and effectively remediate AMD (Abinandan et al., 2017). The CME from Wayoung coal mines at Donghae, South Korea was treated by *S. obliquus* and *C. vulgaris* cultivation with 10% dosage of mine effluent at initial pH 9 and achieved cell density of 0.5 and 1.0 g L⁻¹, respectively (Salama et al., 2016). The comparative assessment of bioremediation and growth performance of microalgae cultures cultivated in different wastewater sources is shown in Table 2.2.

2.2.2.2 Role of microalgae in heavy metal removal

CME contains a significant amount of heavy metal (Cd, Pb, Cu, Cr and Ni) that have negative ecological impacts, including air pollution, soil degradation, eutrophication and consistent health risk to coal miners and aquatic life (Wang et al., 2024). The heavy metal bioremediation performance of different microalgae cultivated in different wastewater resources is presented in Table 2.3. In this direction, the microalgae-based biological method is considered an innovative alternative technology for removing metallic pollutants from coal mine discharge (Elleuch et al., 2021). The three local marine microalgae named *D. salina*, *Navicula salinicola* and *Amphora coffaeiformis* were collected from the Tunisian Coast of Ksour-Essef. Further, they explored Cd, Pb and Cr removal for heavy metals, resulting in a promising metal removal efficiency of nearly 95% for *D. salina* (Elleuch et al., 2021).

Table 2.2 Summary of bioremediation and growth performance of microalgae cultures cultivated in different saline wastewater sources.

Saline wastewater sources	Wastewater characteristics	Microalgae species	Bioremediation performance		Microalgae growth performance		Reference
			Nutrient removal (%)	Salinity removal (%)	DCW _{final} (g L ⁻¹)	Lipid content (%)	
Coal mine wastewater	AMD (pH– 2.33, conductivity – 7.79 mS cm ⁻¹)	<i>Scenedesmus</i> sp.	SO ₄ ²⁻ –83.13 Metal removal – 99.9	37.9	0.65 (AMD with nutrient supply)	ND	Santos et al., 2020
Coal mine wastewater	AMD from coal waste deposit (pH– 2.9, EC – 0.78 mS cm ⁻¹)	<i>Scenedesmus</i> sp.	ND	27.6	0.57	8.9	Nicknig et al., 2024
Coal mine effluent	Coal mine effluent (pH – 6.58, COD –138 mg L ⁻¹)	<i>Scenedesmus</i> sp. NCI	ND	ND	1.02	28.3	Kumar et al., 2021
Municipal wastewater + 3% Coal mine wastewater	Municipal wastewater (pH– 7.28, TOC – 180.6 mg L ⁻¹ , SO ₄ ²⁻ – 83.13 mg L ⁻¹) AMD from coal mine (pH– 4.2, TOC – 24.8 mg L ⁻¹ , SO ₄ ²⁻ – 988.5 mg L ⁻¹)	<i>Microcystium reisseri</i>	NO ₃ ⁻ –97 PO ₄ ³⁻ –83	ND	0.8	17	Ji et al., 2014
Aquaculture water	Saline effluent (pH – 8.30, COD –198.10 mg L ⁻¹ , EC – 28.50 mS cm ⁻¹)	<i>Artthrospira platensis</i>	COD – 69.02 PO ₄ ³⁻ –100 SO ₄ ²⁻ – 55.34	31.7	0.93	ND	Mirzaei et al., 2024
Artificial wastewater	Simulated wastewater with spiked chemicals (TOC – 300 mg L ⁻¹ , NO ₃ ⁻ –60 mg L ⁻¹ , PO ₄ ³⁻ –15 mg L ⁻¹)	<i>Chlorella vulgaris</i>	TOC – 92 NO ₃ ⁻ –95 PO ₄ ³⁻ – 30	15.8 (salt accumulation in microalgae)	0.5	ND	Vo et al., 2019

AMD: Acid mine drainage; COD: Chemical oxygen demand; DCW: Dry cell weight; TOC: Total organic carbon; EC: Electric conductivity; ND: Not detected.

These metal pollutants, i.e., Cd, Pb and Cr show carcinogenic risk to humans via ingestion, inhalation and/or dermal contact (Mishra et al., 2018). In another study, phycoremediation potentials of microalgal consortia was investigated to treat sewage water resulting maximum biomass concentration of 1.53 g L⁻¹ with heavy metal removal efficiency of 98.2% Pb, 75.2% Cr, 85.06% Cu and 99.6% Cd at 50% diluted waste water (Sharma et al., 2020). Further, heavy metal removal was investigated from coal mine discharge via green algae cultivation, resulting in the highest removal of 99%, 95%, and 85% for Cd, Zn and Fe, respectively (Makhanya et al., 2021). The coal mine water from Bhowra abandoned mine (open cast mine) and Sudamdih Shaft mine (underground mine water) located in Dhanbad, India was investigated for heavy metal removal by *Spirogyra* at different dilutions of 100%, 80%, 60%, 40% and 20%. This study reveals maximum Cu, As and Cd uptake as 60%, 40% and 20%, respectively for the Bhowra abandoned mine water (Vetrivel et al., 2017). In another study, cyanobacterium *Nostoc muscorum* isolated from a coal mining site was investigated to remove heavy metals Pb, Zn, Cu and Cd from aqueous solution, resulting a removal efficiency of 98% (Pb), 87.8% (Cu), 82% (Cd) and 67.2% (Zn) at 5 mg L⁻¹ initial metal concentration (Hazarika et al., 2015).

Table 2.3 Summary of heavy metal bioremediation from wastewater using microalgae.

Wastewater resource	Applied microalgae	Heavy metal removal mg g ⁻¹ (%)	Adsorption characteristics	References
Coal mine water	<i>Pediastrum duplex</i>	Mn – 97	Langmuir isotherm	Thongpitak et al., 2019
Wastewater	<i>Chlorella vulgaris</i>	Cr – 23.6	Freundlich isotherm	Aksu and Kutsal, 1990
Mine tailing water	<i>Chlorella sp.</i>	Ni – 24.8 Co – 10.5 Mn – 24.8 Sr – 26.4	ND	Palma et al., 2017
AMD from mine site	<i>Chlorella vulgaris</i>	Fe – 98.7 Al – 94.7 Mn – 93.29	ND	Brar et al., 2022
Simulated aqueous metal rich solution	<i>Chlamydomonas reinhardtii</i>	Cd ²⁺ – 42.6 Pb ²⁺ – 96.3 Hg ²⁺ – 72.2	Freundlich isotherm	Tuzun et al., 2005

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Wastewater resource	Applied microalgae	Heavy metal removal mg g ⁻¹ (%)	Adsorption characteristics	References
Coal mining site water	<i>Nostoc muscorum</i>	Pb ²⁺ – 98.0 Cu ²⁺ – 87.8 Cd ²⁺ – 82.0 Zn ²⁺ – 67.2	Freundlich isotherm	Hazarika et al., 2015
AMD from mine site	Blue-green algae (predominantly <i>Oscillatoria</i> sp.)	Fe ²⁺ – 95 Pb ²⁺ – 88 Cu ²⁺ – 97 Co ²⁺ – 83 Ni ²⁺ – 62 Mn ²⁺ – 45	ND	Sheoran and Bhandari, 2005
Industrial wastewater from coal fired power plants	<i>Chlorella vulgaris</i>	Hg ²⁺ – 97	ND	Peng et al., 2017
Industrial effluent	<i>Scenedesmus obliquus</i> <i>Desmodesmus pleiomorphus</i>	Zn ²⁺ – 22.3 Cd ²⁺ – 60.8 Zn ²⁺ – 83.1 Cd ²⁺ – 58.6	ND ND	Monteiro et al., 2011

AMD: Acid mine drainage; ND: Not detected.

2.2.2.3 Mechanism of biodesalination and heavy metal removal

Reviewing existing literature, it is confirmed that microalgae mediated salt removal and heavy metal removal processes are similar and both involve bioadsorption and bioaccumulation (bioabsorption) processes. The bioadsorption or physical adherence involves rapidly bonding ions or molecules upon the wet or dried algal surface. Bioadsorption is considered a reversible surface phenomenon that depends upon the properties of the adherents without any energy exchange (Patel et al., 2021). Microalgal bioadsorption follows two process mechanisms such as (i) Ion exchange – Na⁺ ion replaces with other cations, bound on the reactive groups of algal surfaces, (ii) Surface complexation – Salt ions and reactive groups are complexed upon microalgal cell surface (Patel et al., 2021). Bioadsorption depends on electrostatic attraction and/or covalent bonding between salt ions and reactive groups such as thiol, hydroxy, carboxyl, amino, phosphate and hydroxyl carboxyl (Patel et al., 2021). The type of reactive group interaction depends upon algal species and their cell wall composition (Leong and Chang, 2020). These studies

confirm that adsorption is a non-metabolic and passive process (Wei et al., 2020). Further, the brackish water desalination mechanism by *S. obliquus* was explored, indicating both adsorption (majorly) and absorption contribute to NaCl removal (Wei et al., 2020). The existing literature confirmed that both non-living and living algal cell surfaces participate in bioadsorption and salt removal application depends upon their availability and cost (Patel et al., 2021). The biodesalination efficiency also depends upon the reactive surface and available sites in the microalgal cell surface (Wei et al., 2020).

Bioaccumulation is an energy dependent process within the living cell that involves salt uptake and accumulation (Wei et al., 2010). It is processed in two stages: passive salt adsorption on the outer cell surface and intracellular diffusion (Patel et al., 2021). Compared to bioadsorption, bioaccumulation is a slower process in which metabolic and physiological changes occur via salt acclimation in living cells (Patel et al., 2021). The ionic gradient between algae and external media is key in entering salt ions into the microalgae cell from outer saline media (Patel et al., 2021). However, microalgae growth and metabolism are negatively affected by higher Na⁺ concentrations (Shetty et al., 2019). The investigation of live and dried microalgae cells of *S. obliquus* revealed that bioadsorption process has a dominant role in the desalination process, although both bioadsorption and bioaccumulation were involved in desalination (Sahle-Demessie et al., 2019).

All possible interactions involved in the desalination process of Na⁺ and Cl⁻ salts by microalgae from saline wastewater are depicted in Fig. 2.4. Among different interactions of bioadsorption, surface complexation involves more stable covalent bonding, followed by ion-exchange which involves both ionic and covalent bonding. Further, ionic interaction involves attraction between ionic species, resulting less stable bonding (Patel et al., 2021). Further, bioaccumulation involves the sequential transfer of both cationic (Na⁺) and anionic

(Cl⁻) species which starts with Cl⁻ to develop the negative membrane potential and further facilitate successive Na⁺ accumulation during a later phase of algal cycle (Fig. 2.4).

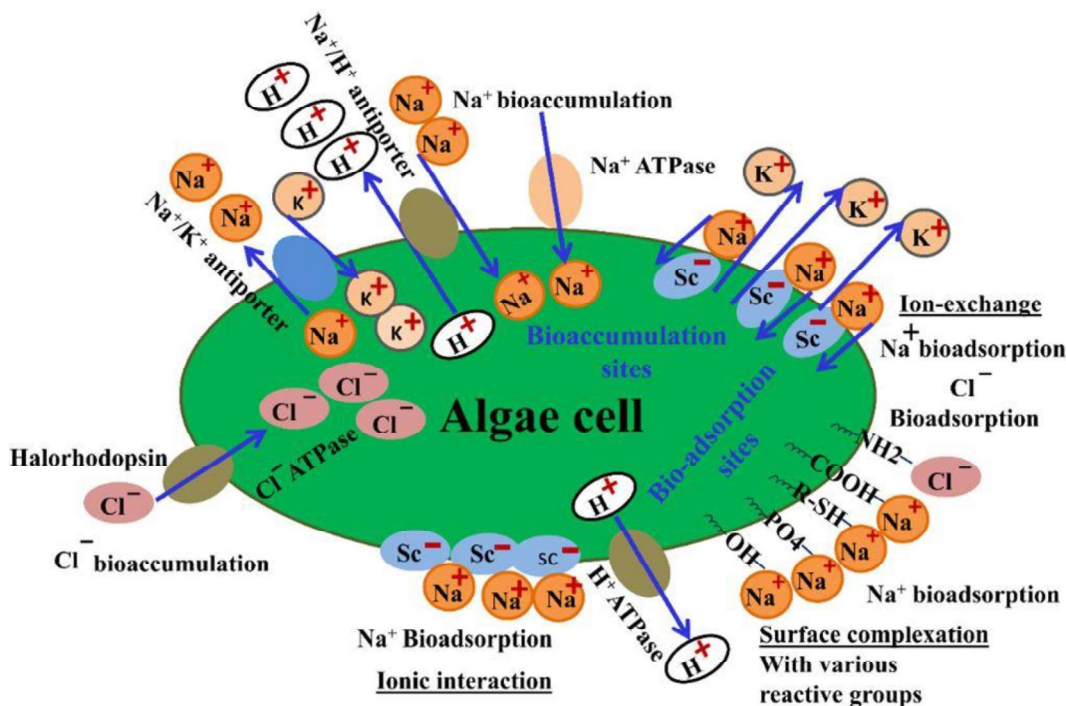


Fig. 2.4 Proposed biodesalination mechanism and type of interactions involved in bioadsorption and bioaccumulation of Na⁺ and Cl⁻ in microalgae cell. Sc⁻ – surface complexation.

The approach to eradicating heavy metal ions from mine discharge is similar to salt removal. Ion exchange, precipitation, membrane processing and adsorption are most commonly applied heavy metal removal mechanisms (Priya et al., 2022). Microalgae can form organometallic complexes, i.e., protein-heavy metal complexes that are further separated inside the vacuoles to control heavy metal concentration and further toxicity (Balaji et al., 2016). Similar to biodesalination, heavy metal removal is attained in two-stage defined as, (i) biosorption via rapid extracellular passive adsorption and (ii) bioaccumulation via slow intracellular positive diffusion (Leong and Chang, 2020). Further, heavy metal removal efficiency depends upon the physiological characteristics of

microalgae and maximum biomass cultivation (Leong and Chang, 2020). The heavy metal removal mechanism is well elucidated in Fig. 2.5.

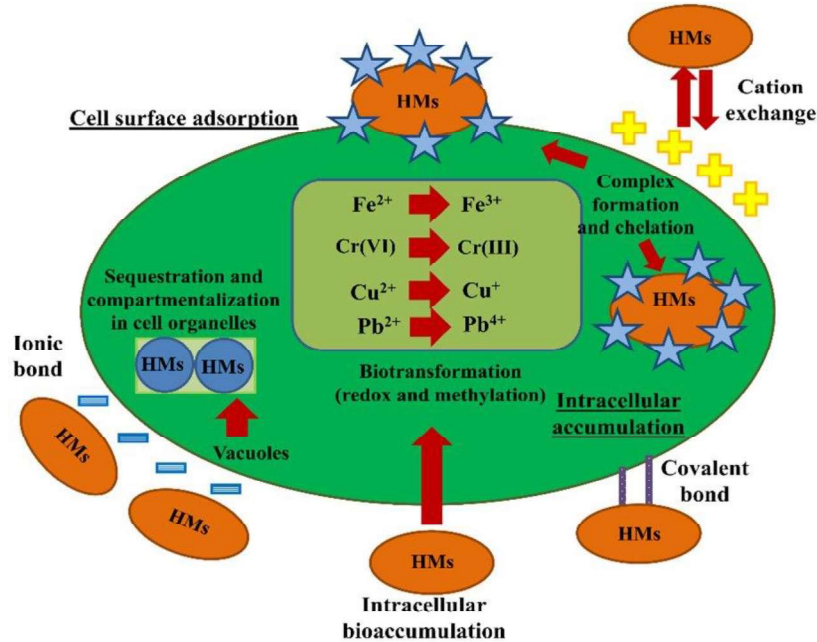


Fig. 2.5 Mechanism involved in heavy metal removal from coal mine effluent by using microalgae.

2.2.3 Biofuel production from harvested microalgae biomass

The concept of circular water economy is very significant in coal mine industries, targeting multiple goals such as (i) unconventional coal mine water treatment and utilization for irrigation and drinking purpose, (ii) high value applications of harvested microalgae from treated mine water, (iii) large scale fish farming in treated coal mine water, (iv) increased carbon capture with reduced GHG emission (Xevgenos et al., 2024). Microalgae-based high value applications are associated with biofuel production utilizing different mechanical and thermochemical conversion processes, biofertilizers and biostimulants production to improve soil quality, natural dyes, and cosmetic production (Levett et al., 2023). Implementing integrated approaches towards wastewater treatment, resource recovery and biofuel production are related to managing materials, products,

components, water and energy till their highest possible intrinsic value (Xevgenos et al., 2024). Therefore, microalgae platform facilitates sustainable and cost-effective coal mine water treatment and biofuel production (Levett et al., 2023). According to the literature survey, a limited number of integrated studies exist related to mine water treatment and biofuel production. In this direction, mine tailings water treatment was investigated by cultivating *Chlorella* sp. with a productivity of $0.77 \pm 0.07 \text{ g m}^{-2} \text{ d}^{-1}$ and showing promising biofuel potential with a total carbohydrate yield of 40.0 % and lipid yield between 6.7–19.5 %. Simultaneously, microalgae biofilm showed potential removal of heavy metals (Co, Mn, Ni, Sr) from mine water (Palma et al., 2017).

To establish a zero-waste microalgae biorefinery, complete utilization of microalgae biomass is the most favorable and sustainable approach to obtain the highest energy value of all components (Klein et al., 2023). The high value microalgae biomass cultivated in water treatment systems includes various beneficial components like proteins, pigments, polyunsaturated fatty acids and polyhydroxyalkanoates (PHAs) (Singh et al., 2024). In sequence of biodiesel production through transesterification of lipids, de-oiled microalgae residues can also be utilized as raw materials for biofuel production (Singh et al., 2024). The microalgae lipid transesterification to produce biodiesel may be integrated with the thermochemical conversion of lipid extracted microalgae residue to produce bio-oil through pyrolysis and bio-gas through pyrolysis/gasification, respectively (Bora et al., 2024). Different processes/routes for biofuel production by utilizing cultivated microalgal biomass from water treatment systems are discussed below:

2.2.3.1 Transesterification for biodiesel production

Biodiesel is considered the most promising and probable replacement for fossil-based diesel and petrol (Pandey et al., 2024). It is a long chain of fatty acid methyl/ethyl esters produced through transesterification. Based on feedstock availability, biodiesel

production has been divided into different generations (Sanjurjo et al., 2024). The first-generation biofuels are derived from edible crops and second-generation biofuels are derived from non-edible seeds, plants, animal fats, along spent cooking oils (Pandey et al., 2024). The microalgae and macroalgae constitute third-generation biofuels and genetically modified algae constitute fourth-generation biofuels (Sanjurjo et al., 2024).

Microalgae are potential candidates for producing biodiesel, which depends upon microalgae biomass productivity and lipids accumulated inside the cell (Cai et al., 2013). Biomass productivity and lipid accumulation are strongly dependent on microalgae species. Microalgae species such as *Chlorella* sp., *Chlorococcum* sp. and *Scenedesmus* sp. have potential to cultivate in wastewater utilizing organic and inorganic nutrients for biomass production coupled with waste remediation (Bora et al., 2024). The microalgae growth and biomass cultivation in wastewater (specifically coal mine water) depend upon various parameters such as temperature, light intensity, pH, aeration, photoperiod and salinity (Brindhadevi et al., 2021). The high biomass cultivation is also coupled with a substantial lipid accumulation inside the microalgal cells, essential for biodiesel production (Pandey et al., 2024). Further, lipid accumulation depends upon nutrient availability, cultivation mode and stress conditions (Goh et al., 2019).

The biodiesel quality depends on pretreatment techniques, lipid extraction methods and transesterification process. The transesterification process involves the conversion of one molecule of triglyceride to three molecules of ester and glycerol in the presence of an acid or a base catalyst. Mostly, methanol is used as alcohol for transesterification to produce fatty acid alkyl ester or biodiesel. The fatty acid alkyl ester quantity depends upon the chemical conversion rate and lipid extraction method (Kumar et al., 2021). The transesterification is mostly carried out by direct and indirect processes. Direct transesterification is carried out without cell disruption with wet microalgae biomass;

however, indirect transesterification involves cell disruption and lipid extraction as the preliminary steps before the transesterification process (Jazzar et al., 2015).

In the direction of biodiesel production from microalgae cultivated in coal mine water, *Scenedesmus* sp. NC1 was isolated from a coal mine, Dhanbad, India. The FAME analysis results indicate that various fatty acids of microalgal lipid ranging from C14-C20 (Kumar et al., 2021). The most abundant fatty acid was palmitic acid (C16:0) with a % composition of 24.54 ± 2.1 %, followed by oleic acid (C18:1) and linolenic acid (C18:3) with % composition of 16.21 ± 1.1 % and 12.32 ± 1.3 % respectively. The remaining fatty acids, such as myristic acid (C14:0), palmitoleic acid (C16:1), stearic acid (C18:0) and linoleic acid (C18:2), cumulatively composed of less than 12 % of total fatty acids. The least abundant fatty acid was arachidic acid (20:0), accounting for 0.98 ± 0.58 % of total fatty acids (Kumar et al., 2021). The lipid characterization results with monounsaturated (18.55 %), polyunsaturated (22.74 %), and saturated fatty acid (35.15 %) indicating *Scenedesmus* sp. NC1 is a promising candidate for biodiesel production (Kumar et al., 2021).

Aiming to utilize coal mine water for microalgae cultivation, two microalgae strains, *Nephroselmis* sp. KGE2 and *Autodesmus obliquus* KGE17 were isolated and cultivated in a livestock wastewater effluent and AMD with dry cell weight of 0.59 g L^{-1} and 0.55 g L^{-1} , respectively, after 20 days of cultivation (Ahn et al., 2022). The transesterification of microalgae biomass cultivated in different wastewater sources for oil production along with detailed process conditions is given in Table 2.4.

Table 2.4 Detail process conditions and fatty acid methyl ester production through transesterification of microalgae biomass for bio-oil conversion.

Microalgae feedstock	Solvent	Catalyst concentration (%) / (mol/mol)	Reaction condition		FAME yield and oil conversion		References
			Temperature (°C)	Time (min)	FAME yield (per biomass)	Oil conversion (per transesterifiable lipid)	
<i>Chlorella</i> sp.	Ethanol	sodium hydroxide (2.0 – 2.5%)	90	6	20.1%	94.3%	Martinez-Guerra et al., 2017
<i>Chlorella vulgaris</i>	Methanol	KF/CaO catalyst (12%)	60	45	ND	93.07%	Ma et al., 2015a
<i>Chlorella sorokiniana</i>	Methanol	H ₂ SO ₄ (0.158:1)	80	19.8	18.0%	77%	Wahlen et al., 2011
<i>Chlorella pyrenoidosa</i>	Methanol	H ₂ SO ₄ (0.5:1)	120	180	93.2%	91.4%	Cao et al., 2013
<i>Chlorella protothecoides</i>	Methanol and Ethanol	Catalyst free supercritical transesterification	320	31	ND	90.8% (Methanol) 87.8% (Ethanol)	Nan et al., 2015
<i>Nannochloropsis</i> sp.	Methanol	Mg – Zr (1.65 :1)	65	240	46.43%	47%	Li et al., 2011
<i>Nannochloropsis gaditana</i>	Ethanol	Catalyst free wet in situ transesterification	185	180	11.65%	91.85%	Kim et al., 2017
<i>Nannochloris</i> sp. <i>Chlorella</i> sp.	Methanol	Catalyst free in situ supercritical transesterification	265	50	ND	21.79% (<i>Nannochloris</i> sp.) 45.62% (<i>Chlorella</i> sp.)	Jazzar et al., 2015
<i>Chaetoceros gracilis</i>	Methanol	H ₂ SO ₄ (0.158:1)	80	19.8	ND	82%	Wahlen et al., 2011
<i>Spirulina platensis</i>	Methanol	MgO/ZSM-5 (3%)	75	60		92.1	Qu et al., 2020
<i>Scenedesmus obliquus</i>	Methanol and hexane	WO ₃ / ZrO ₂ (15%)	50	180	ND	94.58%	Guldhe et al., 2017
Algal biomass	Methanol	H ₂ SO ₄ (0.678:1)	65	120	ND	86%	Haas et al., 2011

FAME: Fatty acid methyl ester; ND: Not detected.

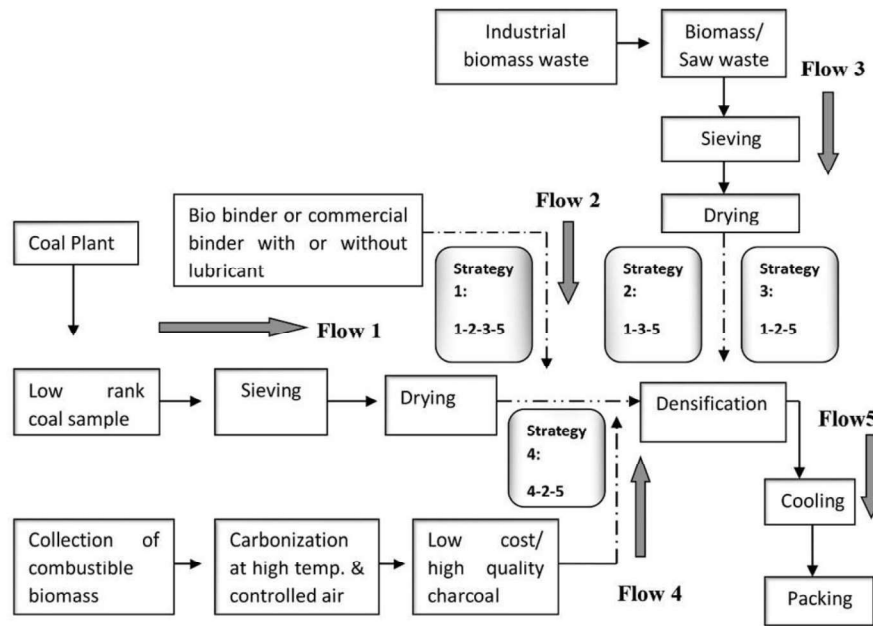
The AMD positively impacts the production of total fatty acids as 0 to 10 % AMD addition increases total fatty acids per biomass. Consequently, *Nephroselmis* sp. KGE2 showed an increment from 508.61 to 813.56 mg/g and *Autodesmus obliquus* KGE17 showed increment from 370.15 to 428.83 mg/g (Ahn et al., 2022). The FAME analysis confirmed 92.4 % of the composition of C16-C18 fatty acid aligned with biodiesel characteristics as a higher CN of 52.31 and IV of 88.26 (Ahn et al., 2022). These results indicate the feasibility of cultivating microalgae in acid mine discharge of coal mine water for biodiesel production. In a similar direction, green alga of *Chlorococcaceae* family was isolated from a coal bed methane production pond, showing highest lipid content of 27 % due to high N and P content. These results indicated nitrate deficiency is correlated with lipid accumulation. However, additional P limitation did not influence lipid accumulation (Hodgskiss et al., 2016). In another study, saline water screened ten microalgae sp. to evaluate biodiesel potential by determining biomass productivity, biochemical components, fatty acid profiling and biodiesel characterization. The biodiesel results indicate *C. vulgaris* as potential species with a specific growth rate of 0.36 d⁻¹, lipid productivity of 7.45g L⁻¹ d⁻¹ and fatty acid profile of 78.3 % C16-C18. Further, biodiesel characteristics showed low viscosity (4.49), high CN (55.38) and low cloud point (4.98) (Khosravinia et al., 2024).

Although large-scale biodiesel production from microalgae is associated with several challenges such as high biomass and lipid productivity, including mono-culture maintenance (Pandey et al., 2024). Incorporation of coal mine water facilitates less complex or low-cost growth medium for monoculture or healthy co-culture lipid-rich microalgae cultivation (Kumar et al., 2021). At coal phase out conditions, microalgae cultivation system may be coupled with coal mine closure plans as a potential opportunity to utilize coal mine water resources, sufficient land and high solar radiation for integrated outcomes of biodiesel production coupled with mine water bioremediation (Levett et al., 2023).

2.2.3.2 Mechanical conversion for solid briquette production

Lipid extraction from microalgae biomass is associated with collecting a surplus by-product defined as de-oiled microalgae biomass/de-oiled cake. In a circular economy context, de-oiled microalgae can be processed for biofuel production in various forms, i.e., solid, liquid and gas (Jaiswal et al., 2021). Mechanical conversion of fuel feedstocks such as de-oiled microalgae, lignocellulosic biomass residue and industrial waste, etc., in the form of briquettes, nodules and pellets can be a cost-effective solution to provide solid fuel for domestic energy supply (Das et al., 2015). In opencast coal mining, coal fines and low-rank coal generation is considered very challenging as these coal residues do not fit in the coal market due to its reduced size (Rawat and Kumar, 2021). The application of these coal fines is very challenging due to storage, handling, transportation and burning problems as a solid fuel (Olugbade et al., 2021). In this aspect, densification of de-oiled microalgae and coal blends in form of briquettes have emerged as a low-cost technology to produce blended solid fuel (Das et al., 2015).

The densification or agglomeration technology may be employed to convert combustible loose material to form a more compact & denser product with increased physical and combustion characteristics (Grover and Mishra, 1996). Any compaction through pressing particles together in a confined volume represents densification. Based on existing research in coal-biomass briquetting, four processing strategies to formulate composites are defined as (i) coal-biomass-binder, (ii) coal-biomass (without binder), (iii) coal-binder and (iv) carbonized biomass in the form of charcoal- binder (Rawat and Kumar, 2021). The process strategy to formulate different coal-biomass composites is presented in Fig. 2.6.



- Strategy 1: Coal- biomass- binder composite
- Strategy 2: Coal- biomass composite
- Strategy 3: Coal- binder composite
- Strategy 4: Carbonized biomass- binder composite

Fig. 2.6 Process strategies to formulate different coal–biomass composites.

Amongst different densification approaches such as briquetting, pelletizing and nodulization, briquetting may be considered as most preferable densification approach due to less investment cost and wide acceptability in developing countries (Jiang et al., 2014; Das et al., 2015). The process design for de-oiled microalgae blended coal briquette production and carbonized biomass or charcoal-binder composite is presented in Fig. 2.7 and Fig. 2.8, respectively.

De-oiled microalgae biomass and coal interaction is synergistic due to the compatible physical properties of both materials, such as moisture content, particle size distribution, and bulk density (Thapa and Engelken, 2020). De-oiled microalgae-blended solid fuels offer improved mechanical performance in the form of compressive strength,

drop strength, and water resistance index (WRI) (Rawat and kumar, 2023a).

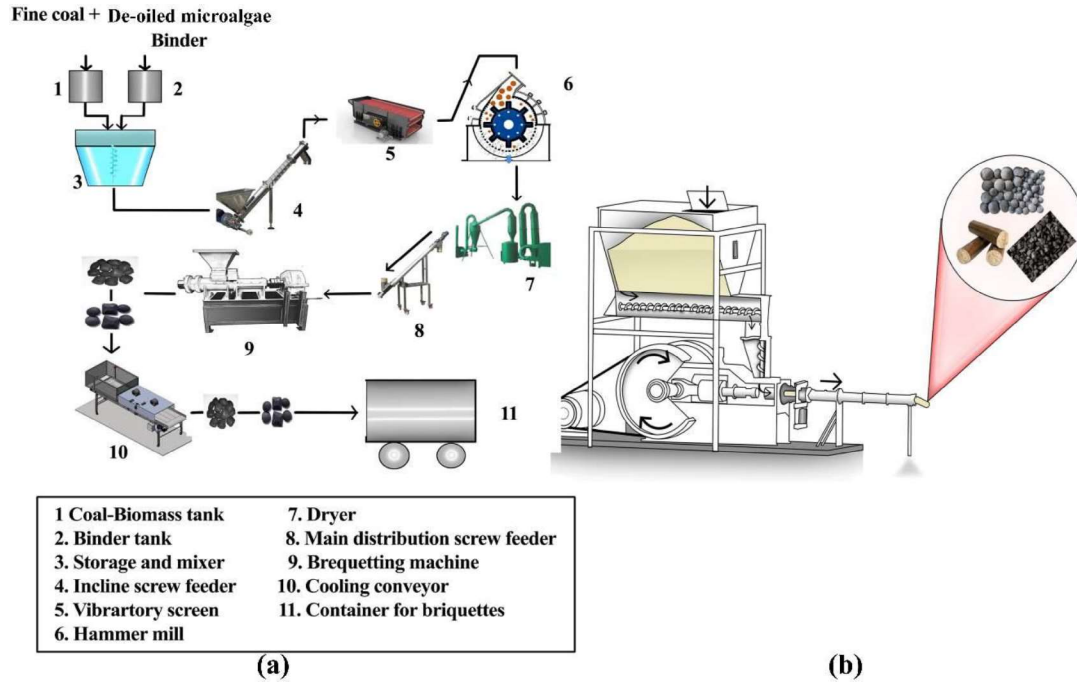


Fig. 2.7 (a) Process design for de-oiled microalgae blended coal briquette production (b) schematic diagram of briquetting machine.

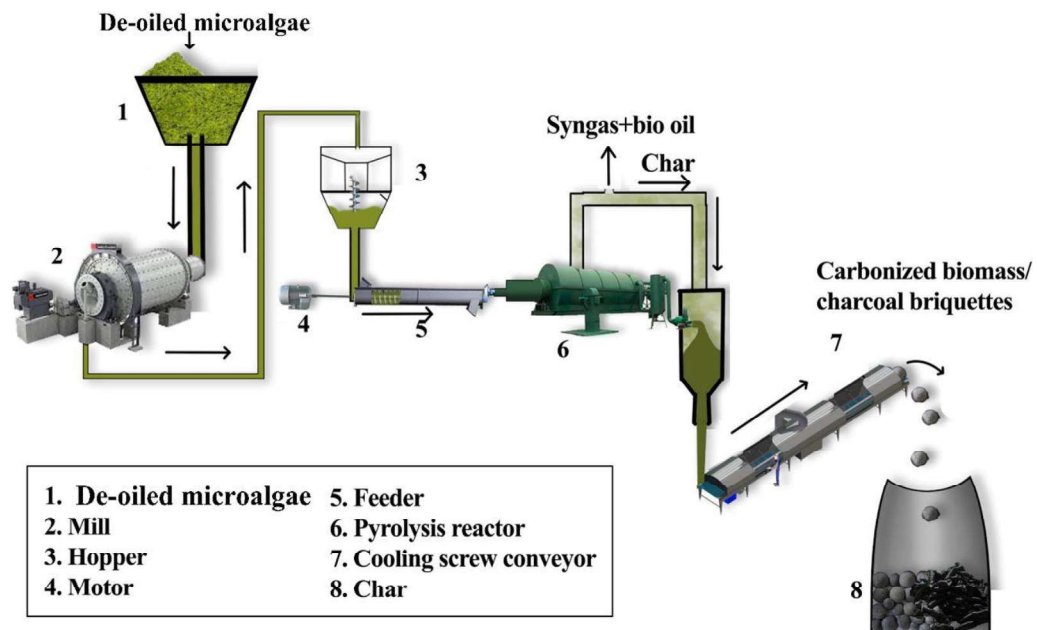


Fig. 2.8 Process design for carbonized de-oiled microalgae biomass or charcoal briquettes production.

In this direction, different freshwater microalgae species (*C. vulgaris*, *C. protothecoides* and *Spirulina*), as well as marine microalgae species (*D. tertiolecta* and *D. salina*), are reported as a promising fuel feedstock to blended with coal (Muazu et al., 2017). Compared to pure coal, the combustion of microalgae blended coal pellets significantly reduces the emission of CO₂, SO_x and NO_x (Nyoni et al., 2020). In a similar aspect, the blending ratio range of *Scenedesmus* (5–20%) to coal reports the reduction of CO₂ (12–29%) and SO₂ emissions (3–19%) during the combustion process (Magida et al., 2022). A recent study has shown that pulverized *C. vulgaris* and coal pellets have better thermal combustion than coal fines or microalgae pellets alone (Chen et al., 2012). These studies indicated that sustainable utilization of waste coal might be possible through microalgae-blended briquettes with minimum adverse environmental impact. However, blending of more than 10 % biomass in coal is not recommended in coal-based boilers due to the possibility of fire hazards at low ignition, feeding issues and the opposite impact on thermal combustion (Rawat and Kumar, 2023a). In the direction of co-pellets production, harvested microalgae from wastewater treatment plants was pyrolyzed to produce biochar and blended with agro-waste to form fuel pellets with improved mechanical strength and thermal properties (Mehdi et al., 2021).

In addition to the direct pelletization of microalgae as a solid fuel, microalgae is also explored as a binder to bind coal fine particles in form of ‘Coalgae’ as a novel application in briquette technology (Gaga and Watts, 2018). However, the suitability of microalgae as a binder also depends upon the nature of raw material, and physical-chemical characteristics such as particle size distribution, moisture content, binding chemistry and compacting pressure (Olugbade and Ojo, 2020). Further, the type and amount of binder positively correlate with the bulk density and mechanical strength of briquettes (Rawat and Kumar, 2021). It is observed that blending of *C. vulgaris* powder (50%) with wood

improved bulk density (1580.2 kg/m³) as well as durability (98%) of pellets under optimum temperature (120°C) and pressure (120MPa) conditions (Cui et al., 2019). In a similar direction, various binders as starch, molasses and biosolids are compared with microalgae to investigate the impact of binder upon pellet strength, confirming that microalgae offer excellent durability of densified products due to the presence of less lignin content (Olugbade and Ojo, 2020). Additionally, it is observed that increasing microalgae proportion interlocks the gaps between loose solid particles and results in enhanced bulk density and durability of reformed pellets (Jabeen et al., 2020).

Therefore, direct briquetting of de-oiled microalgae or de-oiled microalgae blended coal briquetting may be considered a successful attempt towards alternate biofuel production, leading to energy production with environmental acceptability to control GHG emission and particulate discharge. Integrating coal mine water treatment and solid waste management with briquetting technology is highly encouraged in the form of de-oiled microalgae and coal fines briquette production. These low-cost blended briquettes can be directly supplied to coal-based power plants as sustainable and affordable fuels (Rawat and Kumar, 2023a)

2.2.3.3 Thermochemical conversion for bio-oil, bio-char and bio-gas production

Microalgae to biofuel production mostly involves lipid extraction and transesterification of lipids to form biodiesel. However, commercializing microalgae-derived biodiesel is still challenging due to its high cost (Kumar et al., 2024). Thus, the valorization of microalgal biofuel depends upon the utilization of all constituents of microalgae following the zero-waste concept (Wang et al., 2024). The lipid extracted from microalgal biomass constitutes approximately half of the residues because lipid normally contributes 55% of the total microalgal biomass (Yang et al., 2024). The de-oiled or lipid extracted microalgae residue is enriched in proteins, carbohydrates, and some intrinsic

lipids, which possess enormous biofuel potential. Towards maximum carbon utilization and minimum waste generation, thermochemical conversion processes such as pyrolysis, hydrothermal liquefaction, and gasification are potential routes to produce bio-oil, biochar, and gas (Rawat et al., 2024b).

According to extensive literature, a synergistic or additive interaction is reported from the co-pyrolysis of microalgae biomass and coal. In this direction, many researchers investigated the thermal behavior of co-pyrolysis of low-rank coal and microalgae biomass. Wu et al. (2017) suggested that co-pyrolysis of low-rank coal and *Spirulina* simulated *Spirulina* showed higher volatiles yield. Similarly, the synergistic interaction of coal with *D. tertiolecta* also finds the same result with a high volatile yield (Yang et al., 2024). Microwave assisted pyrolysis of low rank coal and *C. vulgaris* with one wt.% HZSM-5 showed high bio-oil yield of 33.8 wt% (Sardi et al., 2022). The fast pyrolysis of *S. platensis* and *Pithophora* sp. produces a maximum pyrolytic oil yield of 45% and 28% in fixed bed reactor at 600 °C and *Botryococcus braunii* produces 28% at 500 °C (Piloni et al, 2021). Recently, conventional pyrolysis of algal biomass was optimized by using Box-Behnken Design of RSM, which results a maximum yield of 20.1% (organic) and 20.6% (aqueous) bio-oil at a pyrolysis temperature of 575 °C, N₂ flow rate of 0.5 l/min and retention time of 45 min (Jeeru et al., 2023). In co-pyrolysis of low-grade bituminous coal and algae biomass, the pyrolysis oil yield is positively correlated with the microalgae/coal blending ratio, and a maximum oil yield of 40% is observed for pure microalgae with a high proportion of fatty acid esters of 28.8–32.6 % (Nyoni et al., 2023).

In addition to coal, the co-pyrolysis of microalgae with waste products has been explored. In this direction, Tang et al. (2020b) explored a synergistic interaction between microalgae and low-density polyethylene, promoting esters and long-chain alcohol formation with reduced bio-oil production of nitrogenous and oxygenated compounds.

Recently, catalytic pyrolysis is explored as an efficient tool for the advancement of co-pyrolysis process via E_a reduction, reaction time shortening and bio-oil upgradation (Lee et al., 2020). The catalytic pyrolysis is performed by in-situ mode, in which raw materials and catalysts are mixed before co-pyrolysis as well as in ex-situ mode, in which pyrolysis volatiles pass through the catalyst surface at an operational temperature (Yu et al., 2019). Recently, the co-pyrolysis of *Nannochloropsis* sp. and polypropylene blends were investigated over HZSM-5 zeolite catalyst in a fixed bed bioreactor at reaction temperature of 500–900 °C, microalgae to polypropylene ratio of 1:0–0:1 and feedstock/catalyst mass ratio of 1:0–1:10 resulting a maximum bio-oil yield of 45% at microalgae to polypropylene ratio of 1:1 (Qi et al., 2018). In a similar direction, Chen et al. (2019) investigated microwave-assisted co-pyrolysis of *C. vulgaris* and wood sawdust, resulting high selectivity of phenols as 43.6 % for wood sawdust sample and a high selectivity of alkenes as 31.2 % for wood sawdust sample. Further, synergistic interaction is observed between co-pyrolysis of *C. vulgaris* and wood sawdust (Chen et al., 2019).

In this direction, microalgae cultivated in wastewater is considered as potential feedstock to produce bio-oil through thermochemical conversion as an alternative to fossil fuels to reduce GHGs emission (Hossain et al., 2022). The co-hydrothermal liquefaction of wastewater-grown microalgae and peat was investigated to yield the highest biocrude of 36.6 wt% for a feed ratio of 50:50 with HHV of 32 MJ/kg (Hossain et al., 2022). Similarly, microalgae *N. elliposporum* grown in municipal wastewater produced bio-oil yield of 24.62% at 300 °C and achieved nutrient removal of 88.31% phosphate and 87.59% nitrogen from wastewater (Devi and Parthiban, 2020). Although bio-oil derived from microalgae pyrolysis are mainly composed of different type of aliphatic and aromatic hydrocarbons as well as undesirable oxygen and nitrogen containing compounds. The oxygenous compounds are responsible for high viscosity, high corrosion and acidity, and high nitrogen,

which can produce nitrogen oxides during combustion (Zainan et al., 2015). Different commercial catalysts can be used to overcome these limitations and upgrade pyrolysis derived bio-oil (Bulushev and Ross, 2011). It leads to the establishment of microalgae biorefineries utilizing de-oiled microalgae, coal, and other waste residues for bio-oil production (Su et al., 2022).

In addition to pyrolysis, gasification is also considered as an efficient thermochemical process due to high conversion efficiency for syngas production (Adnan and Hossain, 2019). Towards establishing a low-carbon bio-economy, the integrated microalgae and coal gasification is considered as an established technology to produce energy-rich syngas as a global energy carrier (Rawat et al., 2024a). In recent years, gasification/co-gasification of microalgae independently or with other waste streams has been widely employed to produce syngas, which is applicable to both power generation and chemical synthesis (Rawat et al., 2024a). Targeting hydrogen and methane as energy rich and high value syngas, gasification of microalgae has attracted more attention than pyrolysis (Adnan et al., 2019). In this direction, an integrated gasification system is developed to evaluate the gasification of *Spirulina* microalgae at various moisture contents of (0–45 wt%) to yield high quality syngas (Adnan et al., 2019). In another study, Indonesian coal and microalgae co-gasification was investigated to evaluate syngas composition, gasification system efficiency and cold gas efficiency (Adnan et al., 2019). Recently, co-gasification of *C. vulgaris* and petrochemical industrial sludge is investigated, which results in a positive correlation between CO and H₂ content with increasing temperature and achieved optimal H₂ at 700 °C (Zhang et al., 2024). The existing literature confirms that microalgae and waste residues co-gasification may be considered an innovative bioenergy production technology to convert feedstocks into energy rich syngas

(hydrogen and methane) targeting zero waste discharge and bio-circular green economy (Zhang et al., 2024).

Considering the existing literature as basis, the pyrolysis of de-oiled *C. pyrenoidosa* (Rawat and Kumar, 2023a), *C. sorokiniana* (Kumar et al., 2023), *Nannochloropsis* sp. (Lu et al., 2023) and *S. obliquus* (Mustapha et al., 2023) have been extensively explored to produce bio-oil, biochar and syngas. In addition to bio-oil and syngas application, lipid extracted microalgae residue is investigated as a precursor to prepare activated carbon/porous carbon material as bio-char for highly efficient catalyst application due to the concentration of active sites, specific surface area and thermal stability (Xia et al., 2024). The reported studies confirm that algae-based biochar and hydrochar have higher porosity and diverse functional groups such as amines, carboxyl and hydroxyl, facilitating improved cation exchange capacity (Arora et al., 2024). Recently, wastewater grown *C. sorokiniana* was investigated for bio-oil and biochar production. The graphitic bio-chars was further explored as bio-adsorbents for multiple heavy metal removals. The graphitic bio-chars derived from oiled and de-oiled biomass were further compared for various heavy metal remediation efficiency (Jaiswal et al., 2021). In another investigation, biochar production was integrated with textile wastewater bioremediation by using *C. vulgaris* which reflects algae-biochar as good biosorbent and biofertilizer (Rehman et al., 2024). Further, various microalgae sp. *Chlamydomonas*, *Desmodesmus*, *Chlorella* and cyanobacteria such as *Spirulina* were investigated for bio-char application with good adsorption capacity (Khan et al., 2022).

Recently, integrated transesterification-pyrolysis was also investigated to explore efficient and complete utilization of microalgae by lipid extraction for biodiesel production and residual de-oiled microalgae biomass utilization for bio-oil and biochar production aiming for circular green economy (We et al., 2024). These integrated strategies, such as

transesterification-pyrolysis (Wei et al., 2024) and pyrolysis-gasification (Fermoso et al., 2018), target efficient conversion of microalgae to biofuel as a potential solution to handle energy security and environmental sustainability issues.

2.4 Identified research gaps

Considering the insights derived from the review of the literature and the need to develop microalgae based integrated facilities towards CME treatment and biofuel production with circular water and energy economy, the subsequent research gaps were identified:

- ❖ Considering country-level coal phaseout commitments by 2040, sustainable microalgae-based bioremediation strategies may be integrated with mine closure plans. In this direction, green initiatives for active/ abandoned coal mine water management have not been investigated properly.
- ❖ Compared to the conventional desalination process, biodesalination processing and mechanisms using a microalgae platform have not been well investigated. Specifically, microalgae-based pilot scale/commercial scale and open or closed system studies of CME treatment lag behind.
- ❖ The integrated process development strategies related to continuous and semi-continuous microalgae cultivation for CME treatment and biofuel production have not yet been investigated.
- ❖ The integrated strategies to evaluate biomass and biofuel potential of microalgae harvested from CME treatment system have not been investigated in a wide spectrum. More specifically, coupled transesterification-pyrolysis, transesterification-gasification, and pyrolysis-gasification have not been explored well to target the efficient conversion of de-oiled microalgae and coal as fuel feedstock to biofuel.

- ❖ Systematic efforts have been lacking to investigate de-oiled microalgae and coal co-pyrolysis for energy-rich syngas production. In this direction, maximizing hydrogen and methane rich syngas emission using machine learning approaches has not yet been investigated. Further, real time monitoring of syngas emission at different pyrolysis stages is very significant towards process development for hydrogen rich syngas generation at slow pyrolysis.
- ❖ In the literature, many studies have been reported on the thermochemical conversion of de-oiled microalgae and coal for bio-oil production. But studies are strictly lagging with an aspect of cleaner co-pyrolysis strategy to produce high quality bio-oil by utilizing low-cost residues such as de-oiled microalgae and coal blends via synthesized catalyst interaction.