



Full length article

# Municipal green waste promotes iron release from steelmaking slag in water

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## ABSTRACT

Shortage of soluble Fe in seawater is a limiting condition for benthic seaweeds growth. Utilizing steelmaking slag as the Fe source for seaweeds growth has been proposed. Aiming to find a cost-effective method to promote Fe release, we investigate the effect of adding municipal green wastes. By conducting leaching experiments in freshwater, a sharp improvement in Fe release was observed with the addition of tangerine peel together with steelmaking slag. The flavonoids supplied from the tangerine peel, vicenin-2, apigenin, hesperidin, vitexin, hesperetin and diosmin were observed to have a promotion effect on Fe release. Formation of stable flavonoid-Fe (II) chelates changes the thermodynamic property of Fe(II) in water and disturbs the equilibrium between Fe(II) in slag and Fe(II) in water, which promotes Fe release from slag. These results demonstrate the feasibility to develop a technology for Fe supply in seawater by utilizing the mixture of steelmaking slag and municipal green wastes.

## 1. Introduction

Accumulation of carbon dioxide (CO<sub>2</sub>) in the atmosphere is the primary reason for global climate change. In 2020, the global emissions reached 34.81 billion metric tons, contributing to a historical highest atmospheric CO<sub>2</sub> of 412.5 ppm (IEA 2021). Lowering the CO<sub>2</sub> level has become an urgent task for human beings, either by reducing the emissions or by capturing the emitted CO<sub>2</sub> (Yang et al., 2021). Ocean cycles about 90 billion tons of CO<sub>2</sub> per year and removes over 30% of carbon in the atmosphere (Nellemann et al., 2009). Marine vegetation has been considered a significant natural carbon sink (Siegenthaler and Sarmiento, 1993) since benthic seaweeds can fix atmospheric CO<sub>2</sub> through photosynthesis. Therefore, mass the cultivation of seaweeds in coastal seabeds is a potential solution to the CO<sub>2</sub> problem. Meanwhile, benthic seaweeds also play the role of a biostimulant. Mass cultivation of seaweeds can boost marine biodiversity by providing shelter, feeding and nursery areas for a highly diverse number of associated fauna (Chai et al., 2018; Visch et al., 2020).

However, the low solubility of iron (Fe) in coastal water has limited seaweed growth. Fe is a micronutrient required for proteins involved in fundamental cellular processes, including photosynthesis and

respiration (Raven et al., 1999). Fe acts a central role in energy production and biochemical catalysis within phytoplankton cells. It is involved in multiple metabolic pathways, either directly via its catalytic role in enzymes, or indirectly via its parts in the production of energy-rich molecules such as NADPH and ATP (Schoffman et al., 2016). Soluble Fe is recognized to be important in regulating the magnitude and dynamics of ocean primary productivity (Martin, 1990; Watson et al., 2000; Martínez-García et al., 2014). However, the concentration of soluble Fe is no more than 56 µg L<sup>-1</sup> in coastal water, because of the easiness to get oxidized to form non-soluble oxyhydroxides under natural conditions (Lu et al., 2012; Achterberg et al., 2001).

Technologies of Fe fertilization by utilizing steelmaking slag have been proposed to enhance seaweed growth, especially for coastal benthic algae. Composed of multiple oxides such as CaO, SiO<sub>2</sub>, FeO<sub>x</sub> and others, steelmaking slag is usually designed to remove impurities in molten steel, and the slag composition depends on the refining conditions. As a major byproduct of the steel manufacturing process, the global output of steelmaking slag in 2020 was estimated at around 200 million tons (World Steel Association, 2021; Fisher et al., 2019). Treatment of such a huge amount of solid waste simply by dumping is against the circular economy mode in the steel industry, which requests

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efficient use of resources and energy, minimization of emissions, cycling of steel products, and reuse or recycling of all byproducts. Critical reviews on the current status of the treatment or recycling of steelmaking slag can be found in the literature (Lobato et al., 2015; Jiang et al., 2018). Rich in ferrous Fe in the form of oxides, steelmaking slag is thought to be a proper Fe source (Kuwahara et al., 2021). Nakata et al. (2003) and Miki et al. (2004) experimentally confirmed that steelmaking slag is basically safe in water because hazardous elements are not released. The conception of cultivating benthic seaweeds in coastal seabed is shown in Fig. 1. By setting artificial block produced from steelmaking slag on the seabed, soluble Fe may be gradually released from slag into seawater by natural leaching, which can be absorbed by seaweeds.

Fundamental studies and field experiments were conducted to put the concept into practice. Through the incubation of green algae chlorella with the culturing media containing eluates from steelmaking slag, Takahashi et al. observed enhanced algae growth (Takahashi and Yokoyama, 2016), possibly because of the soluble iron released from slag. Yamamoto et al. evaluated the continuous effect of steelmaking slag fertilization to a barren ground in coastal areas of northern Japan (Yamamoto et al., 2017). It was found that the distribution of dissolving iron from slag was related to the distribution of seaweed beds. Seaweed proliferation was enhanced in the experimental areas. Researchers of POSCO installed artificial reef “TRITON” produced from steelmaking slag in a coastal area (South Gyeongsang, Korea) and confirmed the apparent increase in the number of individual organisms, biological mass, and plant species (Posco Newsroom, 2020).

Tsukihashi and coworkers conducted systematic studies to clarify the releasing behavior of Ca, Mg, Si, Mg, P and Fe from steelmaking slags into seawater (Zhang et al., 2012; Zhang et al., 2016; Lang et al., 2017). The dissolution behavior of these elements depends on the slag composition. Moreover, since these elements don't react with each other in the water phase and the amounts are limited except for Ca, it is considered that there is little mutual effect among these elements during dissolution. As research continues, researchers gradually realized that direct usage of steelmaking slag in seawater is not ideal, because Fe release from slag to seawater is quite limited. Steelmaking slag usually contains a certain amount of free CaO, which increases the pH of the water phase and causes a sharp decrease in the solubility of Fe. The usage of organics in seawater is considered to be effective in boosting Fe release (Yamamoto et al., 2020; Kawasaki, et al., 2021). Some organics, such as humic acid (Yamamoto et al., 2010) and gluconic acid (Zhang et al., 2014; Zhang et al., 2015; Sakurai et al., 2020; Yang et al., 2021), are reactive with soluble Fe to form chelates, which are stable, soluble

and absorbable for seaweeds. The chelate reaction may disturb the initial equilibrium between slag and water, leading to a significant improvement in Fe release from slag. However, how to add organics together with steelmaking slag into seawater efficiently and cost-effectively in practice remains a challenge. Yamamoto et al. used composts or bamboo powder together with steelmaking slag and observed the acceleration in Fe leaching rate (Yamamoto and Liu, 2016). Kato et al. reported an effective method of mixing steelmaking slag with humus soil (Kato et al., 2015). These studies demonstrated that using an additive capable of releasing functional organics together with steelmaking slag can improve Fe release. Taking into account large-scale utilization, the candidate material must be cheap in price and enormous in quantity.

This work proposes an optimized technology of using steelmaking slag together with municipal green waste as the underwater Fe source, as illustrated in Fig. 2. Fe released from slag in seawater may instantly react with natural organics released from municipal green waste to form chelates, which can be absorbed by seaweeds. Municipal green wastes rich in natural organics have the advantages in eco-friendly, low cost and enormous quantity. Combining the usage of steelmaking slag and municipal green waste may offer a cost-effective solution to promote Fe release from slag to water.

Tangerine peel and used tea leave are two typical municipal green wastes. Global production of tangerine in 2020 was around 33.1 million tons, generating peel waste accounting for approximately 7% to 11% of the total amount. Tangerine peel is rich in flavonoids (up to 4.5%) (United States Department of Agriculture, 2021; Mahato et al., 2019; Marín et al., 2007). Belonging to the family of polyphenolics, flavonoids may react with Fe to form chelates with a high antioxidant ability (Dimitrić et al., 2011; Stanisic et al., 2020; Kostyuk et al., 2004). Used tea leave is another commonly found green waste in daily life. Global production of tea is about 5.73 million tons per year (Food and Agriculture Organization of the United Nations, 2018). Used tea leave contains catechins which may also be reactive with Fe to form stable chelates (Cabrera et al., 2003; Markova et al., 2014).

As a fundamental study to develop a technology for mass cultivation of benthic seaweeds by utilizing steelmaking slag, this work aims to find a cost-effective method to promote Fe release from slag to water. Two municipal green wastes, tangerine peel and used tea leave, are used as additives. By clarifying the leaching behavior of steelmaking slag in freshwater under different conditions, the effects of tangerine peel and used tea leave on Fe release are evaluated and the mechanisms are investigated. A technology for the cultivation of benthic seaweeds by utilizing steelmaking slag and municipal green wastes can

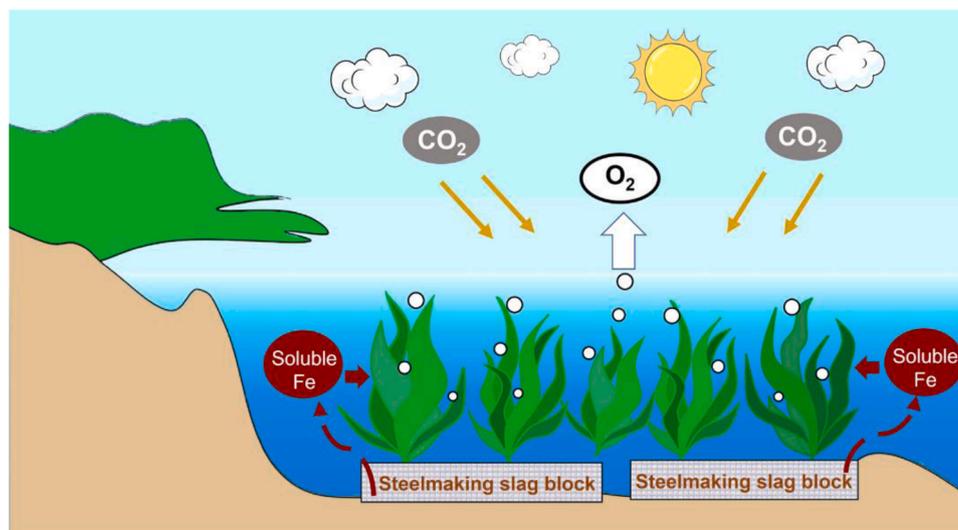


Fig. 1. Cultivating benthic seaweeds by utilizing steelmaking slag as the Fe source in coastal seabed.

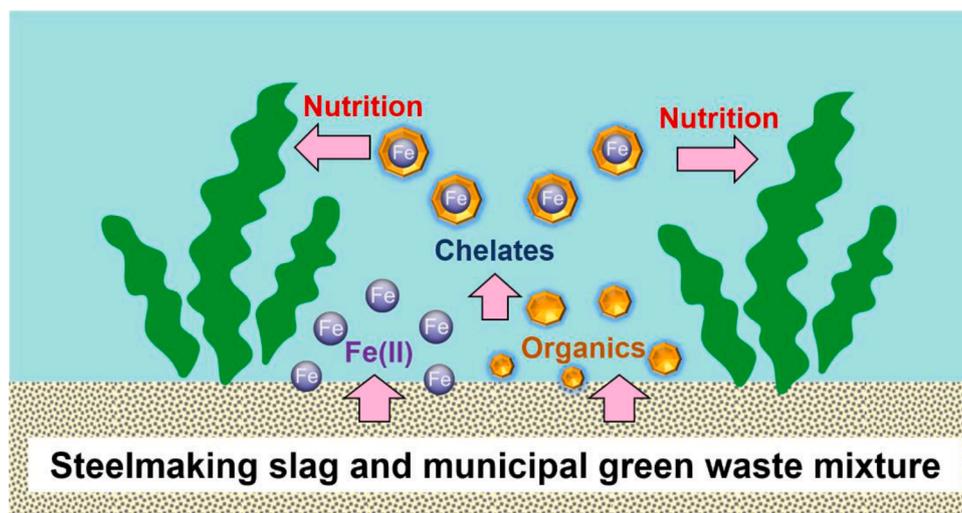


Fig. 2. Scheme of using steelmaking slag and municipal green waste mixture as the underwater Fe source.

simultaneously address the two issues of CO<sub>2</sub> mitigation and waste management.

## 2. Materials and methods

### 2.1. Materials

Steelmaking slag was obtained from a 180-ton basic oxygen furnace (BOF) producing carbon steel in China. Table 1 lists the composition analyzed by an X-ray fluorescence spectrometer (XRF, ARL-9900, Thermo Fisher). The slag was ground and the sieved particles in the size range of 0.28–0.50 mm were used. The slag was also measured by X-ray diffraction (XRD, Cu K $\alpha$ , scanning speed of 12 deg. min<sup>-1</sup> from 10 deg. to 80 deg., Bruker Co. Ltd., D8 Advance). The morphology of slags was recorded with the analytical field emission scanning electron microscope (SEM Gemini 450, ZEISS, Germany). Tangerine peels were obtained from tangerine produced in Guangxi, China. Tea leaves were obtained after consumption (white tea; harvested in Zhejiang, China). Tangerine peels dried in air at room temperature were pulverized to powder with an average size of 0.15 mm. The particle size of the powder is analyzed by a laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd.). The used tea leaves were directly used after drying at 333 K in an oven.

Quercetin, lonicerin, rhiofolin, narirutin, narigin, neohesperidin, hesperidin, hesperetin, vitexin, nomilin, rutin, narigenin, apigenin, limonin were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.; diosmin, obacunone, nobiletin were purchased from Bide Pharmatech Co., Ltd.; and vicenin-2 was purchased from MedChemExpress, Monmouth Junction. These chemicals were used as references to identify the organic released from tangerine peel or used tea leaves and to assess their ability to promote Fe release.

### 2.2. Methods

Release of Fe(II) from steelmaking slag was tested in batch experiments at 298 K. Supplementary Fig. S1 shows an illustration of the experiment. Steelmaking slag (0.50 g), municipal waste (0.10 or 0.30 g), or a mixture of slag and waste were packed into a dialysis bag (flat width

34 mm, MWCO 8000–14000Da). The reason to use a dialysis bag is to avoid the entrapment of ultrafine particles in the solution outside the bag. The permeability of soluble Fe and impermeability of non-soluble Fe [e.g. Fe(OH)<sub>3</sub> and slag particles] through the bag had been confirmed in pre-experiment. The bag poured with 15 mL distilled water was set in a high-density polyethylene bottle (diameter 32 mm, height 28 mm, volume 125 mL) containing 110 mL water. The bottle was set in a shaking bath at 298 K with a shaking speed of 160 RPM. Shaking time ranged from 0.2 h to 648 h.

### 2.3. Analysis and characterization

After shaking, the pH of the solution outside the dialysis bag was immediately measured with a pH meter (DZS-708, Leici Ltd.). Concentrations of elements (Ca, P, Mg and total Fe) in the solution outside the dialysis bag were measured with an inductively coupled plasma mass spectrometer (ICP-MS, iCAP RQ, Thermo Fisher). Concentrations of total Fe in the solution inside the dialysis bag were measured by ICP-MS after passing a filter paper (ashless, 2.5  $\mu$ m pore size). The concentration of ferrous iron [Fe(II)] was determined by the colorimetric method with 1,10-phenanthroline monohydrate (Phygene Biotechnology Co., Ltd.) as the indicator by using an ultraviolet-visible-near infrared spectrometer (UV-Vis-NIR, UV-3600 plus, Shimadzu Co., Ltd.). Total organic carbon concentrations were determined by a total organic carbon analyzer (TOC-L, Shimadzu Co., Ltd.).

To identify the organics released from the tangerine peel, the tangerine peel powder (0.10 g) was soaked in a Ca(OH)<sub>2</sub> solution (pH=11.5). After shaking for 72 h, the solution was treated with a hydrophilic-lipophilic balanced polymer column (Oasis HLB, cartridge column, 3.9  $\times$  150 mm, avg. particle diameter 28.9  $\mu$ m) to remove Ca. Afterwards, the solution sample was analyzed by an ultra-high performance liquid chromatography-time of flight mass spectrometry (UPLC-MS, SYNAPT-G2-Si, Waters).

UPLC-MS was also conducted to study the formation of Fe(II) chelates with flavonoids. After diluting ammonium iron(II) sulfate solution (5600 mg L<sup>-1</sup>) with ammonium acetate (770.8 mg L<sup>-1</sup>) buffer solution 100 times, the Fe(II)-bearing solution was mixed with a flavonoid (200 mg L<sup>-1</sup>) in a ratio of 1: 10 and further diluted with methanol/water (v/v=1) solution. Concentrations of Fe(II) and flavonoid in the sample solution for analysis were 0.5 mg L<sup>-1</sup> and 5 mg L<sup>-1</sup>, respectively. Details of UPLC-MS analysis are given in supplementary material.

Table 1

Composition of a practical steelmaking slag (mass%).

| Total Fe | FeO   | SiO <sub>2</sub> | CaO   | MgO  | P <sub>2</sub> O <sub>5</sub> |
|----------|-------|------------------|-------|------|-------------------------------|
| 21.10    | 17.01 | 12.18            | 44.36 | 7.86 | 3.33                          |

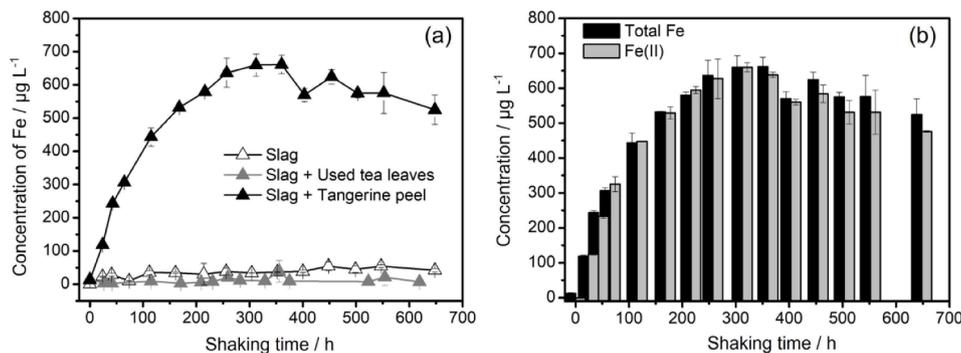
### 3. Results and discussion

#### 3.1. Fe release behavior from steelmaking slag

Supplementary Fig. S2 shows the XRD patterns and SEM images of the slag particles before and after leaching for 168 h. Except the disappeared MgO peaks, there is little noticeable change in the XRD pattern and morphology for the slag after leaching. Effects of microstructure on the reaction behavior of slag in water and structural variation during leaching are not considered in this work.

At first, the leaching behavior of steelmaking slag in distilled water and the effects of adding tangerine peel or used tea leave were clarified. Variation of pH and concentrations of Ca, Mg and P are shown in supplementary Fig. S3. Reaction between CaO-bearing phases in slag and water causes an immediate increase in pH and concentration of Ca in the solution in all cases. According to the slag composition and this result, it is believed that free CaO should be contained in the initial slag, although not detected by XRD. Both Mg and P in the solution are less than  $400 \mu\text{g L}^{-1}$  even after 150 h. Fig. 3a shows the time dependence of Fe concentration in the solution after leaching. The distilled water is free of Fe. The concentrations of Fe in the internal and external solution of the dialysis bag were measured, as shown in Fig. S4. After 24 h, the Fe concentration on both sides reached equilibrium, indicating that the soluble Fe can completely pass through the dialysis bag. When using steelmaking slag without additives, Fe is slightly released from slag, yet the concentration is no more than  $30 \mu\text{g L}^{-1}$  even after leaching for a long time (ca. 684 h). Addition of tangerine peel leads to a remarkable improvement. Fe concentration continues to increase within 300 h and maintains at a high level (no less than  $500 \mu\text{g L}^{-1}$ ) in the subsequent time period. The maximum concentration is approximately  $650 \mu\text{g L}^{-1}$ , 20 times more than the case without adding tangerine peel. Since it had been clarified that tangerine peel itself could not supply Fe, organics released from tangerine peel should be the reason in promoting Fe release. The relationships between Fe concentration and other elements (Ca, Mg and P) in the case of adding tangerine peel are shown in supplementary Fig. S4. As can be seen, Fe increases together with Ca and P, while decreases as Mg increases. This result indicates that these elements play important and interlocking roles with each other during leaching. The reason is considered to be the interconnected thermodynamic properties of soluble ions of these elements in the solution. In a separate study, the used slags were sintered at 1473 K for different time (1 h, 10 h, and 24 h) in Ar to clarify the effect of slag grain size on soluble Fe release. However, no apparent difference was observed.

Fig. 3a also shows that Fe concentration with addition of used tea leaves is extremely low. Although some organics must be released in the solution from used tea leaves, they are not reactive with Fe. Therefore, it is considered that addition of used tea leaves is not effective in promoting Fe release from slag.



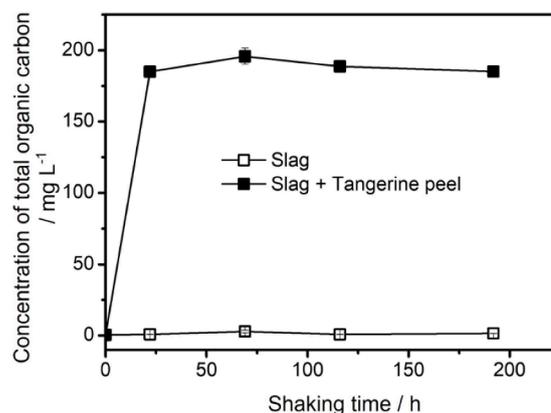
**Fig. 3.** (a) Time dependences of Fe concentration in the solution (125 mL) after leaching steelmaking slag (0.50 g) with or without addition of tangerine peel (0.10 g) and used tea leaves (0.30 g) at 298 K. (b) Time dependences of concentrations of ferrous Fe [Fe(II)] measured by UV-Vis-NIR and total Fe measured by ICP-MS in the solution (125 mL) after leaching steelmaking slag (0.50 g) with addition of tangerine peel (0.10 g) at 298 K.

The valence state of soluble Fe in the post-leaching solution with addition of tangerine peel was investigated. Fig. 3b shows the concentration of ferrous Fe [Fe(II)] measured by UV-Vis-NIR. The concentration of total Fe measured by ICP-MS is also plotted. As shown, most of the soluble Fe in the post-leaching solution occur in the state of Fe(II), whose concentration maintains almost constant at a high level (no less than  $500 \mu\text{g L}^{-1}$ ) throughout the experiment, even in the solution with a pH higher than 11 (supplementary Fig. S3). These results indicate that tangerine peel is an excellent additive in promoting Fe release from slag and making the soluble Fe stable.

#### 3.2. Organics supplied by tangerine peel

During leaching, the solution color when using the mixture of steelmaking slag and tangerine peel gradually changed from colorless to bright yellow, different from the case of using only steelmaking slag. The phenomenon indicates the release of specific organics from tangerine peel, which may be related to the promotion in Fe release. Fig. 4 shows the total organic carbon (TOC) concentration in the leached solutions. There was barely any organic carbon in the solution containing only steelmaking slag. With addition of tangerine peel, the TOC concentration rises to a high level (no less than  $180 \text{ mg L}^{-1}$ ) after ca. 24 h and remains constant. The release of organics from tangerine peel is more efficient than the release of Fe from slag in terms of quantity and rate, which should benefit the chelating reaction of Fe(II).

It is considered that a couple of organics had been released from the tangerine peel powder into the solution. To identify these organics, the tangerine peel powder was soaked into the  $\text{Ca}(\text{OH})_2$  solution (pH=11.5)



**Fig. 4.** Time dependence of concentration of total organic carbon released in the solution (125 mL) after leaching steelmaking slag (0.50 g) with or without addition of tangerine peel (0.10 g) at 298 K.

and the solution was measured with UPLC-MS. By comparing the pattern with those of the solutions containing with pure organics, nine organic species possibly released from tangerine peel can be identified. They are vicenin-2, vitexin, diosmin, hesperidin, apigenin, hesperetin, limonin, obacunone and nobiletin. Characterizations of these organics are shown in Fig. 5 and listed in Table 2.

Effects of each organic on Fe release from steelmaking slag were evaluated. These natural compounds are safe and stable in water. Most of them have effective anticancer activities, and are usually extracted for applications as active constituents of medicinal agents (Nagaprasanthan, et al., 2011; Gerges, et al., 2022; Yan et al., 2017; Gong, et al., 2019). Therefore, tangerine peel is an eco-friendly additive and tangerine peel-based products should be pollution-free to the environment. Experiments of leaching steelmaking slag in distilled water with the addition of these organics individually were conducted. Fig. 6 shows the Fe concentration in the solution after leaching for 72 h. Obvious promotion effects on Fe release from steelmaking slag were observed when adding vicenin-2, apigenin, hesperidin, vitexin, hesperetin and diosmin, while the effects when using obacunone, limonin and nobiletin. In general, species belonging to the family of flavonoids are more effective than others.

### 3.3. Chelating reactions between flavonoids and Fe(II)

It has become clear that tangerine peel promotes Fe release from steelmaking slag in water by supplying flavonoids. The organics belonging to the family of flavonoids usually possess versatile properties such as antioxidant and chelating activities (Kasprzak et al., 2015). To confirm the formation of flavonoid-Fe(II) chelates, species belonging to the family of flavonoids (vicenin, apigenin, hesperidin, vitexin and hesperetin) dissolved in the solution of methanol/water (v/v=1) were mixed with Fe(II)-bearing solution. Fig. 7 shows the electrospray ionization mass spectroscopy spectra of five possible flavonoids-Fe(II) chelates detected by UPLC-MS. In addition to the free ligands, vicenin ( $m/z = 595.1665$ ,  $[\text{Vic}+\text{H}]^+$ ), apigenin ( $m/z = 271.0628$ ,  $[\text{Api}+\text{H}]^+$ ), hesperidin ( $m/z = 611.1973$ ,  $[\text{Hes}+\text{H}]^+$ ), vitexin ( $m/z = 433.1141$ ,  $[\text{Vit}+\text{H}]^+$ ) and hesperetin ( $m/z = 303.0883$ ,  $[\text{Het}+\text{H}]^+$ ), isotopic pattern of flavonoids-Fe(II) chelates were readily detected at  $m/z = 1242.2341$  and  $1243.2362$  ( $[\text{Fe}^{\text{II}}(\text{Vic}-\text{H})_2]^+$  and  $[\text{Fe}^{\text{II}}(\text{Vic})(\text{Vic}-\text{H})]^+$ ), 594.0248

( $[\text{Fe}^{\text{II}}(\text{Api}-\text{H})_2]^+$ ), 1274.2928 and 1275.2961 ( $[\text{Fe}^{\text{II}}(\text{Hed}-\text{H})_2]^+$  and  $[\text{Fe}^{\text{II}}(\text{Hed})(\text{Hed}-\text{H})]^+$ ), 918.1275 and 919.1316 ( $[\text{Fe}^{\text{II}}(\text{Vit}-\text{H})_2]^+$  and  $[\text{Fe}^{\text{II}}(\text{Vit})(\text{Vit}-\text{H})]^+$ ), 658.0751 ( $[\text{Fe}^{\text{II}}(\text{Het}-\text{H})_2]^+$ ), respectively. All chelates are signed to a 2:1 (Flavonoids:Fe(II)) binding formation, releasing one or two hydrogens. There was no 1:1 or 3:2 (Flavonoids:Fe(II)) stoichiometry of Fe(II) chelates spectra to fit well the isotopic pattern. Formation of these chelates can explain why tangerine peel promotes Fe release from steelmaking slag in water.

Most flavonoids contain ortho-phenolic hydroxyl group, or phenolic hydroxyl group with a nearby carboxylate or carbonyl group in a cis conformation. Fig. 8 shows the flavonoid base structure. Phenolic hydroxyl group and the adjacent carbonyl group play a critical role in iron chelation, as reported in detail in the literature (Guo et al., 2007; Kim et al., 2013). Simple Fe(II) ions are easy to be bound with oxygen donors at positions 4 and 5 to form chelates (Uivarosi et al., 2019).

Taking apigenin and vicenin-2 for examples, the possible chelating reactions can be illustrated as shown in Fig. 9. Because the amount of Fe(II) ions released from slag is limited, influence of the chelating reactions on pH of the solution is ignorable. One Fe(II) ion may be coordinated by 4 and 5 oxygen donors on two of flavonoid molecules to form the complex.

### 3.4. Mechanism of tangerine peel promoting Fe release from steelmaking slag in water

The overall equilibrium between soluble Fe(II) in solution and Fe(II) in slag can be written as



The equilibrium after addition of tangerine peel powder must have changed because the chemical states of Fe(II) in solution [right side of reaction (1)] are different.

The equilibrium constant ( $K$ ) can be written as

$$K = \frac{a_{\text{Fe(II)}}^{\text{in solution}} C_{\text{Fe(II)}}^{\text{in solution}}}{a_{\text{Fe(II)}}^{\text{in slag}}} \quad (2)$$

$$RT \ln K = \mu_{\text{Fe(II)}}^{0, \text{in slag}} - \mu_{\text{Fe(II)}}^{0, \text{in solution}} \quad (3)$$

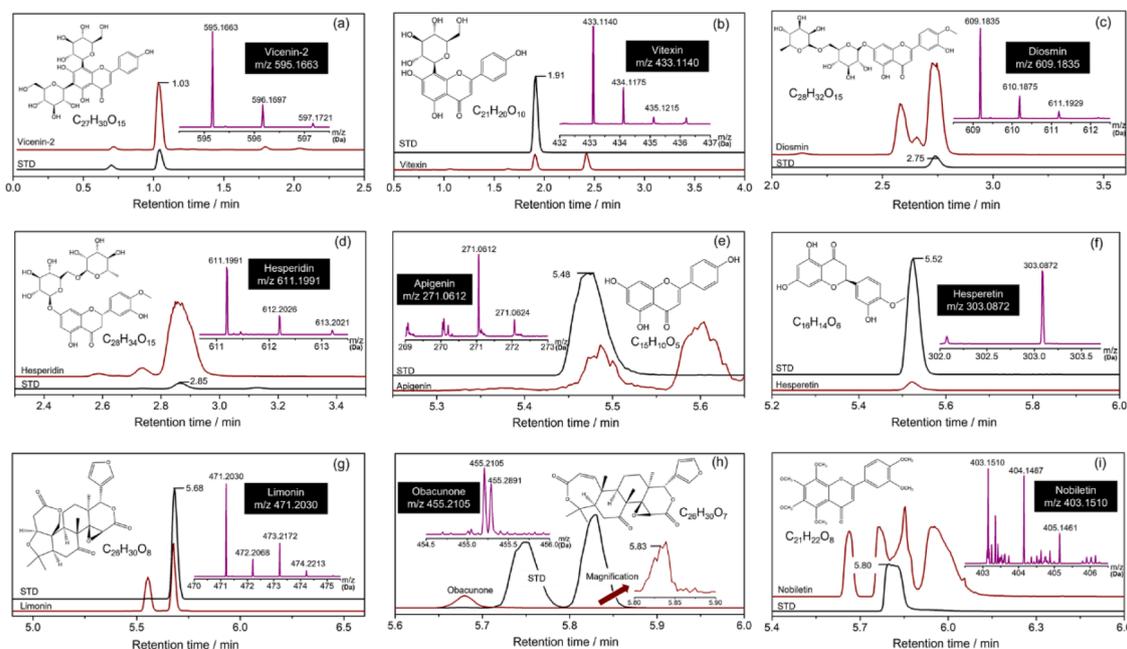
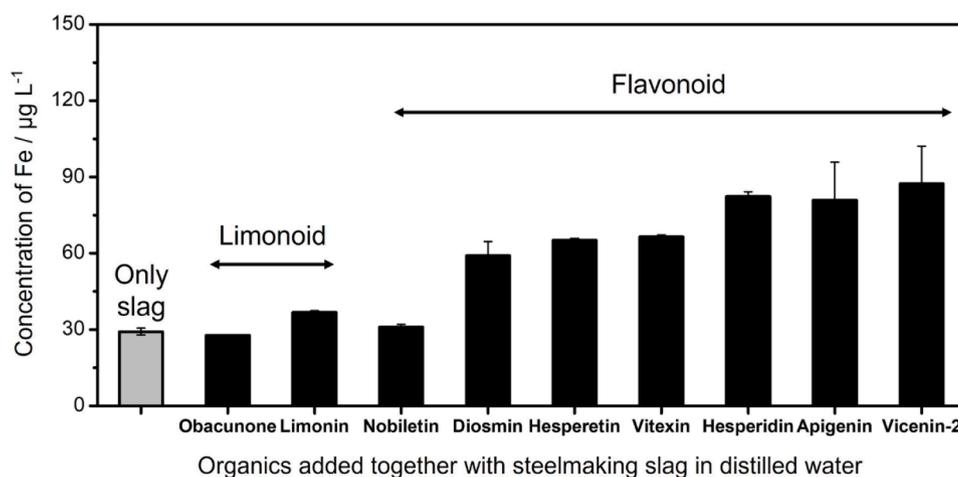


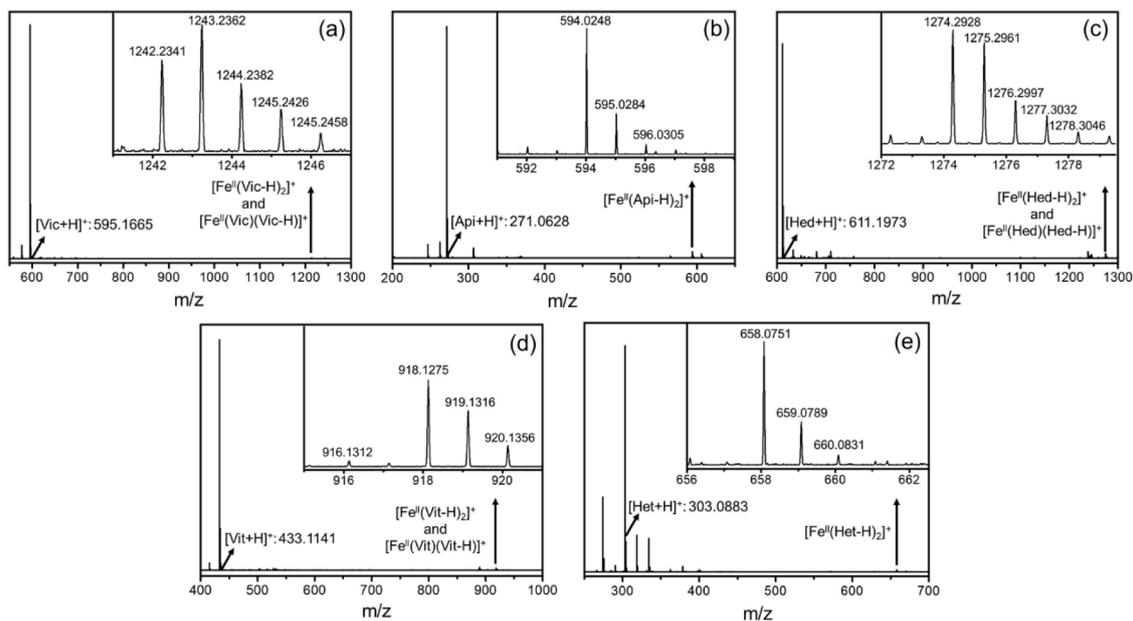
Fig. 5. Chemical structures, representative chromatogram and mass spectra of nine organic species released from tangerine peel in  $\text{Ca}(\text{OH})_2$  solution ( $\text{pH}=11.5$ ), identified by UPLC-MS (STD, corresponded internal standards).

**Table 2**Characterization of the organics released from tangerine peel in the Ca(OH)<sub>2</sub> solution identified by UPLC-MS.

| Analyte identification | Formula   | Retention time / min | [M+H] <sub>t</sub> <sup>+</sup> | [M+H] <sub>a</sub> <sup>+</sup> | Class                    |
|------------------------|---|----------------------|---------------------------------|---------------------------------|--------------------------|
| Flavonoid              |   |                      |                                 |                                 |                          |
| Vicenin-2              | C <sub>27</sub> H <sub>30</sub> O <sub>15</sub> | 1.03                 | 595.1663                        | 595.1663                        | Flavone-C-glycoside      |
| Vitexin                | C <sub>21</sub> H <sub>20</sub> O <sub>10</sub> | 1.91                 | 433.1135                        | 433.1140                        | Flavone-C-glycoside      |
| Diosmin                | C <sub>28</sub> H <sub>32</sub> O <sub>15</sub> | 2.75                 | 609.1819                        | 609.1835                        | Flavone-O-glycoside      |
| Hesperidin             | C <sub>28</sub> H <sub>34</sub> O <sub>15</sub> | 2.86                 | 611.1976                        | 611.1991                        | Flavone-O-glycoside      |
| Apigenin               | C <sub>15</sub> H <sub>10</sub> O <sub>5</sub>  | 5.48                 | 271.0606                        | 271.0612                        | Flavone aglycone         |
| Hesperetin             | C <sub>16</sub> H <sub>14</sub> O <sub>6</sub>  | 5.52                 | 303.0869                        | 303.0872                        | Flavone aglycone         |
| Nobiletin              | C <sub>21</sub> H <sub>22</sub> O <sub>8</sub>  | 5.85                 | 403.1393                        | 403.1510                        | Polymethoxylated flavone |
| Limonoid               |   |                      |                                 |                                 |                          |
| Limonin                | C <sub>26</sub> H <sub>30</sub> O <sub>8</sub>  | 5.68                 | 471.2019                        | 471.2030                        | Limonoid                 |
| Obacunone              | C <sub>26</sub> H <sub>30</sub> O <sub>7</sub>  | 5.83                 | 455.2070                        | 455.2105                        | Limonoid                 |

<sup>t</sup>Theoretical value<sup>a</sup>Actually detected value

**Fig. 6.** Fe concentrations in the solution (12.5 mL) after leaching steelmaking slag (0.05 g) in distilled water with addition of different organics (0.001 g) for 72 h at 298K. Obacunone and limonin belong to the family of limonoid; nobiletin, diosmin, hesperetin, vitexin, hesperidin, apigenin, and vicenin-2 belong to the family of flavonoid.



**Fig. 7.** Electro-spray mass spectra of five chelates formed between Fe(II) ions (0.5 mg L<sup>-1</sup>) and (a) vicenin (Vic), (b) apigenin (Api), (c) hesperidin (Hed), (d) vitexin (Vit) and (e) hesperetin (Het) (5 mg L<sup>-1</sup> each) in the solution of methanol/water (v/v=1), as detected by UPLC-MS.

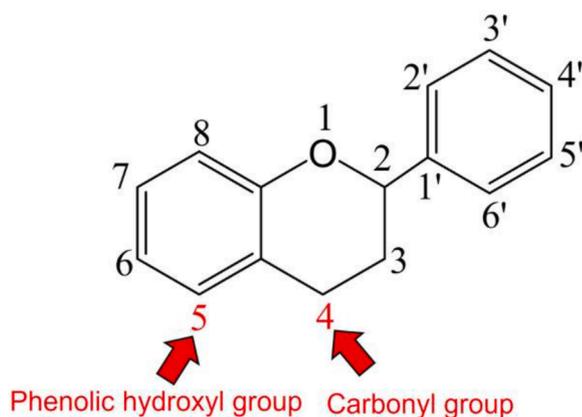


Fig. 8. Flavonoid base structure (red number marks the possible chelate position with Fe(II) ions).

where  $r_{\text{Fe(II)}}^{\text{in solution}}$  and  $C_{\text{Fe(II)}}^{\text{in solution}}$  are activity coefficient and mole fraction of Fe(II) in solution, respectively;  $a_{\text{Fe(II)}}^{\text{in slag}}$  is activity of Fe(II) in slag;  $\mu_{\text{Fe(II)}}^{0, \text{in slag}}$  and  $\mu_{\text{Fe(II)}}^{0, \text{in solution}}$  are chemical potential of Fe(II) in slag and in solution at standard state conditions, respectively. Combination of Eqs. (2) and (3) leads to

$$\ln C_{\text{Fe(II)}}^{\text{in solution}} = \frac{\mu_{\text{Fe(II)}}^{0, \text{in slag}} - \mu_{\text{Fe(II)}}^{0, \text{in solution}}}{RT} + \ln \frac{a_{\text{Fe(II)}}^{\text{in slag}}}{r_{\text{Fe(II)}}^{\text{in solution}}} \quad (4)$$

$\mu_{\text{Fe(II)}}^{0, \text{in slag}}$  and  $a_{\text{Fe(II)}}^{\text{in slag}}$  are considered independent of usage of tangerine peel, given that tangerine peel should not be reactive enough to change the thermodynamic property of the solid phase. Therefore, as can be

seen, the concentration of Fe(II) in solution depends on  $\mu_{\text{Fe(II)}}^{0, \text{in solution}}$  and  $r_{\text{Fe(II)}}^{\text{in solution}}$ , both relevant to the thermodynamic property of Fe(II) in solution. Decrease in  $\mu_{\text{Fe(II)}}^{0, \text{in solution}}$  or  $r_{\text{Fe(II)}}^{\text{in solution}}$  leads to the increase in the concentration of Fe(II) in solution.

Accordingly, the mechanism can be summarized, as illustrated in Fig. 10. When setting the mixture of steelmaking slag and tangerine peel in a water phase, simple Fe(II) ions will be released from steelmaking slag while flavonoids organics will be released from tangerine peel. Fe(II) ions may coordinate with oxygen donors of carbonyl and adjacent phenolic hydroxyl groups on flavonoids to form flavonoid-Fe(II) chelates, which are rather stable even in alkaline solutions.

The formation of flavonoid-Fe(II) chelates must have changed the thermodynamic property of Fe(II) in the solution. Consequently, the initial equilibrium between Fe-bearing solid oxides in slag and simple Fe(II) ions in water is disturbed, leading to a continuous release of Fe from slag until establishing a new equilibrium between Fe(II) in slag and Fe(II) in solution. Therefore, a significant improvement in Fe release from slag is observed when adding tangerine peel together. Given the flavonoid-Fe(II) chelates can be absorbed by seaweeds eventually in a practical application, the mass transfer of Fe from steelmaking slag to seaweeds can be described as  $\text{Fe}_{\text{in slag}}^{\text{oxides}} \rightarrow \text{Fe}_{\text{in water}}^{\text{simple ions}} \rightarrow \text{Fe}_{\text{in water}}^{\text{chelates}} \rightarrow \text{Fe}_{\text{in seaweeds}}$ .

### 3.5. Verification of the effect on seaweed growth

To verify the boosting effect of steelmaking slag and tangerine peel on seaweeds growth, an experiment of cultivating ulva (collected from Jiangsu, China) in artificial seawater was conducted. The seaweeds were set in the sterilized artificial seawater in the incubator for 2 days for acclimation. After that, the collected healthy seaweeds were cut into 11-15 cm<sup>2</sup> rectangle shapes and set into the sterile cell culture flask (culture area 175 cm<sup>2</sup>) with 350 mL artificial seawater. Steelmaking slag (0.50 g)

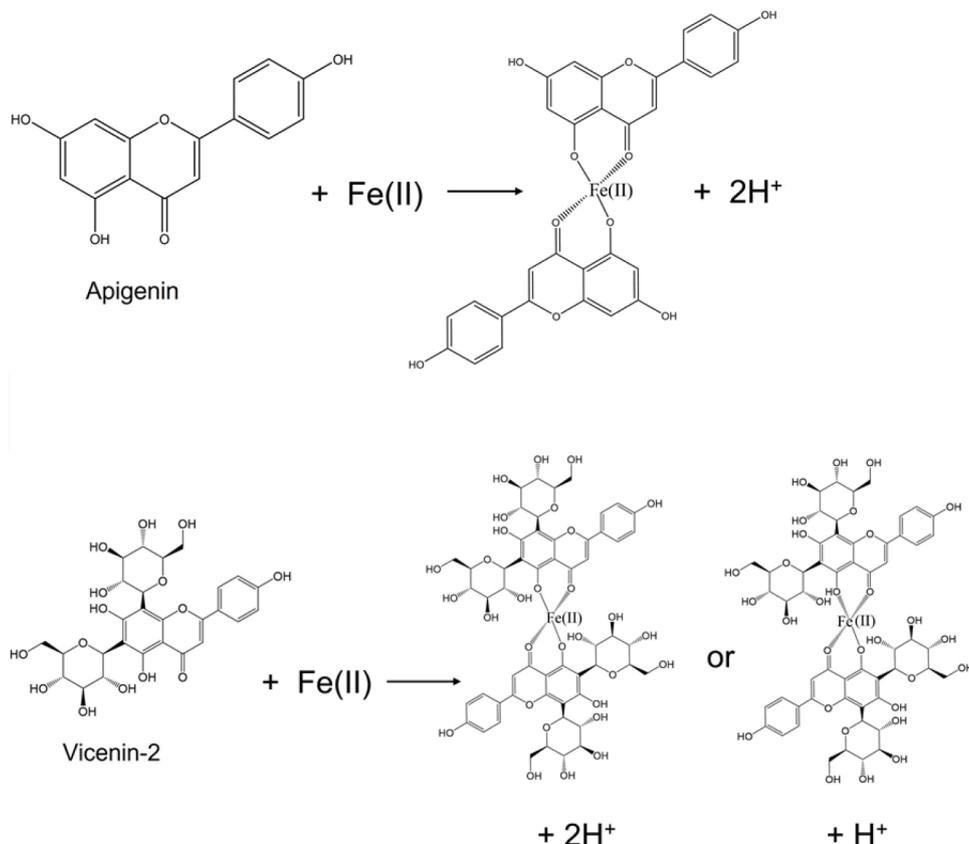


Fig. 9. Possible chelating reactions between flavonoids (apigenin and vicenin-2) and Fe(II) ions.

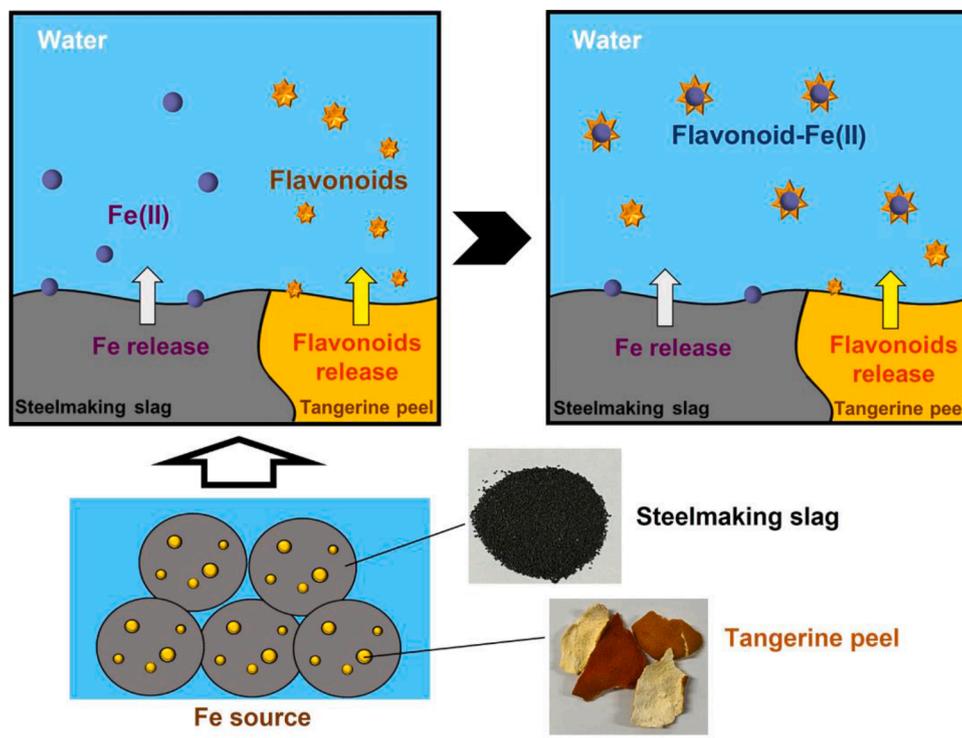


Fig. 10. Mechanism of tangerine peel promoting Fe release from steelmaking slag in water.

or a mixture of steelmaking slag (0.50 g) with tangerine peel (0.10 g) were set in the dialysis bags with 15 mL seawater, which were settled in the seaweeds cultivated flask. The cultivation lasted for 23 days in the incubator at 293 K. The experimental method is shown in Fig. S6. Variation of ulva appearance and fresh mass were taken and recorded. The results are shown in Fig. 11. In the case of adding steelmaking slag and tangerine peel together, boosting effect on ulva growth was the most apparent compared with the other two cases. The seaweed gradually became larger, and its fresh mass increased a lot through the cultivation term. These results sufficiently verify the possibility of cultivating benthic seaweeds in the coastal area by using a steelmaking slag and tangerine peel mixture.

### 3.6. Application prospect

Experiments in this work confirm the efficacy to promote Fe release from slag to water by using tangerine peel as an additive. The method is quite simple. Since both steelmaking slag and tangerine peel are cheap in price, enormous in quantity, and generally safe to the environment, the waste tangerine peels after drying at room temperature and

pulverization can be directly mixed with steelmaking slag to prepare artificial rocks or reefs with added values. Fig. 12 shows the flow chart of processing wastes from steel plant and tangerine orchard into artificial rock or reef. Here, steelmaking slag plays the role of Fe(II) source while tangerine peel is the Fe(II) stabilizer. Fine powders of ironmaking slag function as a binder when forming the product. Since the manufacture and management of artificial rocks or reefs are well-established practices, by simply setting these newly-formulated rocks or reefs in the coastal seabed, enhanced growth of benthic seaweeds in the surrounding area can be expected. Such a recycling technology may lead to a considerable decrease in waste volume and thus ease the management burdens, though new policies for efficient management of treatment and recycling are still needed.

### 4. Conclusions

In an attempt to utilize steelmaking slag as a Fe source for coastal seaweeds, this work evaluates the effects of tangerine peel and used tea leaves on the promotion of Fe release from steelmaking slag. By conducting experiments of leaching steelmaking slag in freshwater, a sharp

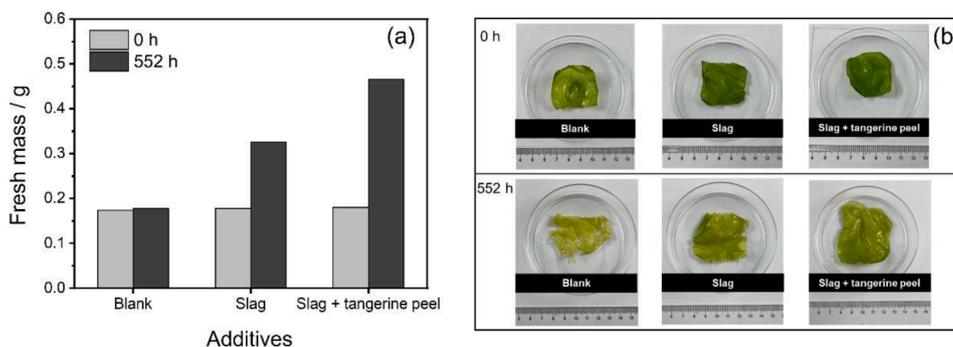


Fig. 11. Variation of (a) fresh mass and (b) appearance of ulva during cultivation at 293 K. Experiments in three solutions (365 ml) were conducted: only seawater, seawater + slag (0.50 g), and seawater + slag (0.50 g) + tangerine peel (0.10 g).



Fig. 12. The flow chart of processing wastes from steel plant and tangerine orchard into artificial rock or reef for seaweeds cultivation.

increase in the concentration of soluble Fe was observed with the addition of tangerine peel, while there was no change with the used tea leaves addition. It was clarified that tangerine peel promotes Fe release from steelmaking slag in water by supplying specific organics belonging to the family of flavonoids. The formation of stable flavonoid-Fe(II) chelates disturbs the initial equilibrium between Fe-bearing oxides in slag and simple Fe(II) ions in water and leads to a continuous release of Fe from slag until establishing a new equilibrium between Fe(II) in slag and Fe(II) in water. This work has thus demonstrated the feasibility to develop a technology for Fe supply in seawater by utilizing steelmaking slag and municipal green wastes.

#### CRediT authorship contribution statement

**Dan Yu:** Data curation, Formal analysis, Investigation, Software, Validation, Writing-original draft. **Fei Liu:** Methodology, Resources. **Changdong Zou:** Data curation, Investigation. **Xiao Yang:** Conceptualization, Data curation, Project administration, Supervision, Writing-review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

#### Data Availability

Data will be made available on request.

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#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.resconrec.2022.106722](https://doi.org/10.1016/j.resconrec.2022.106722).

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