

Preparation and characterization of seaweed and steel slag composite for agricultural application

Submitted in partial fulfillment of the requirements for the award of
Bachelor of Technology degree in Chemical Engineering

By

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**DEPARTMENT OF CHEMICAL ENGINEERING
SCHOOL OF BIO AND CHEMICAL**

**SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Accredited with Grade "A" by NAAC
JEPPIAAR NAGAR, RAJIV GANDHI SALAI, CHENNAI – 600 119**

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BONAFIDE CERTIFICATE

This is to certify that this project is a bonafide work of **ABDUL RAHMAN MARICAR (37190001)** who carried out the project entitled "**PREPARATION AND CHARACTERIZATION OF SEAWEED AND STEEL SLAG COMPOSITE FOR AGRICULTURAL APPLICATION**" under our supervision from September 2020 to March 2021

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DECLARATION

I, Abdul Rahman Maricar (37190001) hereby declare that the project entitled "Preparation and characterization of seaweed and steel slag composite for agricultural application" done by us under the guidance of Dr.Joshua Amarnath and Dr.K.Govindaraju at Jeppiaar Research Park, Sathyabama Institute of Science and Technology is submitted in partial fulfillment of the requirement for the award of bachelor of technology in chemical engineering

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SIGNATURE OF CANDIDATE

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ABSTRACT

The world steel production touched 1,869 MT in 2019. During the iron- and steelmaking processes, several by-products are produced, such as slags, dusts, mill-scales and sludges. By providing 1 tonne of the by-product productions, on average for one tonne of steel 200 kg (in the scrap-based steelmaking) and 400 kg (in the iron ore-based steelmaking) of by-products are produced. Over the past decades, steel production has increased and consequently, the higher volume of by-products (slag) generated necessitates its efficient recycling. In order to mitigate environmental consequences caused by the disposal of a large quantity of slag at landfill sites and to reduce the transportation cost for disposal of slag, steel industries encourage sustainable use of slag in different fields of application, such as in agriculture. Slags are rich in silica, calcium oxide, magnesium oxide and iron oxides. These beneficial properties of the slag can be exploited to improve agricultural productivity. Seaweeds are macroscopic marine algae, which form an important component of the marine living renewable resources. Application of seaweed to manage soil fertility is a traditional practice in many coastal regions, utilizing an inexpensive, abundant, and nutrient-rich resource. Seaweed fertilizers which obviously more effective for plant growth are proved, and the source of seaweeds is harbour and abundant to sustain the fertilizer use without environmental pollution. In the present project, characterization of Induction Furnace Steel Slag using XRD for mineralogical phase's identification, XRF for distribution % of metal and metal oxides, SEM equipped with EDAX for surface morphology and elemental distribution and FTIR for functional groups analysis. Further, preparation of seaweed and steel slag composites [seaweed (100 %), 25 %: 75 % (seaweed: IF slag), 50 %: 50 % (seaweed: IF slag), 75 %: 25 % (seaweed: IF slag), IF (100 %)] and used for seed germination and seedling growth of *Vigna radiata*. Among various composites, 25 %: 75 % (seaweed: IF slag) showing better seedling growth was identified.

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CHAPTER-1: INTRODUCTION

1.1. STEEL SLAG AND TYPES

The utilization of industrial by-products (waste) is a most important challenge globally and hence, in the present research towards the effective management/utilization of industrial by-products is gaining more importance. Slag from steel industry is an industrial byproduct which is generated during steel production by various process majorly involving Electric Arc Furnace (EAF), Blast Furnace (BF) and Induction Furnace (IF). Steel slag (Ss) is one among the industrial by-products available in large quantity and is utilized by the researchers for the following; hazardous ions uptake (Jha et al., 2004), organic pollutants degradation (Zhang et al., 2012), CO₂ sequestration (Yadav et al., 2017), increase crop production (Syeda and Humari, 2014), production of vitreous ceramic tiles (Sarkar et al., 2010) and in concretes (Rondi et al., 2016).

1.2. CHARACTERISTICS OF STEEL SLAG

1.2.1. Physical characteristics

The particle size distribution of steel slag is the most significant physical feature for use as an agricultural liming medium. The smaller the particle, the more reactive it is in neutralizing acidity in the soil. The high proportion of material passing 20 mesh or finer in the White et al. (1937) research shows that these slags were either pre-screened or ground, as in the case of the 20 mesh slag. In comparison to agricultural limestone (2.7-2.9 and 1.4-1.5 g/cm³, respectively), steel slags have high individual gravities (3.2-3.6 g/cm³) and bulk densities (1.6-1.9 g/cm³). As a result of residual metal in the slag, this occurs.

1.2.2. Chemical composition

Steel slags contain many of the same chemical compounds found in Portland cement. They contain calcium silicate and some free CaO and MgO. Chemical composition of steel slag from open hearth and the basic oxygen process is given in Table 1.1.

Table 1.1: General chemical characteristics of steel slag

Constituent	(% by wt.)
CaO	40-52
SiO ₂	10-19
Al ₂ O ₃	1-3
MgO	5-10
Fe(FeO or Fe ₂ O ₃)	10-40
MnO	5-8
TiO ₂	0.5
P ₂ O ₅	0.5-1
Free CaO	2.1
Metallic Fe	0.5-1.0

1.3. IMPORTANCE OF SEaweEDS IN AGRICULTURE

Seaweed extracts (SE) are currently commonly used as plant biostimulants, which are described as "any substance or microorganism added to plants with the goal of improving nutrition yield, abiotic stress tolerance, and/or crop quality traits, regardless of nutritional content. Seaweed extracts account for more than a third of the global biostimulant market, with a forecasted volume of 894 million Euro in 2022. Furthermore, seaweeds or macroalgae are thought to include about 10,000 species, which are classified into three groups based on pigmentation: Phaeophyta (brown), Rhodophyta (red), and Chlorophyta (green) (Green). The biochemical structure of seaweed extracts is complex (polysaccharides, minerals, vitamins, antioxidants, pigments, hormones). As a result, deciphering their mechanism of action is complex and sometimes necessitates a multidisciplinary approach owing to the various interactions between large amounts of bioactive compounds within a single extract. SE may be used as a soil or foliar mist. Marine macro algae *Kappaphycus alvarezii* is rich in fucoids, sulphated polysaccharides and is reported to be used as a food ingredient, animal food and fertilizer. A wide range of biological properties which

including, anti-bacterial (Arivuselvan et al., 2011), anti-inflammatory (Ananthi et al., 2011), antioxidant and anti-coagulant (Vijayabaskar et al., 2011), properties have been reported (Kelman et al., 2012). Marine algae-based materials seem to be the potential candidates for preparing eco and bio-compatible composite due to their non-toxic phytochemical constitutes, economically viable, flexibility and easy in reaction parameters as compared to chemical and physical synthesis methods (Singaravelu et al., 2007; Govindaraju et al., 2009).

1.4. AGRICULTURAL APPLICATION OF STEEL SLAG

Steel slag, an inevitable by-product of iron and steel manufacturing, may soon make its way into agricultural land as a soil nutrient, reducing India's reliance on imported fertilizers. India, the world's third-largest steelmaker, manufactures more than 12 million tonnes of slag per year, but just around 20% of it is used in the cement industry, with the rest piling up at steel mills, while countries like the United States and Japan use slag extensively (more than 70% of the output) in areas like housing and road building, ground and mine filling. The steel ministry has asked the agriculture ministry to look into the feasibility of using these slags, especially in areas with acidic soils and low productivity, such as the eastern part of the country. Acid soils occupy 49 million hectares of India's 142 million hectares of arable land. The use of steel slag can be one of the most environmentally friendly solutions, since it may aid in the treatment of soil for improved crop yields at a low cost, as well as prevent the production of significant wastes in steel plants.

Over the last decades, with the increase in iron/steel production, the higher amount of by-product (slag) generated draw attention to re-use it in an increasingly well-organized way. In recent decade, few studies revealed that slag-based fertilizer used for agriculture applications to improve crop productivity (Wang et al., 2015), mitigate greenhouse gas emissions (GHG) (Gwon et al., 2018), alleviate soil-acidification (Branca and Colla, 2012), and heavy metal stabilization of contaminated soils (Ning et al., 2012), which turns it into a high value-added product in sustainable agriculture production. On the other hand, long-term and continuous cultivation of rice to meet the growing food demand constantly depletes micronutrients in

agricultural fields (Wang et al., 2015), which necessitates the micronutrients fertilizer amendment in agricultural cropping systems for sustainable crop cultivation.

Evidence to date suggests that micronutrients directly involved in regulation of cell functions, increases physical strength of leaves and leaf-sheaths and help plant to sustain yield by counteracting stress and increasing photosynthesis (Ma and Yamaji, 2015). The beneficial roles of micronutrients rich fertilizer to improve biotic and abiotic stresses and to improve crop productivity (Meharg and Meharg, 2015; Luyckx et al., 2017).

1.5 IMPORTANCE OF SEED PRIMING AND SEEDLING GROWTH IN AGRICULTURE

In viable agriculture, fast and uniform seed germination and seedling appearance are important parameters of successful stand establishment. Seed priming has been found to be useful for promote seed quality, seedling organization, crop yields and increasing environmental stress tolerance (Chen and Arora, 2013; Ibrahim, 2016). Seed priming can improve the germination of under adverse environmental condition, aged, weak and damaged seeds (Dragicevic et al., 2013). A variety of priming agents have been widely used which includes, water, nutrients, inorganic salts, polyethylene glycol etc (Butler et al., 2009; Horii et al., 2007; Hussain et al., 2015). Nevertheless, the priming solutions have effectiveness, different properties. Further, optimization of effective priming agents is required for all crops species (Horii et al., 2007). Therefore, there is a growing need to develop new and potent priming agents to enhance seed germination of agriculture crop plants. Recent decade, metal and metal oxide materials copper (Taran et al., 2017), iron (Panyuta et al., 2016), iron pyrite (Srivastava et al., 2014), zinc (Taran et al., 2017), metal oxides nanoparticles such as titanium-di-oxide (Zheng et al., 2005), zinc oxide (Prasad et al., 2012; Latef et al., 2017), cerium oxide (Zhao et al., 2012), iron oxides (Li et al., 2016) have been used for priming agents for enhancing the seed germination, seedling growth, physiological effects and stress tolerance in crops. In the present project, provides new insights to understanding of IF slag and seaweed composite fertilizer effects on germination and seedlings growth of green gram *Vigna radiata*.

CHAPTER-2: REVIEW OF LITERATURES

2.1. OVERVIEW OF STEEL SLAG

In 2019, global steel production reached 1,869 MT. Several by-products, such as slags, dusts, mill scales, and sludge, are created during the iron and steelmaking processes. Through giving some estimates on by-product productions, it is estimated that 200 kg (in scrap-based steelmaking) and 400 kg (in iron ore-based steelmaking) of by-products are produced on average per one tonne of steel. Slags are iron and steel by-products that are processed in the largest quantities, with a global average recovery rate ranging from over 80% (steelmaking slag) to nearly 100% (steelmaking slag) (iron making slag). Steel production has increased in recent decades, and the increased amount of by-products (slag) produced necessitates efficient recycling. Steel companies promote sustainable use of slag in multiple areas of use, such as agriculture, to alleviate environmental effects caused by the dumping of a significant quantity of slag at landfill sites and to minimize shipping costs for slag disposal (Chand et al., 2015). Silica, calcium oxide, magnesium oxide, and iron oxides are abundant in slags. The slag's beneficial properties can be used to improve agricultural production. Appropriate nutrient supply, for example, has been proposed to enhance tissue rigidity and boost plant photosynthesis capability, crop output, and biotic and abiotic stress tolerance (Das et al., 2020). Steel slag wastes are used in agriculture all over the world to improve soil fertility. Converter slag is used to make siliceous fertilizer, phosphorus fertilizer, and micronutrient fertilizer in developing countries such as Germany, the United States, France, and Japan (Wu et al., 2005). In acidic soil, some research was conducted using pulverized slag to grow various vegetables and crops such as tomato, potato, onion, spinach, and wheat (Maslehuddin et al., 2003).

2.2. STEEL SLAG AVAILABILITY IN INDIA AND ITS COMPOSITION

Steel is produced in one of two ways: using iron ore as a raw material in a blast furnace for iron processing, basic oxygen steelmaking (BOF) for steel conversion, and secondary metallurgical process (SMP) for steel refining; and using

scrap as a raw material in an electric arc furnace for steel production and secondary metallurgical process (SMP) for steel refining.

Slags are grouped into three categories: BF slag, BOF slag, and SMP slag. Due to the lower generated volume, the BF slag accounts for about twice the amount of BOF slag, and the SMP slag is comparatively less important in terms of consumption (Meng and Liu, 2000; Das et al., 2007; Wu et al., 2007; Shen et al., 2009). The Linz-Donawitz process generates LD (Linz-Donawitz) slag during the steelmaking or pig iron processing processes in oxygen converters. One of the most critical wastes of all integrated steel plants is LD converter steel producing slag. In India, the overall production rate of LD slag is 150-180kg/t of crude steel (Yadav et al., 2002). SAIL produces 1.28 MT per year (Basu, 2002), and global demand is about 47 MT per year (Takano et al., 2001). Steel melting slag is generated at a rate of over 4 to 4.5 MT per year. In India, just 25% of this is recycled, compared to 70-100 percent in other countries (Umadevi et al., 2010). It has been discovered that 50% of slag is used for road construction, sintering, and iron-making processing in steel plants (Gao et al., 2011).

The composition of stainless steel slag obtained from Taiyuan Iron and Steel (Group) Co., Ltd., Taiyuan, Shanxi, was quantified by Zhuo et al. (2012). The stainless steel slag was alkaline (pH 13.96), with large amounts of CaO (51.84 %), FeO (6.17%), Al₂O₃ (4.39%), MgO (9.74%), MnO (0.29%), S (0.18%), SiO₂ (28.2%), and TiO₂ (0.35%); the apparent density, porosity, surface region, and most likely pore size of stainless steel slag is 2.88 g cm⁻¹ (Ziemkiewicz, 1998).

Steel slag, according to Pettinato et al. (2015), is a complex heterogeneous substance consisting predominantly of total iron (43.14 %), CaO (35.43 %), SiO₂ (10.08 %), Al₂O₃ (3.24 %), MnO (2.52 %), and MgO. (2.06 %). The XRD analysis also revealed that the major constituents of slag were iron and calcium oxides. The specific surface area and pore size of steel slag, according to the Brunauer, Emmett, and Teller (BET) data, are SBET= 12.56 m²/g and 794 nm, respectively.

Ghataora (2015) estimated the chemical composition of refined BOS slag aggregate to be 42–44 % CaO, 27–31 % Fe₂O₃, 10–12 % SiO₂, 5–6 %t MgO, 3–4 % Mn₃O₄, 1.2 % P₂O₅, 1.2 % Al₂O₃, and 0.5 % TiO₂.

BOS slag is usually di-calcium silicate (bredigite) (2CaO.SiO₂), with up to 12% other elements (e.g., Mn, Fe, Mg) present, tri-calcium silicate (3CaO.SiO₂), free lime (CaO), wustite (FeO), calcium ferrite (also di-calcium ferrite and calcium aluminoferrite), and minor concentrations of per (solid solution of FeO and MgO).

2.3. STEEL SLAG UTILIZATION AS FERTILIZER SOURCE

Iron (Fe) chlorosis can affect a wide range of crops grown on calcareous soils, resulting in significant yield losses. In most cases, it has been corrected by adding Fe synthetic chelates, but these are very pricey. Several studies have focused on using various Fe sources to reduce the economic burden and recycle some industrial by-products, such as converter slag (Wallace et al., 1982; Sikka and Kansal, 1994). They are used as a source of essential plant nutrients such as P, K, Mg, and Fe oxides, as well as a soil amendment. The application of a steel by-product (dust containing 430 g Fe kg⁻¹) as fertilizer to alkaline soils, with or without sulphuric acid, improved sorghum dry matter production, according to a 1984 report (Anderson and Parkpian, 1984). Fe chlorosis in corn and alfalfa has been corrected using a related treatment containing a combination of sulphuric acid and iron sulphates (Stroehlin and Berger, 1963). Although converter sludge has been successfully used as a Fe fertilizer in calcareous soils, the use of converter slag as a Fe fertilizer source in some calcareous soils incubation studies has led to the use of waste sludge.

Steel slag was tested at various rates with corn as an iron fertilizer in Fe deficient calcareous soils by Xian and Sheng (2006). Moderate rates of slag or acidified slag (10 and 20 g kg⁻¹) significantly improved corn dry matter yield and Fe absorption, according to the findings. Steel slag application improved the extractable Fe concentration of ammonium bicarbonate-diethylene triamine penta acetic acid (AB-DTPA) in the soils. The rise in extractable Fe was generally proportional to the rate of use, and was supported by slag acidification. Steel slag proved to be a

promising and low-cost source of Fe for reducing crop Fe chlorosis in calcareous soils with low Fe levels.

According to Wang et al. (2014), steel slag fertilizer, a by-product of the steel industry with a high concentration of active iron (Fe), was applied at rates of 0, 2, 4, and 8 Mg ha⁻¹ in subtropical rice (*Oryza sativa* L.) paddy fields in China to determine the impact of steel slag amendment on CH₄ emissions as well as rice growth and yield characteristics.

The application of steel slag fertilizer greatly improved Fe concentrations in paddy soils, according to the findings. Steel slag modification in paddy fields decreased CH₄ output substantially, resulting in lower total CH₄ emissions. Total CH₄ emissions during rice cultivation decreased by 26.6, 43.3, and 49.3 percent, respectively, while steel slag was applied at rates of 2, 4, and 8 Mg ha⁻¹. Steel slag amendment has had a major positive impact on rice crop yield and percentage of ripened grain, most likely due to improved supply of inorganic nutrients including silicate and manganese.

Wang et al. (2017) reported, in a paddy field in subtropical China, the effects of steel slag amendment on nutrient distribution, stoichiometry, and rice production. Higher available N and P in the soil, a lower available-N: available-P ratio, and higher available Ca and Si concentrations were all linked to amendment. High yields were associated with increases in P, Ca, and Mg supply. High yields under steel slag amendment were also linked to high foliar and stem N and P concentrations, lower N: P ratios, and high shoot/root N and P concentration ratios, all of which are traits correlated with healthy habitats that can sustain fast-growing plants. The favorable relationship between steel slag application and yield was due in part to an indirect influence of increased soil Ca, Si, and P supply, both of which were positively associated with yield. By increasing nutrient supply, changing soil and plant stoichiometry, and moving stem:root nutrient distribution, steel slag amendment improved plant growth and yield in this paddy field.

Das et al. (2020) reported that the effect of the LD slag amendment on soil quality (measured by soil physicochemical and biological properties), plant nutrient

uptake, and the strengthening of associations between nutrient uptake and soil bacterial populations. The soil bacterial population was studied using 16 S rRNA illumine sequencing, and soil enzymes involved in C, N, and P cycling were studied using the APIZYM assay. Under flooded conditions, 2 Mg ha⁻¹ of LD slag was added to Japonica and Indica rice. Regardless of cultivar, the LD slag modification increased soil pH, plant photosynthesis, soil nutrient supply, and crop yield. Rice straw absorption of N, P, and Si was greatly improved.

The slag amendment increased soil microbial biomass and enzyme activity, as well as enriching some bacterial taxa with copiotrophic lifestyles and the ability to provide ecosystem services to the plant. The study found that adding LD slag to rice cropping systems for a short time improves soil physicochemical and biological status, as well as crop yield.

CHAPTER-3: MATERIALS AND METHODS

3.1. INDUCTION FURNACE (IF) STEEL SLAG SAMPLE COLLECTION AND PREPARATION

Induction Furnace (IF) slag materials was obtained from Jeppiaar Furnace and Steels, Pvt. Ltd. (JFASPL), Kanchipuram, Tamil Nadu. Collected slag materials were subjected ball milling process for size reduction (Figure 3.1a&b).



Figure 3.1: shows induction furnace (IF) steel slag (a) stone form; (b) powder form

3.2. CHARACTERIZATION OF INDUCTION FURNACE (IF) STEEL SLAG

3.2.1. X-ray diffraction (XRD)

Mineralogical phases of IF slag material were determined using X-ray diffraction (XRD) patterns. XRD patterns were recorded on an X-ray powder diffractometer (BRUKER AXS, D8 Discover) operated at a voltage of 40 kV and a current of 30 mA with CuK α 1 radiations.

3.2.2. X-ray fluorescence (XRF)

The IF slag sample were characterized using X-ray fluorescence (XRF) (XRF, Bruker) for major chemical composition.

3.2.3. Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopic (EDAX)

The surface morphological studies of IF slag material was measured by scanning electron microscope (Supra 55-Carl Zeiss, Germany) equipped with Energy dispersive X-ray spectroscopic analysis (EDAX) was performed to analyze the elemental composition.

3.2.4 Fourier Transform Infrared (FT-IR)

Fourier Transform Infrared (FT-IR) spectra was recorded employing KBr pellet method for the IF slag material to identify the functional groups present in the material using Shimadzu IR Affinity-1S FT-IR spectrophotometer in the range of 3500 - 450 cm^{-1} .

3.3. COLLECTION OF SEAWEED AND PREPARATION

Red algae (Seaweed) *Kappaphycus alvarezii*, were collected from Mandapam Camp, South East Coast of Tamil Nadu. The algal samples were thoroughly washed with tap water and then distilled water to remove the associated biota, salt and other debris. Further, shade dried and powdered using an electric blender for further use (Figure 3.2a&b).



GPS

Latitude	12; 52; 17.3312389999991
Longitude	80; 13; 34.96871899999967529

Figure 3.2: shows induction furnace (IF) steel slag (a) stone form; (b) powder form

3.4. PREPARATION OF IF SLAG AND SEAWEED COMPOSITES

Different composition of IF slag and seaweed powder [seaweed (100 %), 25 %: 75 % (seaweed: IF slag), 50 %: 50 % (seaweed: IF slag), 75 %: 25 % (seaweed: IF slag), IF (100 %)] were used for seed priming assay.

3.5. SEED GERMINATION TEST

Seed germination assay were carried out in quadruplicate using 25 seeds each was analyzed (treated and untreated seeds) in petriplate method as per the rules of International Seed Testing Association. Briefly, all control and experimental seeds were subsequently transferred into sterile petriplates with sterile river soil and 10 seeds/plate were kept in room temperature with 12 h dark and 12 light cycles. The test condition 25 ± 2 °C and 95 ± 3 % RH were maintained in germination room. Numbers of normal seedlings were counted and mean arrived, calculated and expressed as %. The experiment was performed in triplicates.

3.6. ROOT LENGTH

Randomly selected 10 normal seedlings was taken from standard germination test at 10th day were measuring the primary root length. For primary root length was measured from the collar region to the tip of the primary root. The mean was calculated and expressed in mille meter (mm).

3.7. SHOOT LENGTH

Control and experimental seedlings at 10th day used for the measurement of shoot length. The shoot length was measured from the collar region to the growing tip of the shoot. The mean was calculated and expressed in mille meter (mm).

3.8. SEEDLING VIGOR

Vigor index was calculated by method suggested by Abdul-Baki and Anderson (1973) and expressed results as whole number.

Vigor index = Germination (%) × seedling length

CHAPTER-4: RESULTS AND DISCUSSION

Agriculture is now-a-days greatly impacted by climatic change issue which is aggregated by global warming, urbanization and unbalanced use of resources and environmental problems like eutrophication and run off, related to use of conventional chemical fertilizers. Extensive application of chemical fertilizers results in an irreparable damage to the soil structure, mineral cycles, soil microbial flora, plants, and even more on the food chains across ecosystems leading to transmissible mutations in future generations of consumers. To combat with this situation, there is need to introduce new fertilizers based of steel slag and slow-release matrix which provide nutrients to plants slowly thereby reducing nutrient loss and promoting enhanced crop yield.

4.1. X-RAY DIFFRACTION (XRD) and XRF STUDIES

Mineral composition cubic centered phases of components present in IF slag were identified using XRD analysis (Fig.4.1). The presence of major mineral compositions cubic centered phases in IF slag material is quartz (SiO_2 , 2θ value 26.6), iscorite ($\text{Fe}_7\text{SiO}_{10}$, 2θ values of 50.32 and 60.30), almandine ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, 2θ values of 22.20 and 68.48) and hematite ($\epsilon\text{-Fe}_2\text{O}_3$, 2θ values of 36.7 and 39.94). Also, some of minor peaks with less intensity have been identified and is similar to the results reported previous studies (Yildirim and Prezzi, 2015; Nicolae et al., 2007). Other minor phases in IF slag materials is manganocalcite $[(\text{Ca},\text{Mn})\text{CO}_3]$, 2θ value 29.73], merwinite $[\text{Ca}_3\text{Mg}(\text{SiO}_4)_2]$, 2θ values of 31.69 and 34.92], periclase (MgO , 2θ value 46.12) and mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, 2θ value of 55.07) (Yildirim and Prezzi, 2015). Iron silicates, FeSiO_4 (2θ value of 35.10) and FeSiO_{10} (2θ value of 51.48) are along with MnO_2 (2θ value of 42.74) and are also present in IF slag material, and the similar results have been reported previously (Nicolae et al., 2007).

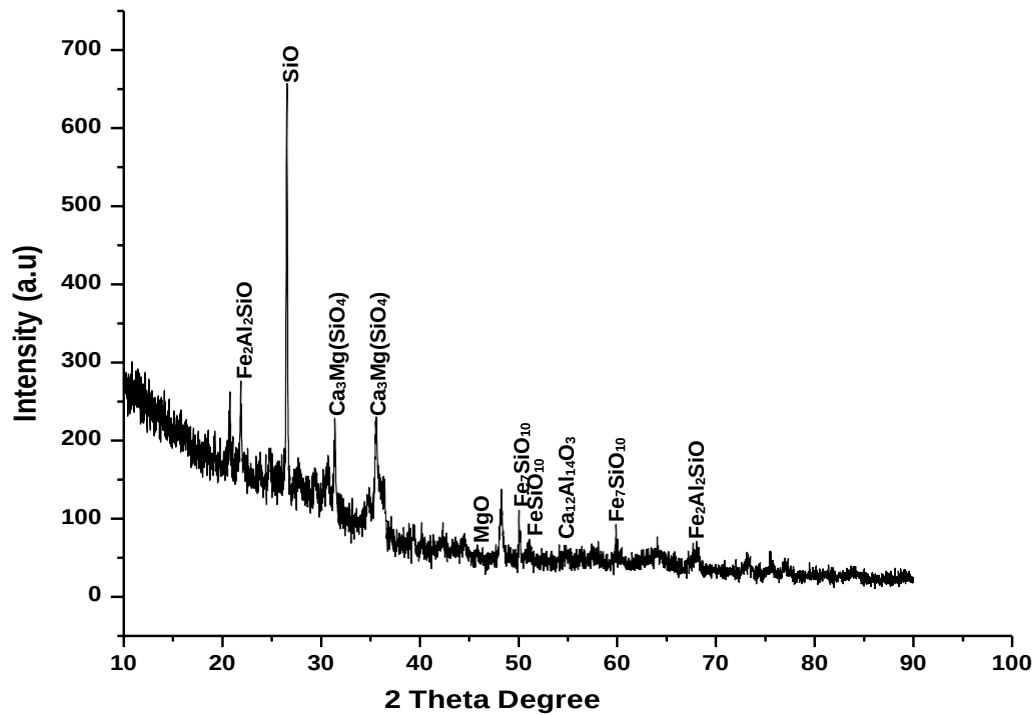


Figure 4.1: shows X-ray Diffraction (XRD) of induction furnace (IF) steel slag

The presence of various metal oxides composition in steel slag has been analyzed using XRF technique and is shown in Figure 4.2 and Table 4.1. The major metal oxides present in slag are Fe_2O_3 (25.739%), MgO (1.893%), Al_2O_3 (1.606 %), MnO_2 (23.794 %), and SiO_2 (7.570 %).

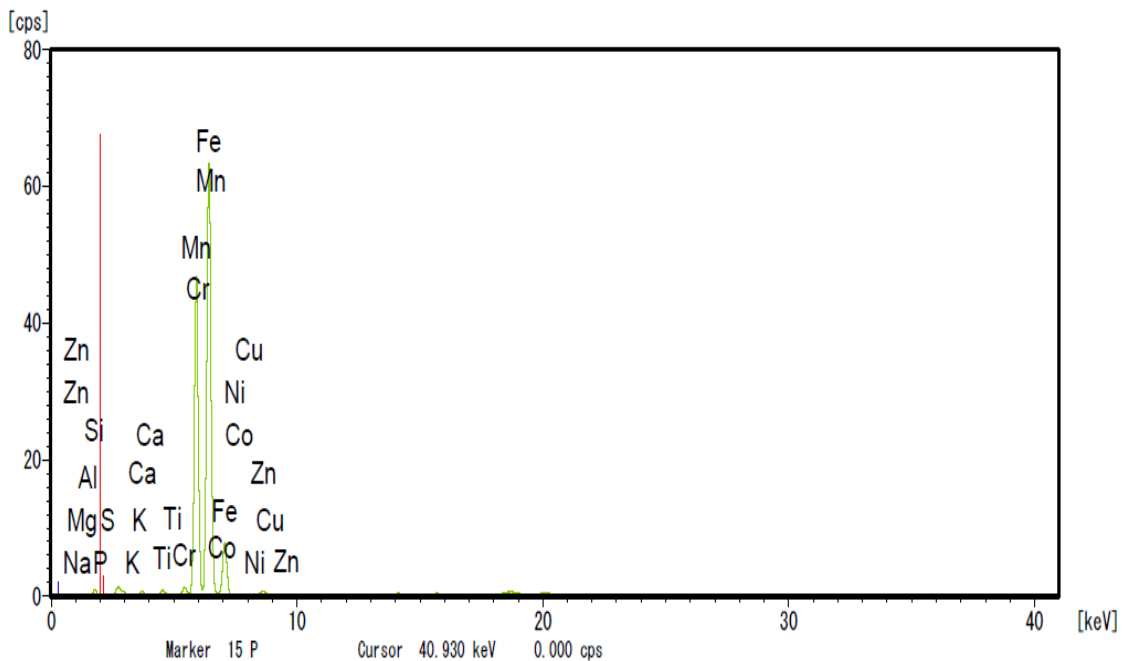


Figure 4.2: shows XRF analysis of induction furnace (IF) steel slag

Table 4.1: shows Element's mass (%) present in the induction furnace (IF) steel slag

Elem.	Line	Mass [%]	2sigma [%]	Atomic [%]	Intensity [cps/mA]	Formula	Mass [%]	Molecule [%]
11	Na K	0.000	3.592	0.000	0.00	Na2O	0.000	0.000
12	Mg K	1.893	2.650	2.119	0.23	MgO	3.138	7.205
13	Al K	1.606	0.587	1.621	1.08	Al2O3	3.035	2.755
14	Si K	7.570	0.695	7.337	13.55	SiO2	16.194	24.943
15	P K	0.042	0.113	0.036	0.15	P2O5	0.095	0.062
16	S K	0.040	0.061	0.034	0.35	SO3	0.101	0.117
19	K K	0.086	0.051	0.060	0.94	K2O	0.104	0.102
20	Ca K	0.676	0.076	0.459	11.17	CaO	0.946	1.561
22	Ti K	0.398	0.048	0.226	11.82	TiO2	0.664	0.769
24	Cr K	0.481	0.051	0.252	20.19	Cr2O3	0.703	0.428
25	Mn K	23.794	1.635	11.791	867.21	MnO2	37.653	40.085
26	Fe K	25.739	1.768	12.546	1089.96	Fe2O3	36.800	21.327
27	Co K	0.001	0.055	0.000	0.01	CoO	0.001	0.001
28	Ni K	0.008	0.050	0.004	0.15	NiO	0.010	0.012
29	Cu K	0.017	0.049	0.007	0.38	CuO	0.021	0.024
30	Zn K	0.430	0.069	0.179	10.80	ZnO	0.536	0.609
8	O	37.219	2.650	63.328				

4.2 SCANNING ELECTRON MICROSCOPY (SEM) WITH ELECTRON DISPERSIVE X-RAY SPECTROSCOPIC (EDXA), FOURIER TRANSFORM INFRARED (FT-IR) AND X-RAY FLOURESCENCE

The morphology of the IF slag material has been investigated by SEM and observed that the IF slag material possess a quasi-spherical shape. The diameter of the poly-dispersed IF slag material and facets on the surface structures appear very smooth and are clearly discriminable (Figure 4.3a&b). EDX spectroscopy of the IF slag material sample indicates the presence of Zn, Al, Si, Mg, C and O composition (Figure 4.3c&d).

FTIR spectroscopy analysis was performed to identify the surface structure of the IF slag material. IR spectra of the IF slag material, the major bands at 3717, 2935, 1547, 1315, 1133, 961, 795 and 465 cm^{-1} observed in the spectrum (Figure 4.4).

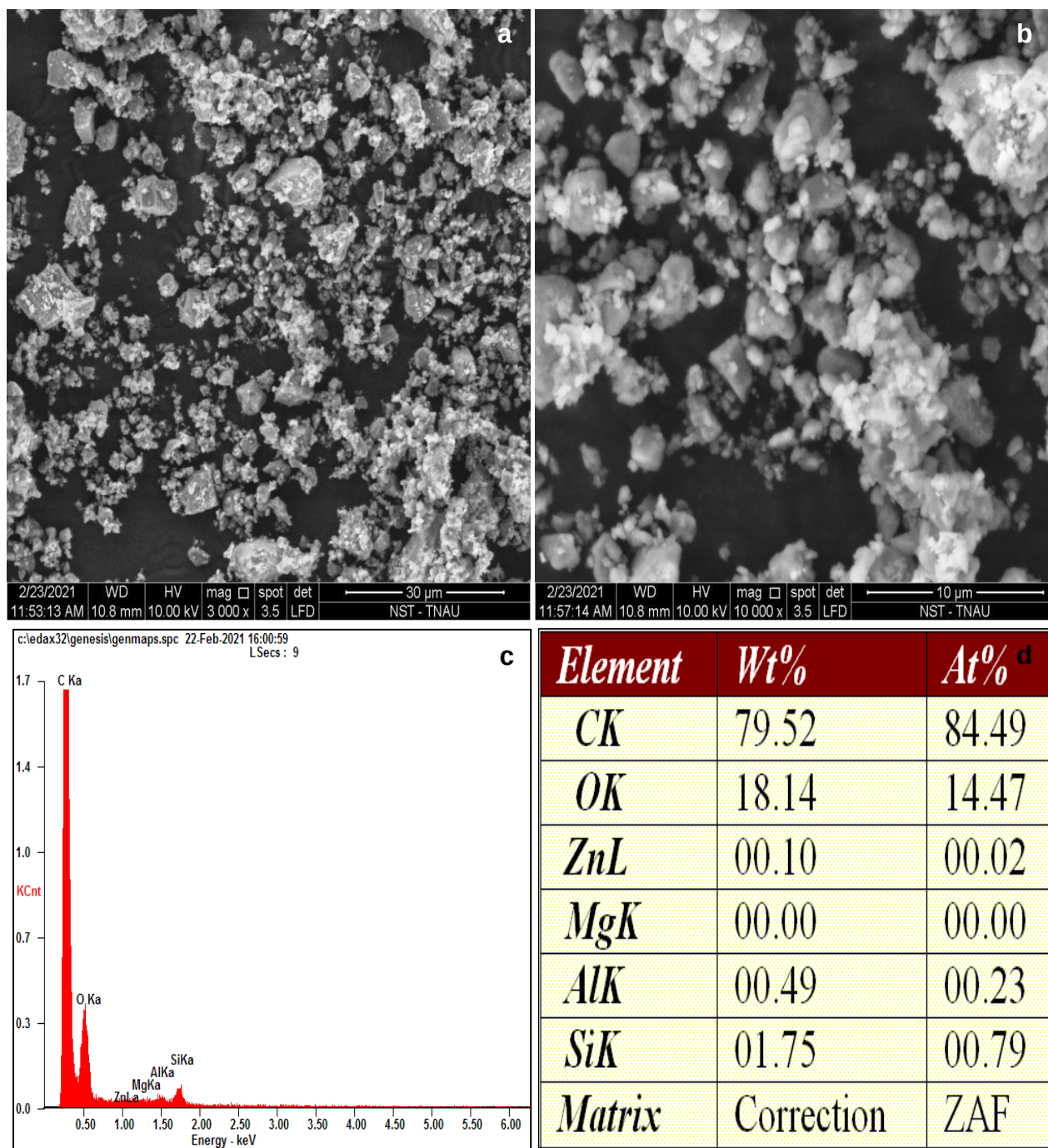


Figure 4.3: shows SEM with EDX analysis of induction furnace (IF) steel slag

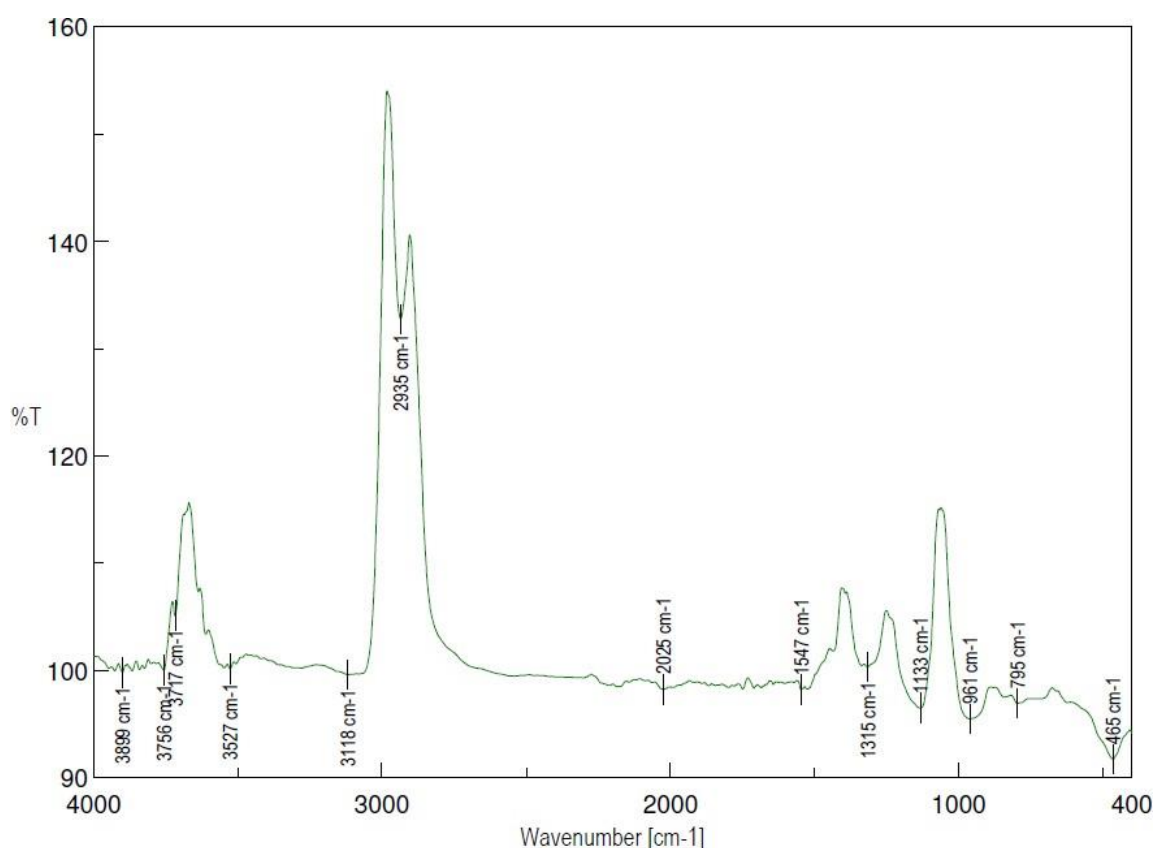


Figure 4.3: shows FTIR analysis of induction furnace (IF) steel slag

4.3 ACCELERATION OF SEED GERMINATION (%) AND SEED QUALITY PARAMETERS

Priming the green gram seeds with different proportion of [seaweed (100 %), 25 %: 75 % (seaweed: IF slag), 50 %: 50 % (seaweed: IF slag), 75 %: 25 % (seaweed: IF slag), IF (100 %)] was significantly accelerating the germination % and seedling parameters (shoot length, root length, and seedling vigour) were conducted in 10th compared those of experimental (control) groups (Figure 4.4a&b; Table 4.1). Among the different proportion, 25 %: 75 % (seaweed: IF slag) recorded comparatively high germination % and seed quality parameters in green gram.



GPS

Latitude 12; 52; 14.0725190000010514

Longitude 80; 13; 33.0661199999740063



GPS

Latitude 12; 52; 16.5349189999977852

Longitude 80; 13; 21.9039590000175366

Fig 4.6: Effect of α -Fe₂O₃ nanoparticles on seed quality parameters after a) 5th day and b) 10th day in rice (*Oryza sativa*) under optimum condition

Table 4.2: Efficacy of steel slag and seaweed composites priming on germination (%), shoot length, root length and and vigor index in green gram *Vigna radiate* on 10th day

Experiments	Germination %	Shoot length (mm)	Root length (mm)	Vigor index
Control	70 ± 0.07 ^e	8.6 ± 0.03	6.7 ± 0.01 ^c	1071.0 ± 0.17 ^e
Seaweed (100 %),	78 ± 0.10 ^d	8.8 ± 0.02 ^{ab}	6.9 ± 0.02 ^b	1368.5 ± 0.18 ^c
25 %: 75 % (seaweed: IF slag)	95 ± 0.01 ^b	11.4 ± 0.01 ^a	8.5 ± 0.02 ^{ab}	1729.0 ± 0.44 ^b
50 %: 50 % (seaweed: IF slag)	87 ± 0.04 ^c	9.9 ± 0.03 ^{ab}	7.3 ± 0.01 ^b	1519.7 ± 0.16 ^b
75 %: 25 % (seaweed: IF slag)	85 ± 0.08 ^c	8.9 ± 0.03 ^{ab}	7.2 ± 0.01 ^{ab}	1336.0 ± 0.27 ^d
IF slag (100 %)	85 ± 0.04 ^c	10.3 ± 0.04 ^{ab}	7.2 ± 0.02 ^c	1368.5 ± 0.18 ^c

Data are mean ± SE of four replicates. Means followed by different letters within a row indicate significant differences (P < 0.05; HSD; Tukeys's Honest Significant Difference post-hoc test)

Controlled and slow-release fertilizers high efficacy fertilizers that release nutrients over a longer period and make their availability better of time as compared to the conventional fertilizers. Combined with nano-scale nutrients and micro to nano structured natural polymer will further increase its efficiency. These may help plants grow efficiently, thereby resulting in higher yields and at lower doses of applications. Major applications of these fertilizers include agricultural areas, commercial lawns and turfs and others. These can be subdivided into nurseries & ornamentals, paddy rice, vegetables, fruits, turf, field crops, arable crops, trees, flowers, garden, vegetables, land scape, agricultural crops, green house and tea, amongst others. Controlled release fertilizers are witnessing higher demand from turf and ornamental application as compared to others. The global controlled and slow-release fertilizers market is estimated to be valued at US\$ 4.2 billion by 2018 end and is expected to reach US\$ 10.1 billion by the end of 2028 while expanding at a CAGR of 9.1% over the forecast period. The global controlled and slow-release fertilizers market is anticipated to represent incremental opportunity of over US\$ 5857 million between 2018 and 2028.

Controlled and slow-release fertilizers are generally used as specialty fertilizers in applications, such as agricultural applications, lawn & turf, fruits and vegetables, nurseries and gardens, among others. Thus, the agriculture industry will hold a dominant share in the demand for controlled and slow-release fertilizers. As per the FMI analysis, the demand from agricultural segment is estimated to grow in tandem with the growing population and agricultural developments in developing economies, such as China and India. The global agricultural industry is anticipated to register a high growth rate of over 3.8% due to increasing population, change in eating habits and improving economies of developing countries. Moreover, increasing penetration of controlled and slow-release fertilizers in the developing markets is anticipated to provide impetus to the growth of the controlled and slow-release fertilizers market during the forecast period. From a regional perspective, the controlled and slow-release fertilizers market is dominated by the Asia Pacific Excluding Japan (APEJ) region owing to the high presence of producers and consumers of controlled and slow-release fertilizers.

APEJ is also projected to be the fastest growing region during the forecast period. This can be attributed to the presence of emerging economies, such as China and India, and agriculture-dependent countries, such as India, Indonesia, Pakistan and China, in the region. Moreover, almost 60% of the global population resides in China and India. Fast-paced infrastructural developments in this region coupled with growing agricultural production are anticipated to help APEJ remain dominant in the global controlled and slow-release fertilizers market during the forecast period. The agricultural segment is anticipated to have a higher impact in the APEJ controlled and slow-release fertilizers market.

Previous literatures reported that, zero valent (ZVI) iron nanoparticles enhanced root elongation (150-200 %) in *Arabidopsis thaliana* by inducing OH radical-induced cell wall loosening compared with control (Kim et al., 2014). Synthesis of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles chemical co-precipitation method and dose dependant experiments were conducted on maize seed germination and noted that increased germination rate, root elongation comparatively control group (Li et al., 2016). Commercial magnetic Fe_2O_3 nanoparticles coated seeds (*Solanum*

lycopersium) have shown significantly enhanced seed germination, root and shoot length (Shankamma et al., 2016). Preparation of engineered ferrihydrite and hematite material using chemical reduction method and effects on the different concentration of nanoparticles (1, 2, 4, and 6 g/L) for maize seed germination and growth were studied. The nanoparticles treatments increased the growth of maize and the chlorophyll content, except for hematite material at 6 g/L, where non-significant effects were found (Pariona et al., 2017).

Calcium (Ca) and silicon (Si) make up the majority of slag, accounting for more than 70% of the overall weight, while N and P concentrations are 10.33 and 0.07 mg g⁻¹, respectively (Yi et al., 2012). Steel slag amendment has been shown to improve soil fertility, rice formation, yield, and grain quality in previous studies (Wang et al., 2013). However, there has been less research on the effects of slag application on soil fertility, rice formation, and yield in subtropical paddy fields. Other nutrients such as Ca and Mg can be restricting in certain terrestrial environments, and C, N, and P interact intensely (Baribault et al., 2012; Lapenis et al., 2013; Naples and Fisk, 2010). Thus, increased Ca and Si inputs, as well as moderate levels of N and P, will modify soil nutrient concentrations, abundance, and stoichiometry, influencing plant growth (Sardans et al., 2012a; 2012b). In Chinese wetlands, plant growth is generally N restricted (Zhang et al., 2013), especially in paddy fields, where periodic inundation restricts access to nutrients due to compromised root metabolism under hypoxia (Kirwan and Guntenspergen, 2012), decreased mineralization rates (Adame et al., 2010), and increased nutrient leaching (Kobayashi et al., 2009).

Steel slag application will improve disease resistance (Ning et al., 2014) thus lowering greenhouse gas emissions (Wang et al., 2015). The present study examined the effect of steel slag and seaweed composites for seedling growth of green gram. Slag has the ability to accumulate and preserve nutrients, delaying nutrient release, avoiding leaching and water eutrophication, and improving the soil's ability to supply nutrients for plant uptake (Zhao, 2012). In reality, due to increased plant growth due to enhanced nutrient supply under steel slag fertilisation, the overall amount of nutrients contained in plants increased. In rice plants, Ca and Si are

involved in a variety of metabolic and physiological processes related to growth, fruit production, and pathogen protection (Cacique et al., 2013; Sano et al., 2015). Furthermore, increasing the abundance of multiple nutrients in the soil at the same time will result in beneficial synergies in crop growth and yield production, as fertilisation of one nutrient increases plant absorption and content of other nutrients (Kim et al., 2005).

CHAPTER-5: SUMMARY AND CONCLUSIONS

Over the past decades, steel production has increased and consequently, the higher volume of by-products (slag) generated necessitates its efficient recycling. In order to mitigate environmental consequences caused by the disposal of a large quantity of slag at landfill sites and to reduce the transportation cost for disposal of slag, steel industries encourage sustainable use of slag in different fields of application, such as in agriculture. Slags are rich in iron, silica, calcium oxide and magnesium oxide. These beneficial properties of the slag can be exploited to improve agricultural productivity. Seaweeds are macroscopic marine algae, which form an important component of the marine living renewable resources. Recent researches proved that seaweed fertilizers are better than other fertilizers; they are very economic and cheap. In the present project steel slag and seaweed composite used to study the effect of seed germination and seedling parameters of green gram.

Mineral composition cubic centered phases of components present in IF slag were identified using XRD analysis. The presence of major mineral compositions cubic centered phases in IF slag material is quartz (SiO_2 , 2θ value 26.6), iscorite ($\text{Fe}_7\text{SiO}_{10}$, 2θ values of 50.32 and 60.30), almandine ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, 2θ values of 22.20 and 68.48) and hematite ($\epsilon\text{-Fe}_2\text{O}_3$, 2θ values of 36.7 and 39.94). Also, some of minor peaks with less intensity have been identified and is similar to the results reported previous studies. Further, mineral composition and their % were studied using XRF.

The presence of various metal oxides composition in steel slag has been analysed using XRF technique and major metal oxides present in slag are Fe_2O_3 (25.739%), MgO (1.893%), Al_2O_3 (1.606 %), MnO_2 (23.794 %), and SiO_2 (7.570 %).

The morphology of the IF slag material has been investigated by SEM and observed that the IF slag material possess a quasi-spherical shape. The diameter of the poly-dispersed IF slag material and facets on the surface structures appear very smooth and are clearly discriminable. EDX spectroscopy of the IF slag material sample indicates the presence of Zn, Al, Si, Mg, C and O composition.

FTIR spectroscopy analysis was performed to identify the surface structure of the IF slag material. IR spectra of the IF slag material, the major bands at 3717, 2935, 1547, 1315, 1133, 961, 795 and 465 cm^{-1} observed in the spectrum.

Priming the green gram seeds with different proportion of [seaweed (100 %), 25 %: 75 % (seaweed: IF slag), 50 %: 50 % (seaweed: IF slag), 75 %: 25 % (seaweed: IF slag), IF (100 %)] was significantly accelerating the germination % and seedling parameters (shoot length, root length, and seedling vigor) were conducted in 10th compared those of experimental (control) groups. Among the different proportion, 25 %: 75 % (seaweed: IF slag) recorded comparatively high germination rate and seed growth parameters in green gram.

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