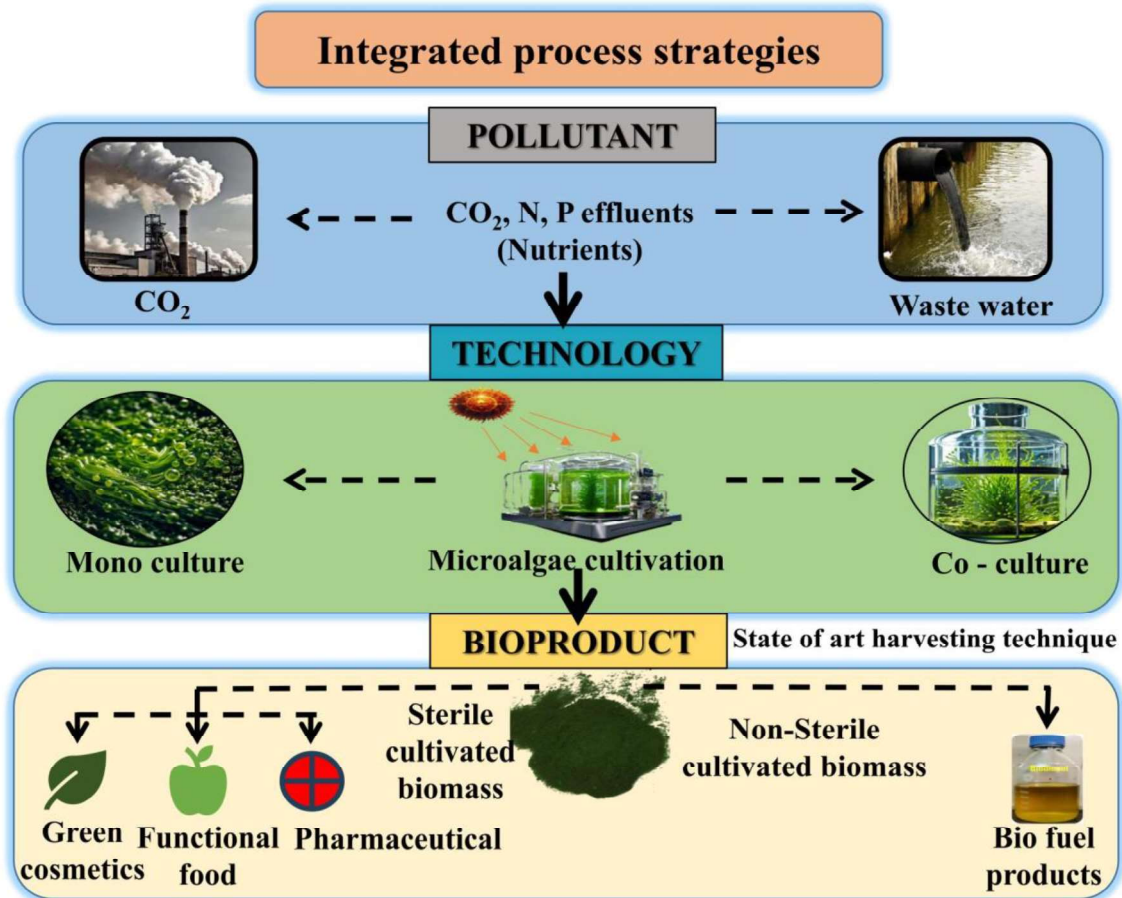


CHAPTER 1

Introduction to integrated strategies for coal mine effluent treatment and biofuel production



Abstract

Water scarcity is considered as a challenging aspect for worldwide security and environmental sustainability. The synergy among water, food and energy sector is interrupted due to the increase of water insufficiency associated with human population. Water unavailability is considered a challenging and triggering factor for the security and sustainability of the water-energy-food domain. In addition to water, energy is considered as an essential ingredient of socio-economic development and economic growth. Considering high electricity and heat production demands, coal mining activities, specifically opencast mining are highly accelerated, which results excess coal fine waste responsible for acid mine drainage (AMD), soil erosion and metal contamination in surface and groundwater resources. The conventional desalination technologies for coal mine effluent treatment such as electrodialysis, reverse osmosis, membrane distillation, forward osmosis, multi-stage flash distillation and multiple-effect distillation, are energy intensive. Further, liquid waste, i.e., corrosive products, pretreatment chemicals, and brine discharge are discussed as negative impacts of conventional technologies interrelated with marine environment and aquatic life. In this aspect, present chapter describes microalgal biomass production coupled with wastewater treatment for biofuel generation as a sustainable and cost-effective replacement of conventional technologies. As a summary, present chapter covers a novel approach applied for microalgae assisted CME treatment and simultaneous biofuel production, along with key objectives and thesis outline.

1.1 Introduction

Water scarcity has risen as a critical threat with a significant negative impact on the sustainability of the ecosystem and human life. Rapidly increasing urbanization, industrialization and global population led to excessive natural resource consumption and acute water scarcity for 40 % of the population worldwide (Mosai et al., 2024). Globally, 700 million people are suffering from the unavailability of clean drinking water. The tremendous environmental pressure is associated with water scarcity, interrupting the synergy between water- food-energy-environment (Schlemm et al., 2024). Because of human population increment and per capita consumption, it is estimated that 30 % increment in water and 50% increment in food resources can fulfill the demand of a potential 9 billion inhabitants by 2050 (UNSDGs, 2022).

All natural resources, such as water, food and energy are deeply interconnected. In the energy sector, coal significantly contributes to global energy supply. Since 2022, increasing oil and gas prices led to fuel switching to coal in power generation (World Energy Outlook, 2023). Considering rising electricity demands aligning with record levels of global coal consumption, coal mining activities are highly accelerated. The coal excavation through opencast mining is the probable reason for generating 20–30% fine and ultrafine coal dust (<1 mm), which may cause a series of negative impacts on the environment as depicted in Fig. 1.1 (Xia et al., 2023). In excessive coal mining, a substantial amount of mine water gets contaminated and accumulates in mine sumps. The coal mine effluent (CME) discharge without any treatment may cause a significant threat to human health and the local aquatic environment (Du et al., 2024). The direct discharge of CME negatively impacts water quality. It causes negative environmental implications in

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different directions, such as groundwater contamination, marine pollution and soil salinization (Fig. 1.2). Further, opencast mining causes the discharge of water with a high concentration of Cu^{2+} , Fe^{2+} , Ni^{2+} and Mn^{2+} due to long-term interaction in between water and rock which involves sulfur-bearing minerals (Mansilha et al., 2021). These processes cause yellow, red or orange sediments and adversely impact water resources and ecosystems. Mine effluents contain high levels of dissolved cations, mainly Na^+ , Mg^{2+} , Ca^{2+} , K^+ and major anions such as HCO_3^- , CO_3^{2-} , Cl^- , F^- , NO_3^- (Mansilha et al., 2021).

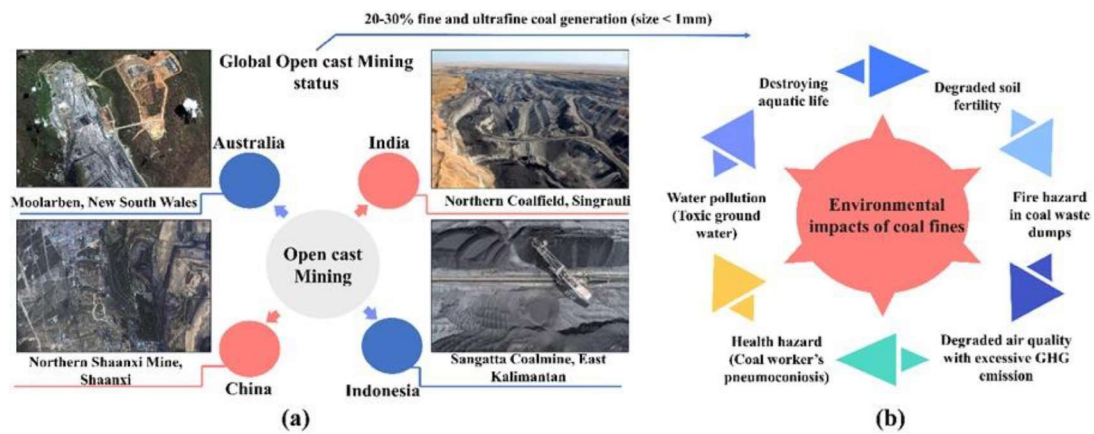


Fig. 1.1 (a) Active coal mines existing in different countries (b) adverse environmental impact of coal fines and water interaction.

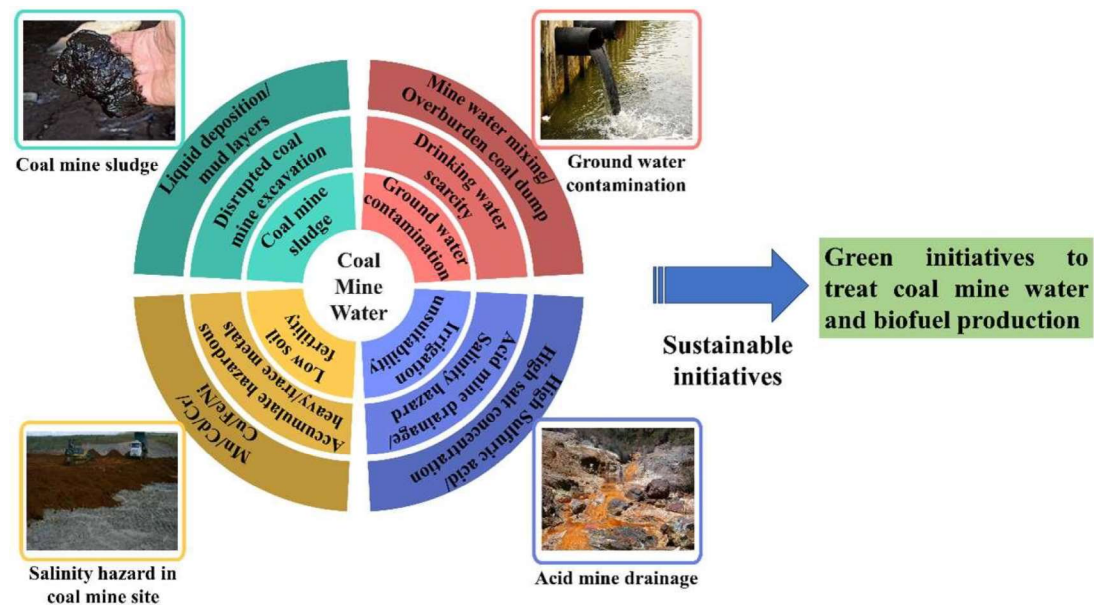


Fig. 1.2 Negative environmental impact of coal mine water drainage.

The CME water enriched with heavy metals and cations can cause crucial problems. Salinity hazards/ high salinity of CME can hinder the transport of nutrients from soil to crop. Infiltration and permeability issues are also associated with CME, which can negatively affect salt infiltration rate and sodium content (Mansilha et al., 2021). Another major concern is the accumulation of specific ions and metals in sensitive crops, which causes plant damage and reduces yields. Further, excessive NO_3^- , HCO_3^- and Fe^{2+} content cause abnormalities in vegetative growth (Lin et al., 2024). Specifically, Fe^{2+} competes with micronutrients in soil and affects plant growth. Irrigation with CME may cause clogging of irrigation equipment and foliar staining due to excess Fe^{2+} and Mn^{2+} ions (Mansilha et al., 2021). In addition to conventional elements, organic pollutants such as polyaromatic hydrocarbon (PAHs) are a source of pollution released to CME due to excessive mining activities and long-term coal storage (Chen et al., 2024). Carcinogenic PAHs and heavy metals may enter the human body through the food chain. The intermixing of heavy metal enriched CME may contaminate groundwater and causes critical health problems, including skin and bladder cancer, kidney problem, liver cirrhosis, hypertension and skin irritation (Wang et al., 2024).

Considering all the above issues, economic and sustainable treatment of CME is crucial to utilize water for irrigation purposes and fulfill water reuse guidelines of the United States Environmental Protection Agency (EPA) as well as the Food and Agriculture Organization (FAO) (Du et al., 2024).

1.2 Conventional strategies for coal mine effluent treatment

Considering salinity hazard as a prime concern in CME, conventional desalination technologies such as electrodialysis, reverse osmosis, membrane distillation, forward osmosis, multi-stage flash distillation and multiple-effect distillation can be applied for efficient water treatment (Sharan et al., 2022). Multi-stage flash distillation and multiple-

effect distillation are considered as thermal-based technologies. Reverse osmosis, high-pressure reverse osmosis and nanofiltration are the main membrane-based technologies. These pressure-driven techniques depend upon membranes with different pore sizes that exclude the passage of salts, microbes and particulate pollutants (Sharan et al., 2022). Thermal- and membrane-based technologies aim to achieve maximum freshwater recovery (Panagopoulos et al., 2024). However, the performance of conventional technologies depends upon the type of water resource, efficiency and economic viability (Panagopoulos et al., 2024). Desalination facilities designed to support single desalination techniques such as reverse osmosis, multiple-stage flash distillation and multiple effect distillation hold limitations of high cost, high energy requirement and lower performance with an aspect of water production capacity (Almasoudi et al., 2024). As an advancement, desalination facilities may be integrated with two or more techniques operating at a single location. These hybrid systems enhance treated water recovery, reduce brine production and lower the cost and energy requirement (Panagopoulos et al., 2024).

1.3 Environmental impacts of conventional treatment

Conventional technologies are energy-intensive and require substantial quantities of fossil fuels for power generation. These processes can directly or indirectly impact the environment. Due to excess fossil fuel application during the process, treatment plant contributes to NO_x , SO_x , CO_x and particulate matter emissions (Panagopoulos et al., 2024). Excess brine production and discharge during membrane-based desalination can negatively impact the marine environment and aquatic life. This liquid waste includes corrosive products, pretreatment chemicals and filter backwash (Eltawil et al., 2009). Hence, it is necessary to investigate the properties of the produced brine before its discharge. Compared to the membrane-based process, thermal-based desalination generates more brine (five times) for a similar plant capacity, which causes negative impacts on

aquatic life. Thermal desalination consumes more seawater due to a lower recovery ratio (Saavedra et al., 2021). The discharged brine temperature is usually 5–15 °C higher than the marine environment and thermal shock results a higher mortality rate in marine aquatic life (Almasoudi et al., 2024).

1.4 Renewable energy technologies integrated with coal mine effluent treatment

Considering the unavoidable negative environmental impacts of conventional treatment technologies, such as fossil fuel dependency, brine discharge problems, excessive greenhouse gas emission (GHGs) and high energy consumption, wastewater treatment technologies are switched towards renewable energy-based processes (Eltawil et al., 2009). Such sustainable energy systems are framed by integrating technical, social, economic and environmental aspects. In the direction of renewable energy driven desalination systems, solar thermal energy harnessed solar stills have been successfully applied to water desalination. Other integrated processes include wind, photovoltaic and geothermal energy for water treatment (Schlemm et al., 2024).

Recently, there have been intense attempts to develop alternative sustainable green techniques for wastewater treatment along with energy production (Wang et al., 2024). One potential approach in this direction is microalgae-assisted CME treatment and harvesting biomass for biofuel production.

1.5 Approach

The present work targeted sustainable and cost-effective means of CME treatment and simultaneous biofuel production using a microalgae platform. The CME enriched with organic/ inorganic compounds and trace metal ions is used as a natural growth medium supplemented with a few essential nutrients termed nutrient supplemented coal mine effluent (NSCME) for mass-scale microalgae cultivation. Two-stage systematic screening was performed to select candidate microalgae from fresh and marine microalgae samples

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to assess the potential of CME bioremediation. In the first stage, fresh and marine microalgae samples cultivated in NSCME were investigated in detail to determine nutrient removal, biomass production, lipid production and biochemical composition. In the second stage, lipid extracted microalgae samples were reinvestigated with aspect of fuel characteristic analysis, thermal behavior and kinetic analysis for bioenergy application. Considering bioremediation potential and biofuel characteristics, *C. pyrenoidosa* (NCIM 2738) was selected as a candidate microalgae to treat NSCME. Further, semi-continuous cultivation of *C. pyrenoidosa* was performed in a reactor scale to investigate NSCME treatment. The hydraulic retention time (HRTs) of 4 d, 6 d and 9 d are considered as operational parameters to investigate nutrient removal as COD and salinity removal efficiency along with growth parameters as biomass and lipid productivity in BCR and ORP. Fatty acid methyl esters (FAME) characterization was conducted to determine the biodiesel applicability of oil. Further, Energy dispersive X-ray spectroscopy (EDS) revealed salt and metal ion deposition on the surface of harvested microalgae samples to investigate the desalination mechanism.

Aiming for a circular economy, the CME treatment combines green energy building and sustainable resource management. Therefore, harvested microalgae biomass was recovered from treated CME as valuable energy feedstock. Further, lipid extracted microalgae residue was co-processed with low rank coal fines to generate green energy with a vision to decarbonize the global energy system. Mechanical and thermochemical energy conversion strategies were applied to produce all energy forms, such as solid, liquid, and gaseous, towards carbon-lean future energy security.

De-oiled microalgae residue as a binder was densified with low rank coal fines to produce biomass-blended coal composites. The multi-objective optimization strategy is used to optimize the molding pressure, average particle size and binder ratio to maximize

the mechanical performance indicators such as compressive strength and drop strength of prepared composites. Further, thermogravimetric analysis, derivative thermogravimetric and differential thermal analysis (TGA-DTG-DTA) are conducted to determine a thermal characteristic of biomass-blended coal composites as solid fuel. An in-depth investigation of the mechanical-thermal aspect of the coal-biomass energy system was crucial to directly applying these composites in thermal power plants as sustainable and affordable fuels.

In the next two stages, co-pyrolysis-based valorization of de-oiled microalgae and low rank coal blend was performed via thermochemical conversion. Initially, response surface methodology (RSM) and artificial neural network-based multi-objective genetic algorithm (ANN-MOGA) were applied to optimize process parameters, i.e., blending ratio and heating rate for enhanced production of hydrogen and methane (hymethane) rich syn gas. Modernization of co-pyrolysis by using ANN-MOGA as an optimization tool may be considered an efficient approach towards worldwide energy transition from fossil fuels to a hydrogen-rich economy. At last, bio-oil production and quality upgradation were explored through co-pyrolysis of low rank coal (CL), de-oiled microalgae (ALG), and their blends (CLALG). In this regard, the ion-exchange method synthesized heavy metal-loaded Cu-Cr-ZSM-5 catalyst. Catalytic and non-catalytic pyrolysis was performed at operating conditions as a temperature – 600 °C, heating rate –10 °C/min and residence time – 60 min. The catalytic and non-catalytic bio-oil was quantitatively estimated through gas chromatography-mass spectrometry (GC-MS) analysis to evaluate bio-oil quality. The strategic developments towards low-cost catalyst preparation, catalyst feed interaction and thermocatalytic cracking were performed, aiming for industrial-scale upgrade of bio-oil to engine fuels.

1.6 Objectives

Following a thorough review of the literature and identified research gap outlined in Chapter 2, the objectives of the study were determined which are:

❖ **Screening and selection of candidate microalgae based on coal mine effluent bioremediation and thermal properties assessment**

- a) Screening and comprehensive characterization of fresh and marine microalgae cultures in NSCME.
- b) Fuel characteristic analysis by using physicochemical properties of fresh and marine microalgae cultures.
- c) Thermal decomposition analysis based on TG-DTG profiles of microalgae at a different heating rate.
- d) E_a estimation by a model-fitted and model-free approach.
- e) New hybrid deep neural network (DNN) model design to predict and verify TGA data of microalgae pyrolysis.

❖ **Coal mine effluent treatment by semi-continuous cultivation of candidate microalga in reactor scale**

- a) Reactor scale study through semi-continuous cultivation of candidate microalgae to investigate nutrient removal and lipid production.
- b) Biodesalination and heavy metal remediation from NSCME using candidate microalgae.
- c) Large scale implementation strategy of developed water treatment process at coal mine site using microalgae platform.

❖ **Co-investigation of mechanical performance and thermal behavior of de-oiled microalgae blended coal composites.**

- a) Selection and pre-processing of waste feedstock followed by fuel characterization using proximate and ultimate analysis.
- b) Individual and multi-objective optimization study using RSM to formulate composites of high compressive and drop strength at optimized binder ratio and particle size of feedstock material.
- c) Impact of mechanical strength optimizing parameters upon thermal decomposition behavior of processed raw material and composites.
- d) TGA-DTG-DTA of raw coal, microalgae and optimized coal composites.
- e) ANN modelling and validation of thermal profiles of coal, microalgae and multi-objective optimized composites.

❖ **Hydrogen and methane rich syngas emission analysis through co-pyrolysis of low-rank coal and de-oiled microalgae biomass**

- a) Real-time syngas emission analysis during pyrolysis of coal and de-oiled microalgae feedstocks at different blending ratios and heating rates.
- b) Optimization of process parameters using statistical and ANN-MOGA model to maximize hydrogen carrying ratio at three different characteristic temperatures.
- c) Analysis of syngas product distribution (H_2 , CH_4 , CO and CO_2) at different pyrolysis stages.

❖ **Co-pyrolysis of low rank coal and de-oiled microalgae biomass for bio-oil production using synthesized catalyst**

- a) Novel bimetallic Cu and Cr incorporated ZSM-5 catalyst synthesis and characterization.
- b) Product yield distribution of bio-oil from noncatalytic and catalytic pyrolysis.
- c) Comparative quality estimation of bio-oil from noncatalytic and catalytic pyrolysis.

- d) Possible reaction mechanism proposal for catalytic upgradation of bio-oil applying synthesized Cu-Cr-ZSM-5 catalyst.

1.7 Thesis outline

The thesis has been outlined in six chapters as follows:

Chapter 1: This chapter deals with the rising concern about clean water and energy scarcity, influence of coal mining activities upon discharged water quality and negative impact of untreated CME on human health and the local aquatic environment. Further, conventional treatment technologies and their limitations are explored along with outlines and objectives of the study.

Chapter 2: This chapter focuses on the physicochemical characteristics and heavy metal concentration of some representative coal mines. In first stage, biological, specifically microalgae mediated wastewater treatment are explored. The role of microalgae and mechanism of biodesalination and heavy metal removal from saline wastewater sources is highlighted. Integrating with bioenergy application and circular water economy concept, microalgal biomass from water treatment system and low rank coal fines from coal mines are considered as potential fuel feedstocks. In this direction, biochemical conversion (transesterification), thermochemical conversion (pyrolysis/gasification) and mechanical conversion processes are described for sustainable fuel production. Then, research gap is identified after an extensive review of the literature.

Chapter 3: This chapter deals with CME sampling, physicochemical characterization, irrigation suitability guidelines and systematic screening of candidate microalgae strain for CME treatment and biofuel production. Nutrient removal potential and growth kinetics are considered as decision parameters to evaluate CME treatment potential of microalgae samples. Secondly, suitability of cultivated microalgae samples as fuel feedstock is

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investigated based on fuel characteristic analysis. Further, thermal kinetic analysis and kinetic modelling is performed to select most suitable microalgae for bio-fuel production.

Chapter 4: This chapter focuses on the semi-continuous cultivation of candidate microalgae isolate in a reactor scale as BCR and ORP to investigate NSCME treatment. Simultaneously, lipid extraction from dried algal powder and transesterification is explored to extract FAMES. Outdoor large-scale microalgae cultivation is planned at coal mine sites for 30–35 yr lifespan targeting sustainable water treatment.

Chapter 5: This chapter presents the densification of de-oiled microalgae with low-rank coal as blended composite. The fuel characteristic analysis, mechanical performance and thermal behavior of blended composites are investigated.

Chapter 6: This chapter delivers co-pyrolysis of de-oiled microalgae and low-rank coal blends to generate hydrogen and methane rich syngas, strategic optimization of process parameters to maximize hydrogen carrying ratio at three different characteristic temperatures, pyrolysis kinetic modeling to evaluate apparent E_a and detail analysis of syngas product distribution (H_2 , CH_4 , CO and CO_2) at different pyrolysis stages.

Chapter 7: This chapter provides a catalytic co-pyrolysis of de-oiled microalgae and low-rank coal blend for high quality bio-oil production. It explores catalyst synthesis, characterization, quality estimation of non-catalytic/catalytic pyrolysis derived bio-oil and catalytic co-pyrolysis mechanism.

Chapter 8: This chapter concludes the significance of the current study and provides insights into future perspectives.