


Review

A Review on the Effect from Steel Slag on the Growth of Microalgae

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Abstract: As a by-product from the metallurgical industry, steel slag contains a large amount of metal elements. In many developing countries, the output of steel slag is huge and the comprehensive utilization rate is low, hence the development of a novel application method for steel slag is of great significance to increase its utilization rate to improve the environment. This paper reviewed the dissolution behavior of Fe, P, Ca and silicate of steel slag under seawater and acidic solutions as an application in the cultivation of different microalgae, such as diatoms, spirulina, and chlorella. This review clarifies that proper pre-treatment of steel slag can effectively increase the dissolved elements of steel slag in the solution and provide more nutrients for the growth of microalgae. Microalgae cultivated with steel slag as a nutrient can be used to produce biodiesel which has a very broad application prospects for cleaner production and environmental protection.

Keywords: steel slag; microalgae; biodiesel; cleaner production; solid waste utilization



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1. Introduction

According to the 2020 Iron and Steel Statistical Yearbook, the world's crude steel production reaches 1.875 billion tons in 2019. Crude steel production in China (54.3%), Europe (10.5%), Japan (5.3%), South America (2.22%), Australia (0.29%), Russia (3.85%), India (5.9%) and the United States (4.7%) accounts for 87.6% of the world's total crude steel production (World Steel Association). Steel slag is a by-product in the metallurgical process [1] which can be divided into blast furnace slag, converter slag and electric furnace slag. There are more than 300 million tons of steel slag that have not been effectively used in China. Compared with Japan and the United States, the utilization rate of steel slag in China is at a lower level, only 29.5% [2]. The accumulation of a large amount of steel slag has caused problems such as land occupation, environmental pollution, and waste of resources [3]. Compared with Japan, the United States, and Europe, China still has more room for development in the recycling rate of steel slag. Due to the different raw materials and smelting processes of various iron and steel enterprises, there were many restrictions on the recycling of steel slag. When steel slag is used for secondary use, the most obvious problem is the enrichment of phosphorus and sulfur [4]. At present, steel slag is mainly used for the preparation of cement [5], carbon dioxide capture [6], plant fertilizers [7], coral reef restoration [8], and other fields. Li et al. [9] showed that 1 kg steel slag can store 77 g of carbon dioxide when the carbon dioxide flow rate was 1, while omale et al. [10] used 1 kg EAF slag to store 58.36 g of carbon dioxide. Ukwattage et al. [11] found that 1 ton of steel slag can absorb 29.47 kg of carbon dioxide. Studies have shown that by adding 3 g of steel slag to 1 kg of dry weight soil, the grain yield of Rice No. 1 increased by 44.7% compared with the control group (5.5 g/dry rice weight). The yield of Rice No. 2 was 36.2% higher than that of the control group (5.17 g/dry rice weight) [12]. Hisham Qasrawi found that when the ratio of steel slag to natural aggregate reached 0.45, the strength of cement increased by 20% [13]. Chen et al. studied the preparation of cementitious materials with

carbonated steel slag instead of part of cement. Calcium carbonate in carbonated steel slag was filled with Portland cement-based materials to improve the volume stability of steel slag [14]. Steel slag was an ideal material for catalysts when a large number of metal elements were used. Guo et al. impregnated steel slag with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (10 wt %) and calcined at 900 degrees Celsius. The tar conversion rate obtained from pyrolysis of biomass was 90.9–97.5% [15].

Steel slag contains Fe, Ca, Mg, P, Si and other elements, which can be used as nutrients for microalgae. Microalgae are ancient low-grade plants widely distributed in oceans, freshwater lakes and other waters. They have the characteristics of fast growth, short reproduction cycle and rich nutrition, and can directly use sunlight, carbon dioxide and simple nutrients such as nitrogen and phosphorus to grow quickly. At present, the main application fields of microalgae are medicine and food [16], renewable energy [17], wastewater purification [18], etc. Studies have shown that when a mixed microalgae community was cultivated at a flue gas concentration of 1% CO_2 , the FAME content produced by the algae was 280.3 $\mu\text{g/L}$, and the lipid productivity was 14.3 $\mu\text{g/L/day}$ [19]. Suarez Garcia et al. extracted soluble protein at room temperature and $\text{pH} = 6.5$ with a yield of 22.5% and a required energy consumption of 0.6 $\text{kWh/kg}_{\text{DW}}$. Compared with whey protein isolate, the protein extract contained 50.4% (DW) protein and 26.4% carbohydrate, and showed superior surface activity [20]. Chen et al. observed shear thinning at a higher concentration of *Chlorella pyrenoidosa* up to 20% w/w. At a shear rate of 215 s^{-1} , the viscosity no longer depended on the shear rate, reaching the cross model. The predicted infinite viscosity can be used in the research of microalgal biomass as food coagulant [21]. Hafse et al. studied the antioxidant, antimicrobial and cytotoxic properties of polysaccharides extracted from microalgae. Polysaccharides had antioxidant activity (41.45–59.07%), anti-cancer activity to human Hela cancer cells, anti-cholinesterase activity to butyrylcholinesterase enzymes, antibacterial to Gram-negative bacteria, Gram-positive bacteria and three *Candida* species active [22]. Yang et al. co-cultured fungi and microalgae at 35 °C with an inoculation rate of 100 the biomass yield was the highest (4.215 g/L). The fungi and microalgae were driven by electrostatic force to capture some suspended solids in the wastewater and attached them to the cell surface. On the 5th day of co-cultivation, 88.39% of the total phosphorus in the wastewater was removed and the total phosphorus concentration was reduced to 3.6 mg/L to achieve the restoration of wastewater [23].

2. Steel Slag Characteristics

2.1. Chemical Composition and Physical Properties of Steel Slag

Due to the difference in steelmaking raw materials and smelting processes, the chemical composition and mineral phase types of steel slag from different producing areas will be different, but most of the chemical components were composed of phosphorus-containing compounds, such as calcium oxide (CaO), and magnesium oxide (MgO), Silicon oxide (SiO_2), aluminum oxide (Al_2O_3), iron oxide (FeO), ferric oxide (Fe_2O_3), manganese oxide (MnO), free calcium oxide (f-CaO), free magnesium oxide (f-MgO). The main mineral composition of steel slag was dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$), tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$), dicalcium ferrite ($2\text{CaO} \cdot \text{Fe}_2\text{O}_3$), and RO phase ($\text{CaO}-\text{FeO}-\text{MnO}-\text{MgO}$ solid solution) [24–29]. Table 1 shows the steel output and steel slag output of some Chinese steel companies in 2019.

Steel slag contains a lot of metal elements such as calcium oxide and silica and has good compressive performance. When the standard effort was $600\text{ kN} \cdot \text{m/m}^3$, the optimal water content and maximum dry bulk density of steel slag were 8.5 % and 21.8 kN/m^3 [30]. In addition, steel slag has three characteristics: (i) gelling activity: the mineral composition of steel slag silicate, iron aluminate, and aluminate determines the cementing performance of steel slag; (ii) poor stability: calcium oxide and magnesium oxide in steel slag were prone to volume expansion after hydration, which was the main factor affecting the stability of steel slag; (iii) wear resistance: the wear resistance of steel slag was related to its own structure and mineral composition [31].

Table 1. Crude steel output and slag forecast of some Chinese iron and steel enterprises in 2019.

Company Name	Steel (Million Tons)	Steel Slag (Million Tons)	Address
China BaoWu Steel Group	9547	1432.05	Shanghai
HBIS Group	4656	698.4	Shijiazhuang
Jiangsu Shagang Group	4110	616.5	Zhangjiagang
AnSteel Group	3920	588	Anshan
JianLong Group	3119	467.85	Beijin
ShouGang Group	2934	440.1	Beijin
Shandong iron & Steel Group Company Limited	2758	413.7	Jinan
VALIN Group	2431	364.65	Changsha
BenXi Iron & Steel Group	1618	242.7	Benxi
FangDa Group	1566	234.9	Nanchang
BaoGang Group	1546	231.9	Baotou
LiuZhou Steel Group	1440	216	Liuzhou
RiZhao Steel Group	1420	213	Rizhao
CITIC PACIFIC Special Steel Group	1355	203.25	Jiangyin
JingYe Group	1258	188.7	Shijiazhuang

(Slag (year/one million t) = steel production \times 15%).

2.2. Dissolution Behavior of Steel Slag in Solution

Researchers extracted slag samples from 58 different steel plants in the United States. The samples were subjected to leaching tests under acidic and neutral conditions. None of the leached materials exceeded the safety standards set by the US government. Steel slag can be classified as a harmless by-product of the steel industry and may be recycled and used elsewhere [32]. Mombelli et al. [28] found that the ratio of water to steel slag is a key factor affecting the release of heavy metals. Understanding the dissolution behavior of elements in steel slag was of great significance to the resource utilization of steel slag.

2.2.1. Dissolution Behavior of Iron, Phosphorus and Calcium in Steel Slag

Steel slag contains a great number of oxides and metal components with high activity, and the ion exchange capacity is large. Steel slag can easily cause higher pH when dissolved in water. In order to continuously supply silicon, phosphorus, iron and other nutrients to the seawater for phytoplankton reproduction, understanding the dissolution behavior of certain elements in steel slag in aqueous solution was of great significance to the growth and reproduction of microalgae. The dissolution behavior of elements in steel slag varies. The maximum amount of iron dissolved in steel slag after 30 days in seawater was 0.1~0.2 mg/L, the concentration of silicon and phosphorus increase to 15 and 4.8 mg/L, respectively, and the dissolution rate of phosphorus depends on its crystal phase type [33]. In another study, five kinds of synthetic steel slags with different Fe^{2+} /T-Fe ratios were leached with citric acid. When citric acid with a pH of 6 was used, after 120 min, the ratio of Fe^{2+} /T-Fe in the steel slag was 0, and the slag contains only Fe_2O_3 . The dissolved concentration of phosphorus was about 70 mg/L, which was 80% of P_2O_5 in the steel slag. The ratio of Fe^{2+} /T-Fe was 1, the dissolved concentration of phosphorus was less than 20 mg/L, and the ratio of Fe^{2+} /T-Fe was inversely proportional to the dissolution rate of phosphorus [34]. In order to improve the solubility of iron in steel slag and the stability of iron in aqueous solution, gluconic acid, as a widely existing organic ligand, can form complexes with iron in alkaline aqueous solutions. Gluconic acid combines with the iron element in the steel slag to form an iron gluconate complex, which promotes the dissolution of the iron element in the steel slag in the solution. However, due to the photoreduction reaction of the iron

gluconate complex during the daytime oscillation, the soluble iron concentration decreased slightly. Gluconic acid has little effect on the change of pH and the increase of dissolved Si and P concentration. The phosphorus element in the steel slag was dissolved in the seawater gluconic acid solution between 0.13–1.39 mg/L, and the concentration of soluble silicon in the synthetic steel slag has no obvious relationship with the concentration of gluconic acid [35].

When the steel slag provides nutrition for marine microalgae, it is important to prevent harmful slag elements from dissolving in the seawater as they can pollute the environment. The final content of calcium in the steel slag in dissolved seawater varies between 400–1400 mg/L. The dissolution rate of manganese was very slow, and the maximum content of manganese was 2 mg/L; the Mg^{2+} ions originally contained in the seawater have a significant buffering effect on the pH increase process caused by the dissolution of Ca, regardless of whether the fluorine leaching rate was positive. The fluorine in some samples does not dissolve, while the fluorine in other samples dissolves more than 15 mg/L [36]. The ratio of CaO/SiO_2 was closely related to the dissolution of calcium in seawater. The dissolved concentration of calcium in the slag with a large CaO/SiO_2 ratio was much greater than that in the slag with a small CaO/SiO_2 ratio. For the ratio of CaO/SiO_2 , the dissolved amount of phosphorus at 1 h increases with the increase of the slag/seawater ratio. When the ratio of CaO/SiO_2 was 2, no dissolved phosphorus was found [37]. In addition, the leaching solution of calcium in the steel slag increases the CO_2 concentration [38].

2.2.2. Dissolution of Silicate in Steel Slag

Researchers in Japan measured the silicic acid content of carbonated steel slag and non-carbonated steel slag in sodium chloride solution. In the 0.5 mol/L sodium chloride solution, the pH value of the carbonized slag solution was slightly higher after the non-carbonized slag and the carbonized slag were stirred for one week. The concentration of silicic acid extracted from carbonized slag was higher than that of non-carbonized slag. Both solutions contain high concentrations of calcium ions. The chemical forms of silicic acid in non-carbonic acid and carbonated slag solutions were identified by fast atom bombardment mass spectrometry. Silicic acid has several chemical forms in the solution: $[Si(OH)_2O_2Na]^-$, $[Si(OH)O_3Ca]^-$, $[Si_2(OH)_5O_2]^-$, $[Si_2(OH)_4O_3Na]^-$, $[Si_4(OH)_7O_5]^-$, $[Si_4(OH)_6O_6Na]^-$, $[Si_4(OH)_9O_4]^-$. In all these complexes, diatoms absorb $[Si_2(OH)_5O_2]^-$ and $[Si_4(OH)_9O_4]^-$. $[Si(OH)_2O_2Na]^-$, $[Si(OH)O_3Ca]^-$, $[Si_2(OH)_5O_2]^-$ and $[Si_4(OH)_9O_4]^-$ and $[Si_4(OH)_7O_5]^-$ in two silicic acid solutions the peak intensity ratio of was also basically the same [39]. Therefore, studies believe that carbonized slag was more suitable as a supplier of silica in seawater than non-carbonized slag. When the ratio of CaO/SiO_2 was 1, the amount of dissolution of silicon increases with the increase of the ratio of slag/seawater. When the ratio of CaO/SiO_2 was 2, the dissolution of silicon appears at the maximum value on the first day of the entire oscillation period, and the dissolution rate of silicon was inversely proportional to the ratio of slag/seawater [37].

3. The Effect of Metal Ions on the Growth of Microalgae

Steel slag contains metal elements with high activity, such as Fe, Ca, Mg and other metal elements, which can be used as nutrients for the growth and reproduction of microalgae. Different iron sources have different effects on the growth of microalgae.

Fe was an important electron acceptor in the photosynthetic process of algae, and can also improve the nitrogen reduction and fixation properties of algae [40]. Different iron sources have different effects on the growth of microalgae. Ferric chloride was the most toxic to *Auxenochlorella protothecoides*, the biomass of ferrous sulfate was the highest (1520 mg/L), and the specific growth rate of ferric EDTA was the highest (1.2891/d). The saturated fatty acid content of microalgae was more than 75% in 1.15 mM ferric chloride solution. The quality of the microalgae cultured at the 0.2 and 14.4 mM ferrous sulfate and 7.19 mM ferric EDTA reached the standard [41]. In another study, three different

iron source reagents (ferric chloride, ammonium ferrous sulfate and iron EDTA) were prepared based on iron. When ammonium ferrous sulfate was 3.25 mg/L, the growth rate of microalgae was 0.3 g/L/d, while when 1.95 mg/L Fe EDTA was used, the lipid content of microalgae was 35%. When the iron concentration increased, the growth rate and lipid content of *Dunaliella tertiolecta* increased simultaneously to a certain extent, and then decreased at higher doses. The best cell growth rate can be obtained by using ferrous sulfate. Ferrous sulfate was conducive to the accumulation of carbohydrates. In the presence of EDTA iron, the lipid content was higher than other iron sources and the carbohydrate content was reduced. EDTA iron was beneficial to microalgae accumulation of lipids has an obvious effect and was expected to be an ideal nutrient for the production of biodiesel by microalgae [42].

Using steel slag as a nutrient source, if the heavy metal ions in the steel slag solution is too high, it will have a toxic effect on the microalgae cells. High concentrations of heavy metals induce an increase in microalgae reactive oxygen species (ROS), which were harmful to algae cells. Under the condition of 100 μ M Al, aluminum induced the imbalance of reactive oxygen species (ROS) level in *Scenedesmus* sp. in order to eliminate the excessive ROS in microalgae cells, the antioxidant system of cells produced ROS scavenging enzymes including glutathione reductase (GR), catalase (CAT), superoxide dismutase (SOD) and ascorbate peroxidase (APX) [43]. For example, Pb^{2+} stimulates ascorbic acid accumulation, and ascorbic acid peroxidase converts H_2O_2 to H_2O to protect cells from oxidative stress [44]. The content of total carotenoids (TCC) in *Dunaliella salina* cells treated with phenol increased, and TCC, as a copigment, could resist the photochemical induction of reactive oxygen species [45]. The toxicity of zinc seems to be related to the cell membrane. It may disrupt the absorption of calcium necessary for the activity of calcium ATPase during cell division. The toxicity may be mainly due to the destruction of protein structure. High-zinc conditions severely inhibited the growth of *Spirulina platensis*, while low-zinc conditions showed little change in biomass. The content of chlorophyll a and carotenoid reached the maximum when the Zn^{2+} concentration was 4.0 mg/L and 1.0 mg/L. The ratio of saturated fatty acids and polyunsaturated fatty acids increases continuously with Zn^{2+} exposure [46]. When the Zn^{2+} concentration was 0.0, 0.5, 1.0, 2.0, 4.0, 6.0 and 8.0 mg/L, biomass productivity of *Coelastrrella* sp. was inversely proportional to Zn^{2+} concentration, and it was 7.79 and 3.48 mg/L/d corresponding Zn^{2+} concentration of 0.0 and 8.0 mg/L, respectively. The protein and glutathione contents (protein/biomass g/g) were 0.207 g/g and 189.9 mg/g, respectively. When the concentration of Zn^{2+} was 6.0 mg/L, the maximum value of superoxide dismutase (SOD) was 55.5 U/mg protein. When the concentration of Zn^{2+} was 8.0 mg/L, the maximum value of ATP content was 1589 ± 57 μ mol/g prot [47].

Studies have shown that heavy metal ions can help increase the lipid content of some microalgae. Under photosynthetic autotrophic conditions, the peak lipid content of *Monoraphidium* sp. FXY-10 added with 100 μ M Mg^{2+} reached 59.8% [48]. Polat et al. obtained the highest lipid content by culturing *Auxenochlorella protothecoides* under the conditions of 18.5 mg/L Mg^{2+} and 5.0 g/L NaCl according to the response surface method [49].

The accumulation of lipids was not inhibited by heavy metals. On the contrary, after adding cadmium and copper, the lipid content of *Chlorella minutissima* UTEX 2341 was significantly increased by 21.07% and 93.90% [50], *Desmodesmus* sp. MAS1 and *Heterochlorella* sp. MAS3 accumulated a large amount of microalgae biomass on the cadmium-containing medium with a pH of 3.5. Fourier transform infrared spectroscopy analysis of cadmium-containing microalgae showed that a large amount of fatty acids were produced esters of biodiesel [51].

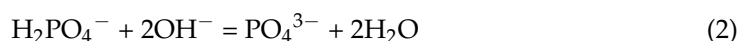
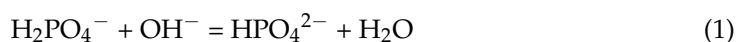
Studies have shown that microalgae will increase the consumption of calcium after being poisoned by aluminum. Calcium was an important component of the cell wall. Changes in the lipid metabolism and degradation of the cellular organelles occurred under Al stress. Aluminum element damages the antioxidant enzyme activity in microalgae, leading to oxidative stress [43].

Some heavy metals in steel slag can promote microalgae and help increase the lipid content of microalgae. Using steel slag to cultivate microalgae helps reduce the cost of microalgae cultivation.

4. Study on the Growth Characteristics of Steel Slag on Microalgae

Iron was an essential trace element in the metabolism of microalgae such as photosynthesis and respiration. However, in the ocean, especially in the high seas, photosynthesis was limited by iron deficiency due to limited land supply and dissolved iron. Due to the rapid oxidation and sedimentation of iron, marine phytoplankton can use steelmaking slag as an iron source to actively grow under this iron stress [52]. The study found that the iron source released in 20 mg/L of steel slag was enough for two kinds of marine diatoms *T. nordenskiöldii* and *T. oceanica* to grow for 50 days. Taking the time (day) of the abscissa and biological growth rate as a vertical coordinate, the regression equation was obtained by the least square method. The maximum growth rates of *T. nordenskiöldii* and *T. oceanica* were 1.5/d and 2.3/d, respectively. The iron or ferrous ions were released in the steel slag and inorganic iron reagent ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), both can effectively promote the growth rate of two diatoms [53]. The iron element in the steel slag forms a colloidal iron ion with the solution to maintain the iron ion concentration in the culture medium. The dissolution of iron in the steel slag was significantly different from inorganic iron reagents, ensuring that the steel slag was used as an iron fertilizer for microalgae. It lasts longer than inorganic iron fertilizer, and the extended Redfield ratio of phosphorus, silicon and iron released by steel slag into the solution was 1:15:0.0075, which was the average ratio of the main nutrients that constitute phytoplankton cells [54]. Another study showed that the ferrous element used for the growth of the diatom *Thalassiosira guillardii* was about 1% of the iron content of the steel slag, the utilization efficiency of phosphorus was less than 68% of the phosphorus content in the steel slag, and the addition of steel slag was below 50 mg/L. It was confirmed that the pH that affects the proliferation of phytoplankton has not changed [55]. Therefore, in the process of producing algae biofuels, steel slag was a promising ingredient to promote the growth of phytoplankton.

Studies have shown that the lack of phosphate limits the growth rate of most microalgae. When the external environment phosphorus was depleted, the microalgae consumes their own phosphorus reserves to proliferate until they reach the minimum phosphorus cell content suitable for growth [56]. In order to further study the possibility of steel slag as a nutrient resource for marine microalgae, to test the growth-promoting effect of decarburized steel slag and dephosphorized steel slag on the growth of the diatom *Thalassiosira guillardii*, 33 mg/L of steel slag was added, and the released phosphate and silicate on silicon. The relative fluorescence of chlorophyll-a was used to indirectly express the biomass of microalgae, and the relative fluorescence of chlorophyll-a was about 70. The growth effect of the alga *Thalassiosira guillardii* was significantly enhanced. When the steel slag concentration (3300 mg/L) is increased to 100 times, the relative fluorescence of chlorophyll-a was about 0.6, and the growth of microalgae was inhibited. The steel slag contains a large number of oxides. Excessive steel slag increases the pH value of the seawater culture medium. The increase of the pH value may greatly reduce the iron in the steel slag and the solubility of the element [57]. Existing studies have shown that adding 50–150 $\text{mg} \cdot \text{L}^{-1}$ steel slag will significantly increase the pH of the solution. Two marine diatoms *Skeletonema costatum* and *Alexandrium tamarense* were too sensitive to the increase in pH caused by the addition of steel slag and cannot grow [58]. The reaction process was shown in the formula:



In order to increase the dissolution rate of iron, silicon, phosphorus and other elements in steel slag, the researchers lowered the pH value. A carbonation of steel slag was used to cultivate microalgae. As iron ions and carbonate ions promote each other to hydrolyze to

form precipitation, the non-carbonated steel slag was significantly higher than the content of silicate, phosphate and iron in carbonated steel slag. The nutrients released from the chemical slag can promote the growth of *Nitzschia laevis*, but the sharp increase in pH inhibits its growth trend. The pH value of non-carbonated steel slag solution at 5.0 g/L and 10.0 g/L was about 8.5 and 9.0, respectively, and the cell density was 20×10^5 and 15×10^5 cells/cm², respectively. On the contrary, although the carbonized slag has a certain alleviating effect on the increase of pH, it has no obvious promotion effect on the growth of *Nitzschia laevis* due to the low nutrients released in the carbonized slag [59].

As we all know, the growth and proliferation of microalgae were inseparable from nitrogen. There was no nitrogen in steel slag or nitrogen was not detected in the solution. Municipal sewage contains a lot of nitrogen (T-N 1780 µM). The researchers combined the steel slag with urban sewage to cultivate microalgae to reduce economic costs. The ammonia nitrogen in urban sewage was used as a nitrogen source. Its effect was the same as nitrate nitrogen. The relative fluorescence variation of chlorophyll a in *Thalassiosira guillardii* cells was more than 100. Iron, phosphorus and silicon in steel slag effectively promoted the proliferation of microalgae, there was no significant difference in the demand for iron from the diatom *Thalassiosira guillardii* [60]. Haraguchi et al. determined that under the condition of 10 °C, the chlorophyll fluorescence value of *Skeletonema costatum* was 3.1 times of that of control group (fluorescence value 0.49) at 20% sewage and 20 mg/L steel slag, which was the best dose to promote the growth of *Skeletonema costatum*. The pH values of 20 mg/L and 200 mg/L steel slag solutions were 8.5–8.6 and 9.4–9.7, respectively. The increase of pH value resulted in the presence of unionized NH₃ in the solution, which inhibited the growth of phytoplankton [61].

Spirulina platensis contains amino acids, vitamins, unsaturated fatty acids and trace elements, all of which have certain biologically active functions, including anti-oxidation and improving human immunity [46]. *Spirulina platensis* contains more unsaturated fatty acids and can be used as one of the raw materials for the production of biodiesel. The use of microalgae was limited by expensive costs, including the supply of nutrients [62]. The study found that the growth effect of *Spirulina platensis* M135 with 500 mg/L steel slag added to the culture medium was 1.27 times that of the control group (growth promotion rate 100%). As the concentration of steel slag increased, the fat content of *Spirulina platensis* M135 decreased, and the carbohydrate content did not fluctuate much. The protein content of *Spirulina platensis* M135 was positively correlated with the concentration of steel slag after 45 days of cultivation, but the protein content decreased at 60 days [63].

The metal nutrient elements in the steel slag were not easily leached under neutral conditions, which makes it difficult for microalgae to use the nutrients in steel slag. In order to maximize the use of steel slag, the researchers used granular blast furnace slag (sample A) and ladle slag (sample B), five samples of blast furnace aggregate (sample C), converter slag-aggregate (sample D), and flat-bottom furnace slag-aggregate (sample E) were leached under acidic conditions to study the effects of two microalgae *Desmodesmus subspicatus* and *Chlorella vulgaris* growth impact. Samples A and B caused the growth of *Desmodesmus subspicatus* and *Chlorella vulgaris* to be inhibited. Sample C has a slight stimulating effect on both algae. The growth inhibition of *Desmodesmus subspicatus* was observed in samples D and E, and the highest growth inhibition effect of sample B on *D. subspicatus* was observed, which may be related to the increase in Zn concentration and the salinity of the extract [64].

Takahashi et al. used two different processes of electric arc furnace slag (EAFs) to leach the metal components in the slag with HCl and filtered it with a 0.45 µm pore filter to eliminate slag particles. The leachate filtered from the residue. After treating the microalgae with each extract for one week, the microalgae were quantitatively detected with a hemocytometer. The concentration of heavy metal ions in the leaching solution of electric arc furnace slag, such as total Ni 0.001 mg/L, total Se 0.012 mg/L, total Zn 0.0143 mg/L, were all lower than the Japanese EQS standard, and had no obvious toxicity to the growth of algae. The growth rate of *Chlorella vulgaris* was 150% when more than 30% of steel slag leaching solution was added to the culture medium. The growth rate of

Chlorella vulgaris was 100% without steel slag leaching solution as the control group. On the contrary, adding steel slag extract to the culture medium did not directly promote the proliferation of *Chlorella*. The calcium in the extract increased the concentration of CO₂, and the increase of CO₂ increased the photosynthetic rate and proliferation rate of algae [38].

Nogami et al. used steelmaking slag (SMS) and blast furnace slag (BFS) to cultivate freshwater microalga *Botryococcus braunii*, and when comparing the addition of 5 g·L⁻¹ SMS and BFS, the growth effect of microalgae at OD_{680nm} was 1.74 times and 2.39 times that of the control group (OD_{680nm} = 0), respectively. In the application of 5 g/L SMS and BFS, the lipid content of microalgae was 2.16 times and 4.47 times higher than that of control group (SMS: 0.08 g/L, BFS: 0.15 g/L). By eluting iron from SMS and eluting other components from BFS, the biomass and lipid productivity of *Botryococcus braunii* were improved. In terms of productivity of metabolites, BFS was more effective than SMS [65].

Fe is an important electron acceptor in the photosynthetic process of algae and can also improve the nitrogen reduction and fixation performance of algae. A proper iron ion concentration was beneficial to promote the growth and proliferation of microalgae. Add 25 and 300 mg/L to the reactor for desulfurization steel slag, the addition of desulfurization steel slag significantly increases the total iron content of the reactor. The total iron ion concentration reaches 1.1 and 4 mg/L. The concentration of iron ions increases with the increase of steel slag concentration. The iron content was only 0.1–0.2 mg/L. Because steel slag contains more oxides, the pH value of the solution gradually increases with the increase of the concentration of desulfurized steel slag. When more than 100 mg/L steel slag was added to the solution, the pH value will rise to above 11, which will inhibit the growth of algae. The results showed that the total iron concentration was 1.1 mg/L in the solution with 25 mg/L desulfurized steel slag. Compared with the control group with only 0.1–0.2 mg/L total iron concentration, the iron ion concentration increased significantly, and the total organic carbon concentration of *Chlorella vulgaris* was 56 mg/L. The results show that the total iron concentration in 300 mg/L desulfurized steel slag solution was 4 mg/L, and the total organic carbon concentration of *Chlorella* was 41 mg/L. The released iron element and very-low dose of heavy metal elements promote the growth of *Chlorella*. The high concentration of steel slag releases more heavy metal ions and the higher pH value inhibits the growth of microalgae. The microalgae in the reactor consumes total iron for growth through absorption or biological condensation mechanisms [40].

The growth of 12 kinds of microalgae in different concentrations of steel slag solution will be studied. The steel slag was dissolved in artificial seawater for 10 days with shaking, adjusted to pH 8 by adding HCl, and divided into four groups according to the growth response of microalgae: Group 1: *Thalassiosira angulata* (bacillaliophyte), *Amphidinium cartae* (Dinophyte), the microalgae that grow best at the highest concentration of steel slag solution; Group 2: microalgae that grow best in a medium-concentration slag solution, but not a 100% slag solution—*Skeletonema costatum* (bacillaliophyte), *Thalassiosira allenii* (bacillaliophyte), *Chlorella* sp. (chlorophyte), *Isochrysis galbana* (haptophyte); Group 3: microalgae that grow best when the slag solution concentration was low, organisms that were inhibited when the concentration was higher than 60%, *Chaetoceros gracile* (diatom), *Rhodomonas lens* (cryptophyte), *Emiliania huxleyi* (haptophyte); Group 5: regardless of the concentration, microalgae that grow well in the slag solution, *Dunaliella tertiolecta* (chlorophyte), *Tetraselmis tetrathela* (chlorophyte), *Synechococcus* sp. (cyanophyte). The slag solution concentration of group (I) was 100%, that of group (II) was 80–60%, that of group (III) was 60–20%, and that of group (IV) was 100–20%. The results show that the growth of almost all microalgae was enhanced, and the growth effect of diatoms in the steelmaking slag solution was significantly better than other phytoplankton [66]. Different types of microalgae have different tolerances to different concentrations of steel slag. Among them, diatoms perform best in the use of metal elements and nutrients in steel slag. Table 2 showed the effect of steel slag types on the growth of microalgae.

Table 2. The influence of steel slag on the growth of microalgae.

Types of Microalgae	Nutrient Types	Growth Conditions	Growth Effect	Reference
<i>T. guillardii</i>	A	33 mg/L	Positive	[57]
	B	33 mg/L	Positive	[57]
	A	50 mg/L	Positive	[55]
	B and M	20 mg/L, Sewage 20%	Positive	[61]
	A and M	50 mg/L, Sewage 40%	Positive	[60]
<i>D. subspicatus</i>	D	Not shown	Negative	[64]
	E	Not shown	Negative	[64]
	F	Not shown	Positive	[64]
	G	Not shown	Negative	[64]
	H	Not shown	Negative	[64]
<i>C. vulgaris</i>	D	Not shown	Negative	[64]
	E	Not shown	Negative	[64]
	F	Not shown	Positive	[64]
	G	Not shown	Positive	[64]
	H	Not shown	Positive	[64]
<i>Chlorella</i>	I	100 mg/L	Positive	[38]
	C	25 mg/L	Positive	[40]
	J	60–80% Steel slag solution	Positive	[66]
<i>Skeletonema costatum</i>	B	200 mg/L	Positive	[58]
	B	100 mg/L	Positive	[58]
	J	60–80% Steel slag solution	Positive	[66]
<i>Botryococcus braunii</i>	J	5 g/L	Positive	[65]
	F	5 g/L	Positive	[65]
<i>Nitzschia laevis</i>	K	10 g/L	Positive	[59]
	L	5 g/L	Positive	[59]
<i>Alexandrium tamarense</i>	B	50–100 mg/L	Negative	[58]
<i>Spirulina platensis</i>	J	500 mg/L	Positive	[63]
<i>T. oceanica</i>	A	20 mg/L	Positive	[53]
<i>T. nordenskiöldii</i>	A	20 mg/L	Positive	[53]
<i>Thalassiosira angulata</i>	J	100% Steel slag solution	Positive	[66]
<i>Amphidinium cartae</i>	J	100% Steel slag solution	Positive	[66]
<i>Thalassiosira allenii</i>	J	60–80% Steel slag solution	Positive	[66]
<i>Isochrysis galbana</i>	J	60–80% Steel slag solution	Positive	[66]
<i>Chaetoceros gracile</i>	J	20–60% Steel slag solution	Positive	[66]
<i>Rhodomonas lens</i>	J	20–60% Steel slag solution	Positive	[66]
<i>Emiliania huxleyi</i>	J	20–60% Steel slag solution	Positive	[66]
<i>Tetraselmis tetraethala</i>	J	20–100% Steel slag solution	Positive	[66]
<i>Dunaliella tertiolecta</i>	J	20–100% Steel slag solution	Positive	[66]
<i>Synechococcus</i> sp.	J	20–100% Steel slag solution	Positive	[66]

A: decarburized steel slag; B: dephosphorized steel slag; C: desulfurized steel slag; D: granulated blast furnace slag; E: steel ladle slag; F: blast furnace slag; G: oxygen converter slag-aggregate; H: open-hearth furnace slag-aggregate; I: electric arc furnace; J: steelmaking slag; K: carbonated Steel Slag; L: non-carbonated steel slag; M: sewage.

5. Assess the Impact of Microalgae on the Natural Environment and Social Benefits

When the heavy metal ions in steel slag threaten microalgae they will induce various protective mechanisms [67], such as increasing the activity of antioxidant enzymes and

stimulating the accumulation of ascorbic acid. The absorption rates of *Chlorella vulgaris* at 0.1 mg/L Cd^{2+} were 70.27% and 40.73%, respectively [68]. The removal efficiency of Pb^{2+} by Pham et al. using *Scenedesmus* sp. was also significant—the absorption rate at 0.2 mg/L Pb^{2+} was 84.2% [69]. Another microalgae, *P. typicum*, had an absorbance at 3.31 mg/L Pb^{2+} concentration of 70% [70]. Li et al. [71] found that the removal rate of Ca, Zn, and Mn in industrial high nitrate nitrogen wastewater by *Chlorella* reached 97.91%, 99.37%, and 99.44%, respectively. The results show that microalgae can effectively adsorb metal ions, and the main mechanism is the combination of negative charged groups in cell wall with positively charged metal ions [72]. The leaching experiment of steel slag shows that the impurities (heavy metals) in the steel slag conform to the safety standard, that the microalgae has the ability to adsorb heavy metals, and that the steel slag impurities have little effect on the microalgae. In order to release more nutrients from steel slag, citric acid, gluconic acid, EDTA and other organic acids could be used for pretreatment.

Microalgae can carry out photosynthesis like most green plants, and a large number of microalgae can reduce global carbon dioxide levels. Sadeghizadeh et al. [73]. The effect of high gas superficial velocity on the *Chlorella vulgaris* microalgae growth and CO_2 removal efficiency in an airlift photobioreactor was investigated. CO_2 removal efficiency by *Chlorella vulgaris* was achieved equal to 80% in the gas superficial velocity of 7.458×10^3 m/s. Similarly, Sun et al. [74]. studies have shown that adding raw microalgae and defatted microalgae can improve the CO_2 capture stability of calcium oxide-based particles; the optimum doping ratio was only 2 wt % defatted microalgae. Guo et al. [75] transformed microalgae into porous carbon hydrophilic and stable carbon quantum dots to capture CO_2 . The microalgae based porous carbons show excellent CO_2 capture capacities of 6.9 and 4.2 mmol/g at 0 and 25 °C respectively, primarily due to the high micropore volume ($0.59 \text{ cm}^3/\text{g}$) and large specific surface area ($1396 \text{ m}^2/\text{g}$). Microalgae have a remarkable effect in reducing carbon dioxide in the atmosphere.

The price per kilogram of dry algae was EUR 35, and the production cost was EUR 2.01 [76]. According to the previous research, the iron content in steel slag is about 30–50% [28]. In the steel slag with 30% Fe, the concentration of Fe in 100 mL seawater is 0.3–0.4 mg/L for every 0.2–2 g [37]. In 96 h, 0.8 g of dry algae was harvested with 0.65 mg of iron [42]. Assuming that iron accounts for 30% of steel slag and 0.4 mg of iron ion is dissolved in every 2 g of steel slag, steel slag accounts for 15% of steel output. According to the above data, it is estimated that 690.09 million tons of microalgae can be harvested in 2019 when all steel slag is used for microalgae cultivation. The economic benefits were huge.

Microalgae was an important source of organic matter and oxygen in nature. A large number of microalgae for photosynthesis can help reduce global carbon dioxide. Microalgae are important primary producers in aquatic ecosystem and key links in aquatic food chain. Microalgae provided food for aquatic animals. In addition, microalgae can purify water and prevent water from being polluted. If a large number of microalgae are used to produce biodiesel, it will greatly alleviate the global energy crisis.

6. Conclusions

Steel slag contains Fe, P, Si, Ca and other nutrients, which can be used as nutrients for microalgae. However, we should also pay attention to the chemical composition determination of steel slag before use.

Steel slag contains more oxides, which increase the pH of the solution. The pH environment for most microalgae growth was around 6–8. When using steel slag to culture microalgae, adjust the corresponding pH value appropriately according to the pH environment of the required microalgae. It was not recommended to use carbonic acid to adjust its pH value. Carbonic acid and the Fe, Ca in the steel slag will form precipitates, reducing the amount of water in the aqueous solution nutrient. The use of organic acids such as citric acid and gluconic acid can not only adjust the pH value, but also form iron complexes with the dissolved Fe in the steel slag, improve the solubility of iron and the stability of the iron

in the aqueous solution, and make the microalgae sustainable Use Fe element. The release of iron in steel slag was conducive to the accumulation of microalgae oil content, and steel slag can be used as a nutrient for microalgae production of biodiesel. On the other hand, steel slag does not contain nitrogen required for the growth and reproduction of microalgae in the dissolved elements in the aqueous solution, which was beneficial to increase the fat content of microalgae. Studies have shown that the lack of nitrogen, phosphorus or sulfur in microalgae will lead to reduced protein synthesis and photophosphorylation, resulting in a large amount of carbon being converted from protein or other macromolecules into energy storage molecules. The lipid content in the cell was relatively high. Productivity was still improved. Nitrogen deficiency, phosphorus deficiency and sulfur deficiency can all increase the oil content and quality of biodiesel [77].

Steel slag as a nutrient for microalgae has made great progress in recent years. Most researchers have only noticed the effect of a certain element in the steel slag on the growth of microalgae. Steel slag is rich in many elements and promotes the growth of microalgae, however, it has not been clearly pointed out whether the growth is a single element or multi-element synergistic effect. The heavy metal elements in steel slag were less toxic to microalgae. The steel slag does not contain nitrogen. It is possible to consider using dilute nitric acid as the leaching agent to extract the elements in the steel slag for cultivating microalgae, and even if nitrogen is provided, it can effectively avoid the increase of pH.

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