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Environment-enhancing process for algal wastewater treatment, heavy metal control and hydrothermal biofuel production: A critical review

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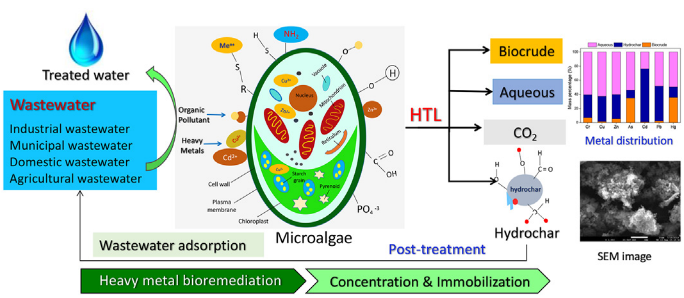
GRAPHIC ABSTRACT



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ABSTRACT

Coupling algae growth on wastewater with hydrothermal liquefaction (HTL) is regarded as an environment-enhancing pathway for wastewater management, biomass amplification, sustainable energy generation and value-added products generation. Through this integrated pathway, microalgae can not only recover nitrogen and phosphorus, but also absorb heavy metals from the wastewater. The migration and transformation of heavy metals need to be specifically assessed and considered due to the environmental concerns associated with metal toxicity. This work reviewed recent advances with respect to bioremediation mechanisms. Particular emphasis was placed on the heavy metal migration, transformation, and the key factors involved in algal wastewater treatment and biomass conversion. Additionally, the challenges of coupling algae wastewater treatment, hydrothermal conversion, and heavy metal control were addressed. Finally, a paradigm involving enhanced algal wastewater treatment and bioenergy production for field application was proposed.

1. Introduction

Microalgae is a promising candidate for biofuel production due to its high biomass accumulation rate, high photosynthetic efficiency, high resistance to harmful substances in wastewater, and its efficient capability to capture CO_2 (Zhou et al., 2014). Wastewater treatment via microalgae cultivation is considered to be a promising pathway to produce biofuel, due to the fact that microalgae have the capability of recovering nitrogen, phosphorus, organic compounds, and even heavy metals in the wastewater (Cai et al., 2013; Chan et al., 2013; Renuka et al., 2015). The major steps involved in wastewater treatment via microalgae growth for biofuel generation are shown in Fig. 1.

Heavy metals pose a great danger to the ecosystem and human health due to their permanent toxicity. The excessive concentration of

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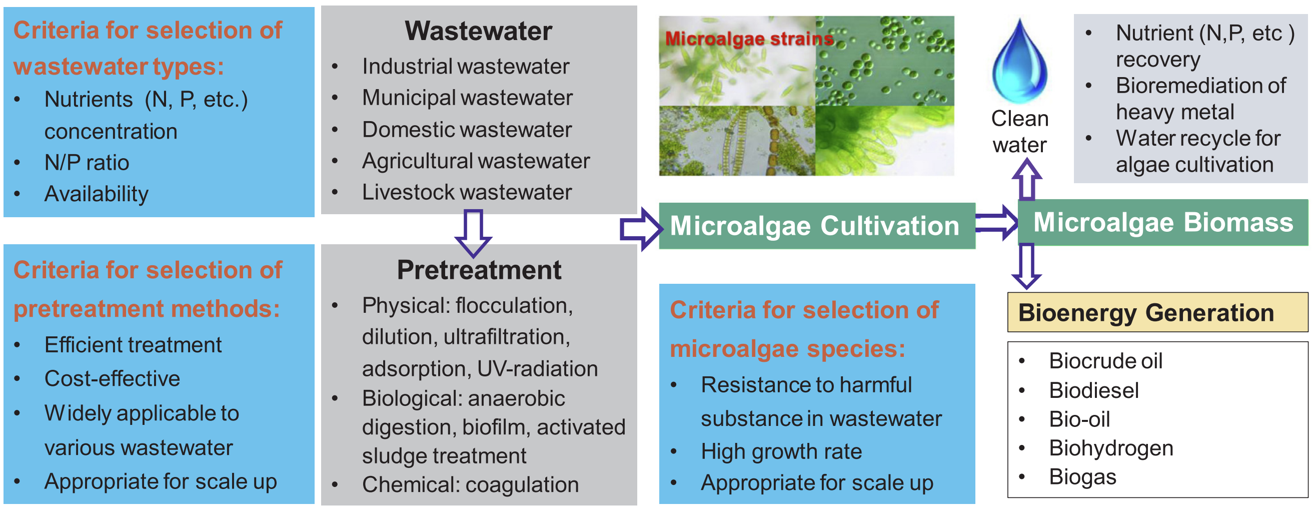

Fig. 1. Main processes from wastewater to algae cultivation and biofuel generation.

heavy metals in wastewater is an extremely concerning problem. Microalgae are able to remove these hazardous metals effectively which can be attributed to their special affinity for metals. Microalgae cultivated in metal-polluted wastewater contain a certain concentration of heavy metals due to the bioaccumulation effect. Currently, many researchers only focus on the recoveries of nitrogen and phosphorus associated with wastewater-grown microalgae. However, the concentration of heavy metals as well as their subsequent migration and transformation during hydrothermal treatment are another important point that needs to be explored in order to achieve the reliable valorization of wastewater-cultivated microalgae. The mechanisms behind heavy metal biosorption, including metal uptake and release routes through metabolism and non-metabolism dependent processes during photosynthesis have been previously systematically summarized. The uptake and release pathways of heavy metals are of great importance during the cultivation and valorization of wastewater fed microalgae, in order to control the speciation and eventual disposal techniques for this process. The mechanism of microalgae biosorption and bioremediation grown with wastewater has been widely studied (Salama et al., 2017). However, the migration and transformation pathways of metals during thermochemical conversion was seldom reported.

The purposes of this work are: 1) to summarize the changes of heavy metals during algal wastewater treatment and hydrothermal treatment; 2) to discuss the key parameters impacting the migration and transformation of heavy metals during hydrothermal treatment; 3) to address the challenges of integrated system coupling algae biomass growth on wastewater, hydrothermal conversion, and heavy metal control.

2. Heavy metal uptake during wastewater treatment via algae growth

The discharge of huge quantities of wastewater from industrial, agricultural, municipal and animal plants pose a great threat to the environment on account of the high risk associated with the toxic heavy metals present within wastewater. The discharge of wastewater into the environment is also harmful to public health if the concentration of heavy metal exceeds the permissible discharge limits for aquatic environments. For instance, the maximum discharge value for Hg, Pb, Cr, Cu, Cd, Zn and Ni concentrations in drinking water should not exceed 0.002, 0.015, 0.1, 1.3, 0.005, 5, and 0.04 mg·L^{-1}, respectively (Suresh Kumar et al., 2015). It is reported that tannery effluents and saline wastewater contained a high concentration of Cr (VI), amounting to 155 mg·L^{-1} and 100 mg·L^{-1}, respectively (Dönmez and Aksu, 2002). It has also been reported that the concentration of Pb^{2+} and Cd^{2+} in some types of industrial wastewater has greatly exceeded the discharge standard of municipal water (Table 1). Conventional heavy metal treatment technologies generally include ion exchange, lime precipitation, chemical precipitation, and adsorption. Practical utilization of these techniques is often ineffective, incomplete, costly and energy inefficient, especially for large volumes of wastewater with a low heavy metal concentration (Jacinto et al., 2009). Growth of microalgae to remove heavy metals offers several unique advantages over traditional techniques, including microalgae's rapid metal uptake capability, energy-saving potential, eco-friendly usage, low cost of implementation, and availability to absorb both high and low concentration levels of metals. The distinct advantages of microalgae over traditional treatment techniques make it an effective candidate for the bioremediation of polluted wastewater. Various species of microalgae (*Chlorella vulgaris, Spirulina maxima, Spirulina platensis, Scenedesmus quadricauda, Coelastrum sp.*, etc) have demonstrated the capability of removing heavy metals (Table 1). The total removal rate of the investigated heavy metals for acid mine drainage wastewater was reported to be 94.89%, 95.60%, 94.19%, 89.22%, 87.50% and 95.00% for Fe, Cu, Zn, Mn, As, and Cd, respectively (Choi, 2015). The main biosorption and metabolism mechanism of microalgae for heavy metals and trace metals is presented in Fig. 2. Theoretical analysis showed that the functional groups conferred a negative charge onto the algae cell surface, due to the accumulation of various functional groups, including carboxyl, hydroxyl, phosphate, amino and sulfhydryl groups. It was demonstrated that these functional groups played vital roles in metal biosorption and uptake by microalgae. In addition, various plasma membrane metal transporters, such as ZIP, CTR, HMA1/HMA6 were responsible for moving Zn^{2+}, Cu^{2+} and Cu^{+} into the cytoplasm (Salama et al., 2017). The cell wall and membrane of microalgae usually is made up of polysaccharides, proteins, and lipids. The membrane transporters are pivotal to facilitating the interaction of microalgae with a concentrated heavy metal environment. The mechanism for heavy metal bioremediation includes non-metabolism dependent uptake and metabolism-dependent uptake. The non-metabolism-dependent process mainly consists of cell surface adsorption (ion exchange, complexation, physical adsorption, and precipitation) and extracellular adsorption (precipitation) (Salama et al., 2019; Suresh Kumar et al., 2015). The metabolism-dependent precipitation process was generally favored by the intracellular adsorption associated with an active metal transportation across membrane process (He and Chen, 2014).

The characteristics of the ultimate analysis and proximate analysis of wastewater-cultivated microalgae are summarized in Fig. 3. The lipid, protein, and carbohydrate of *Chlorella* sp. cultivated in anaerobic digestate were 22%, 60% and 18% (based on a dry ash-free content),

Table 1
Heavy metals removal efficiency during microalgae grown in wastewater reported in the literature.

Wastewater type	Algal species	Initial concentration of heavy metals (ppm)							Removal capacity (%)							Reference
		Cu	Zn	Cd	Cr	Pb	Ni	As	Cu	Zn	Cd	Cr	Pb	Ni	As	
Domestic treatment plant wastewater	*Chlorella* sp.	0.06	0.41	–	–	–	–	–	56.5	82.6	–	–	–	–	–	Mishra et al., 2018
Secondary effluent from wastewater treatment plants	*Chlorella vulgaris; Spirulina maxima;*	56.6	31.6	–	–	–	–	–	81.7	94.1	–	–	–	–	–	Chan et al., 2013
Mixture of sewage, well water and sea water	*C. vulgaris C. salina*	56.73–81	27.11–36.8	–	0–27.09	–	14.7–21	–	55.9–100	64.96	–	21.7–66.5	–	51.11–100	–	El-Sheekh et al., 2016
Pb-containing aqueous solution	*Spirulina platensis*	–	–	–	–	100	–	–	–	–	–	–	91	–	–	Al-Homaidan et al., 2016
Synthetic solutions containing $CdCl_2 \cdot H_2O$ and Pb $(NO_3)_2$	*Scenedesmus quadricauda*	–	–	1000	–	1000	–	–	–	–	66	–	82	–	–	Kipigroch et al., 2015
Industrial effluents	*Phormidium* sp.	–	–	–	–	10	–	–	–	–	–	–	92.5	–	–	Das et al., 2014
Heavy metal adsorbate Cd solution	*Coelastrum* sp.	–	–	1000	–	–	–	–	–	–	32.8 mg g^{-1}	–	–	–	–	Zheng et al., 2016
Acid mine drainage wastewater	*Chlorella* sp.	22.8	19.8	0.27	–	–	–	0.45	95.6	94.2	95	–	–	–	87.5	Choi, 2015
Mixed solution containing both Cu and Ni	*Desmodesmus* sp.	18.9	–	–	–	–	13.8	–	43	–	–	–	–	95	–	Rugnini et al., 2017
	Chlorella vulgaris	18.9	–	–	–	–	13.8	–	39	–	–	–	–	90	–	Rugnini et al., 2017
Copper mine wastewater	*Sargassum*	20	–	–	–	–	–	–	87	–	–	–	–	–	–	Jacinto et al., 2009
Industrial effluent	*Desmodesmus* sp.	9.4	–	–	–	–	7.4	–	94	–	–	–	–	85	–	Rugnini et al., 2018
Tannery effluents	*Anabaena, Oscillatoria, Phormidium,* and *Spirogyra*	–	–	–	155	–	–	–	–	–	–	74.8%-80.64	–	–	–	Balaji et al., 2015
Saline wastewater	*Dunaliella* sp.	–	–	–	100	–	–	–	–	–	–	53.6	–	–	–	Dönmez and Aksu, 2002

respectively. The accumulated concentration of Cu and Zn was approximately 10 ppm and 250 ppm in dry microalgae biomass, respectively (Li et al., 2018a, b, c). The mixed microalgae grown in a wastewater treatment plant had a relatively higher Cu (200 ppm) and Zn (3000 ppm) content (Roberts et al., 2013). This was mainly attributed to the distinction between different microalgae species, cultivation choices, as well as the initial heavy metal concentration. Researchers in Australia cultured three species of algae (*Hydrodictyon, Oedogonium, Rhizoclonium*) in the contaminated wastewater from an ash dam. The average concentration of Cu, Zn, As, Cd, Pb and Cr in these three microalgae species were 42–85 ppm, 2003–4355 ppm, 44–55 ppm, 3.5–8.1 ppm, 2.4–2.9 ppm and 4.2–5.4 ppm, respectively (Saunders et al., 2012). Compared with other kinds of biowaste (e.g. sewage sludge, swine manure, and some hyperaccumulators), the concentration of heavy metals in almost all of the wastewater-fed microalgae was below the threshold disposal standards in China (Wang et al., 2016a,b).

The existence of essential nutrients (carbon, nitrogen, phosphorus and microelements) makes wastewater a promising cultivation medium for microalgae (Luo et al., 2019; Mennaa et al., 2015; Wang et al., 2016a,b). The aim of removing the high concentration of nitrogen and phosphorus from wastewater is to prevent eutrophication in water body. Nitrogen is vitally important for microalgae growth as it is an integral part of the formation of proteins, peptides, enzymes, ATP/ADP and other biological molecules. Microalgae offer several unique advantages, including a high growth rate, an effective photosynthetic process to make energy, and an excellent resistant to harmful substances in wastewater (Luo et al., 2016). The excellent characteristics of microalgae make it a suitable candidate for effectively recovering nitrogen and phosphorus in wastewater. In recent years, researchers have reported the nitrogen and phosphorus removal efficiency by various microalgae species from municipal, agricultural, industrial and other types of contaminated wastewater. The cultivation of *Chlorella vulgaris* in anaerobically-treated piggery wastewater in an open raceway pond led to a nitrogen and phosphorus recovery of 85.3% and 89.5%, respectively (Wang et al., 2016a,b). Inorganic nitrogen, including nitrate (NO^{3-}), nitric acid (HNO_3) and ammonium (NH^{4+}), could be transformed into organic nitrogen through assimilation (Fig. 3). The inorganic phosphorus (e.g. HPO_4^{2-}/$H_2PO_4^{-}$) in wastewater could be easily utilized by microalgae. ATP and glutamate were transformed into ADP and PO_4^{3-} by phosphorylation during microalgae metabolism. The removal rate of phosphorus in microalgae varied with the algae species and wastewater type (El-Sheekh et al., 2016). Microalgae could potentially eliminate organic pollutants, such as phenolic compounds and surfactants, primarily by biosorption and enzymatic degradation (Xiong et al., 2016).

3. Transformation and distribution of heavy metals during hydrothermal treatment

The valorization of algae and biowaste via hydrothermal treatment to produce valuable products, (e.g. biocrude oil, hydrochar, etc.) is considered an energetically favorable and environmentally sustainable practice (Chen et al., 2018). The concentration of heavy metals within the raw feedstock and thermochemical outputs are vitally important for the future application of these products. Additionally, the speciation of the heavy metals plays a vital role in determining their migration and transformation behavior. In order to better understand the application potential of the hydrothermal products, heavy metal speciation should be conducted in order to evaluate the environmental risk associated with these products. The environmental risk of hydrochar and biocrude oil could potentially affect their value and also their downstream utilization potential. Therefore, it is necessary to investigate the distribution and transformation of heavy metal species.

Furthermore, the treatment conditions during hydrothermal treatment have a notable impact on the distribution and immobilization of heavy metals within the hydrothermal treatment products. The main

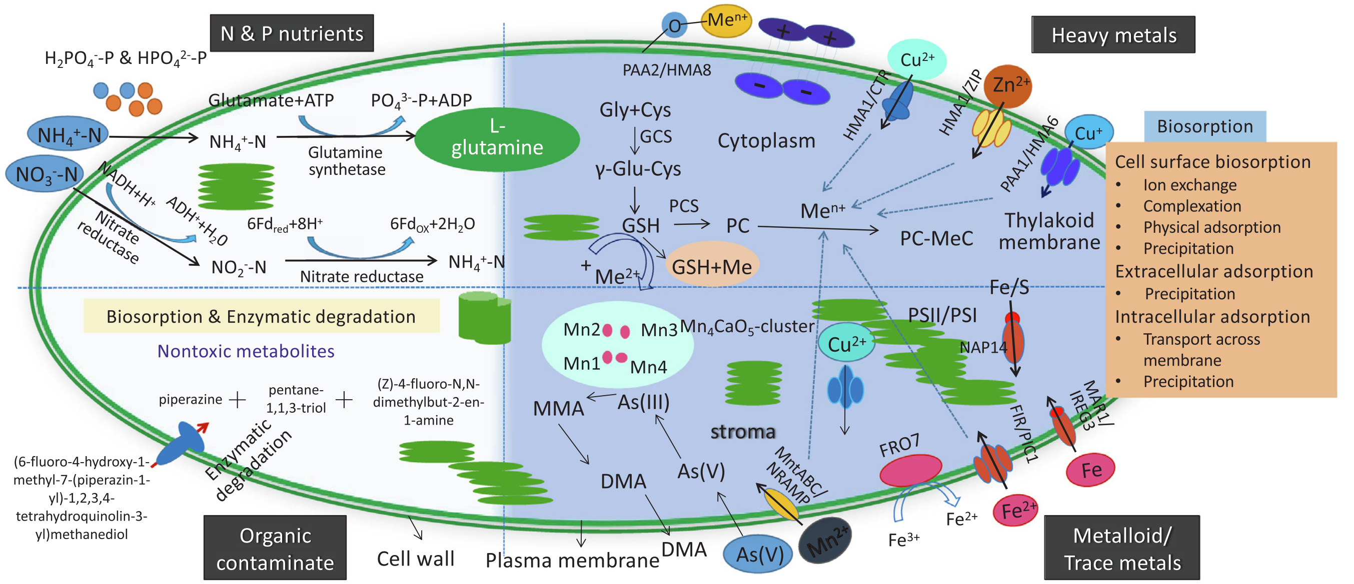

Fig. 2. Mechanism diagram for the uptake of metals, nitrogen, and phosphorus absorption throughout the algal wastewater system (Hwang et al., 2016; Mantzorou et al., 2018; Salama et al., 2017; Suresh Kumar et al., 2015). NRAMP, CTR, ZIP and FTR are metal-ion transporters. Me^{n+}, metal ions; Glu, glutamic acid; Cys, cysteine; GSH, glutathione; PCS, Phytochelatin synthase; PC, Phytochelatins. NADH, nicotinamide adenine dinucleotide; ATP, Adenosine triphosphate; ADP, Adenosine diphosphate.

factors affecting the distribution and transformation of heavy metals during hydrothermal treatment have been summarized in depth.

3.1. Heavy metal transformation and distribution of microalgae and biowaste during HTC/HTL

Microalgae has an excellent ability to sequester metals via bioaccumulation. The functional groups present on the microalgae cell surface influence the uptake rate and the specific metals species able to be absorbed in the wastewater. The main mechanism behind this is described in Section 2. Previous studies have demonstrated that the heavy metal species with the highest concentration in microalgae include Cu, Zn, Pb, Cd, As and Cr. In particular, Cu and Zn were two of the most abundant metals reported in preceding studies. Several studies have noted that the concentration and chemical speciation in the microalgae from wastewater were primarily dependent on the initial concentration of the wastewater and microalgae species (Chan et al., 2013; El-Sheekh et al., 2016). Arsenic is one of the most toxic metal that has been reported in polluted wastewater. Microalgae (such as *Chlorella* sp.) could efficiently absorb As (V) and As (III) via phosphate transporters, aquaglyceroporins (AQP) and hexose permeases (Zhang et al., 2014). As shown in Fig. 4A, the majority of Cu, Zn, Pb, Cd, and Cr in anaerobic digestate wastewater-grown microalgae were distributed in the hydrochar and aqueous phase during continuous HTL conducted at 300 °C. Arsenic was mainly transferred into the aqueous phase and biocrude oil. 34.7% of the Arsenic in the feedstock migrated into the bio-oil. The distribution trends of arsenic were obviously different from other heavy metals (such as Cu, Zn, Pb, Cd and Cr). This was partially attributed to the speciation of the arsenic that accumulated in algal biomass (Wang et al., 2015). In a simplified European Community Bureau of Reference sequential extraction method (BCR) procedure, the unstable fraction (F1) and stable fractions (F234) of the heavy metals was extracted in sequence. The results showed that over 82% of Cu, Zn, Cr, Pb and Cd in the biocrude oil was in a stable state. Meanwhile, nearly 50% of the unstable fraction consisted of Arsenic. The environmental risk of heavy metals in the biocrude oil from HTL of raw microalgae needs to be assessed before downstream transportation and utilization of biocrude oil.

Bio-oil production from wastewater-grown algae and biowaste via hydrothermal treatment is a promising route for the valorization of the biomass. However, heavy metals present within biowaste feedstock may migrate into the bio-oil phase during thermochemical conversion. This is a severe problem, because heavy metals can exacerbate problems associated with corrosion and wear in engines. Additionally, metal emissions from the combustion of biofuel has an adverse effect on the surrounding environment and human health (Lim et al., 2007). Thus, determining the concentration and speciation of heavy metals in bio-oil is vitally important. Despite the harmful effects of metals in biocrude oil, only a small fraction of the heavy metals within the feedstock have been proven to transfer into the biocrude oil. A notable exception is arsenic associated with the acetone dissolved arsenic in biocrude oil. A preceding study confirmed this trend, noting that only a small fraction of the heavy metals in sewage sludge was transferred into the bio-oil during hydrothermal treatment (Fig. 4A). The simple BCR method for heavy metal species separation revealed that over 83% of the heavy metals (Pb, Cd, Zn, Cu, and Cr) in the biocrude oil derived from the HTL of microalgae was in a stable state (Fig. 4B). Furthermore, large quantities of heavy metals (e.g. Pb, Cd, Zn, Cu, Ni, and Cr) in the bio-oil obtained from HTC of sewage sludge was also in a stable speciation state (Leng et al., 2018).

Previous studies have examined the speciation and mobility of heavy metals by using sequential chemical extraction methods during hydrothermal treatment (Leng et al., 2018; Li et al., 2018a, b, c; Shi et al., 2013; Wang et al., 2016a,b). However, chemical extraction methods are considered to be a destructive approach that is not able to reveal accurate metal speciation information due to the fact that the mobility of heavy metals can be affected with transformation of the metal species through the use of HNO_3/H_2O_2 during the extraction steps. The detailed speciation of Cu and Zn during thermochemical conversion has been characterized via combining synchrotron-based X-ray absorption spectroscopy (XAS), micro-X-ray fluorescence (m-XRF) imaging, absorption spectroscopy (m-XAS) and sequential extraction. Linear combination fitting (LCF) analysis of X-ray absorption fine structure (EXAFS) data could quantitatively determine the fractions of heavy metals present after thermochemical conversion (Huang et al., 2018; Wu et al., 2017). Heavy metals in the microalgae can exist in various and complex physicochemical fractions. The detailed speciation of heavy metals with a low concentration (< 0.01%) in microalgae

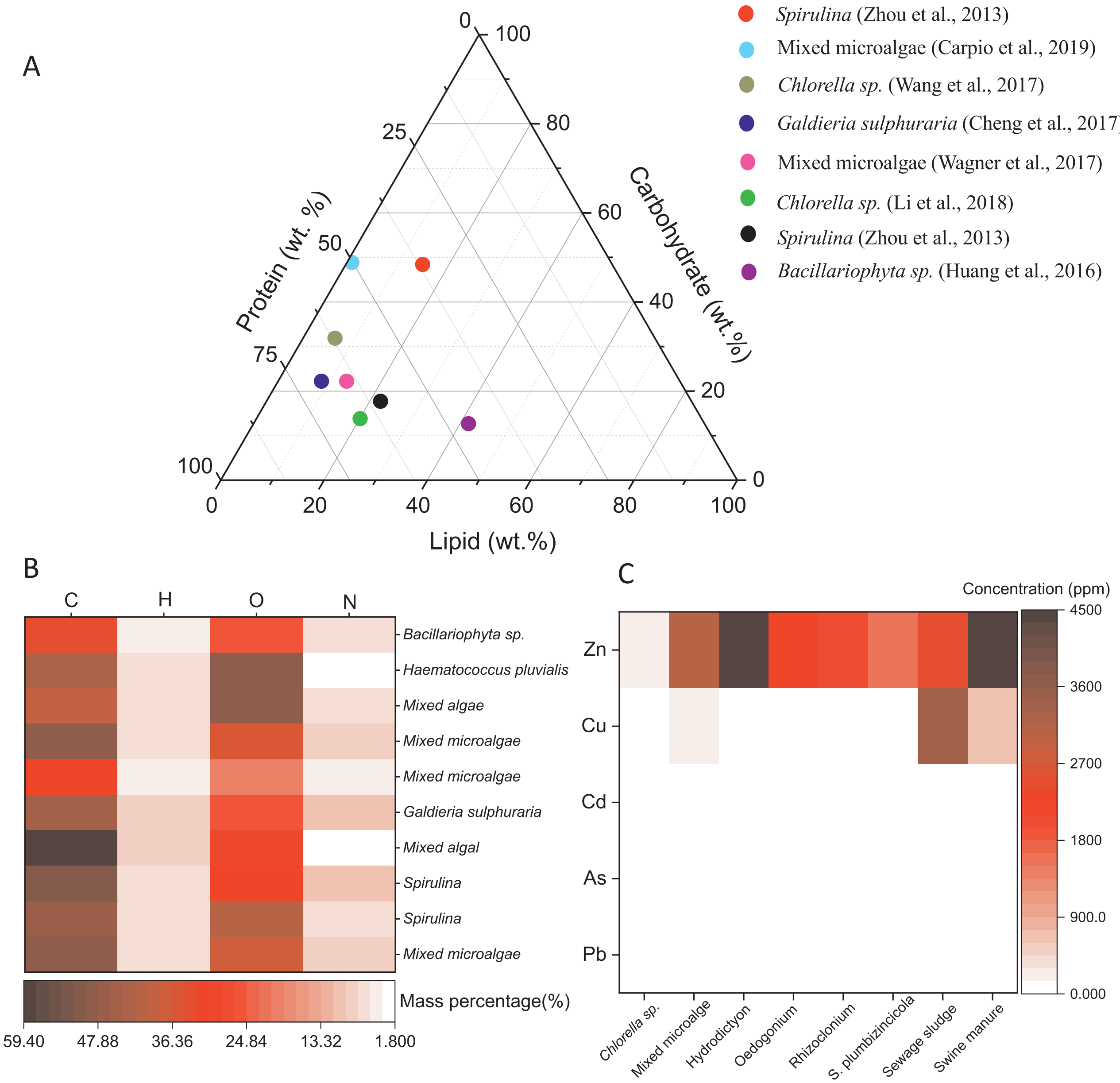

Fig. 3. Average proximate analysis (A) and ultimate analysis (B) results for wastewater-fed microalgae reported in preceding studies (Carpio et al., 2019; Chen et al., 2017; Cheng et al., 2017; Haque et al., 2017; Huang et al., 2016; Li et al., 2018a, b, c; Novoveská et al., 2016; Roberts et al., 2013; Wagner et al., 2017; Zhou et al., 2013). The concentration of heavy metals in algae biomass (Li et al., 2018a, b, c; Roberts et al., 2013; Saunders et al., 2012) were compared with other organic wastes (Li et al., 2018a, b, c; Qian et al., 2018; Wang et al., 2016) in previously reported studies (C).

could potentially be characterized by non-destructive methods.

3.2. Important factors

3.2.1. Temperature

Temperature is considered to be a primary factor affecting the heavy metal distribution and transformation behaviors during hydrothermal treatment. It was reported that the migration behavior of Zn in the *S. plumbizincicola* plant and products was obviously affected by the HTL temperature (Qian et al., 2018). A high temperature generally enhanced the ability of the heavy metal species to be released into hydrochar. A large percentage of Zn was released into the liquid phase at 220 °C (Fig. 4). The distribution of Zn in the products via HTL of *S. plumbizincicola* was significantly affected by the reaction temperature (Fig. 4A). 90% of the Zn was released from biomass into the hydrochar at 220 °C. Nearly 10% of the Zn in the feedstock was transferred into the hydrochar at a temperature range of 220–280 °C. This was primarily attributed to the fact that the low pH of the liquid phase had the capability of promoting the release of metals form the microalgae cell surface by ion exchange. An acid solution can provide an ample amount of H^+ ions thereby enhancing this process (Qian et al., 2018). Temperature not only affects the distribution of heavy metals during HTL, but it also plays a vital role in determining the heavy metal transformation pathway. A preceding study found that a much higher percentage of unstable Zn fractions (such as the acid-exchangeable fraction and reducible fraction) was transformed into a relatively stable fraction (oxidizable fraction) and stable fraction Zn (residual fraction) in the hydrochar (Qian et al., 2018). The release of heavy metals, including Cu, Zn, Cd, and Ni in sewage sludge during hydrothermal treatment exhibited a very similar tendency (Wang et al., 2016a,b). Another study found that the F1 and F2 speciation fractions of metals were much more easily dissolved into the liquid phase at a higher temperature.

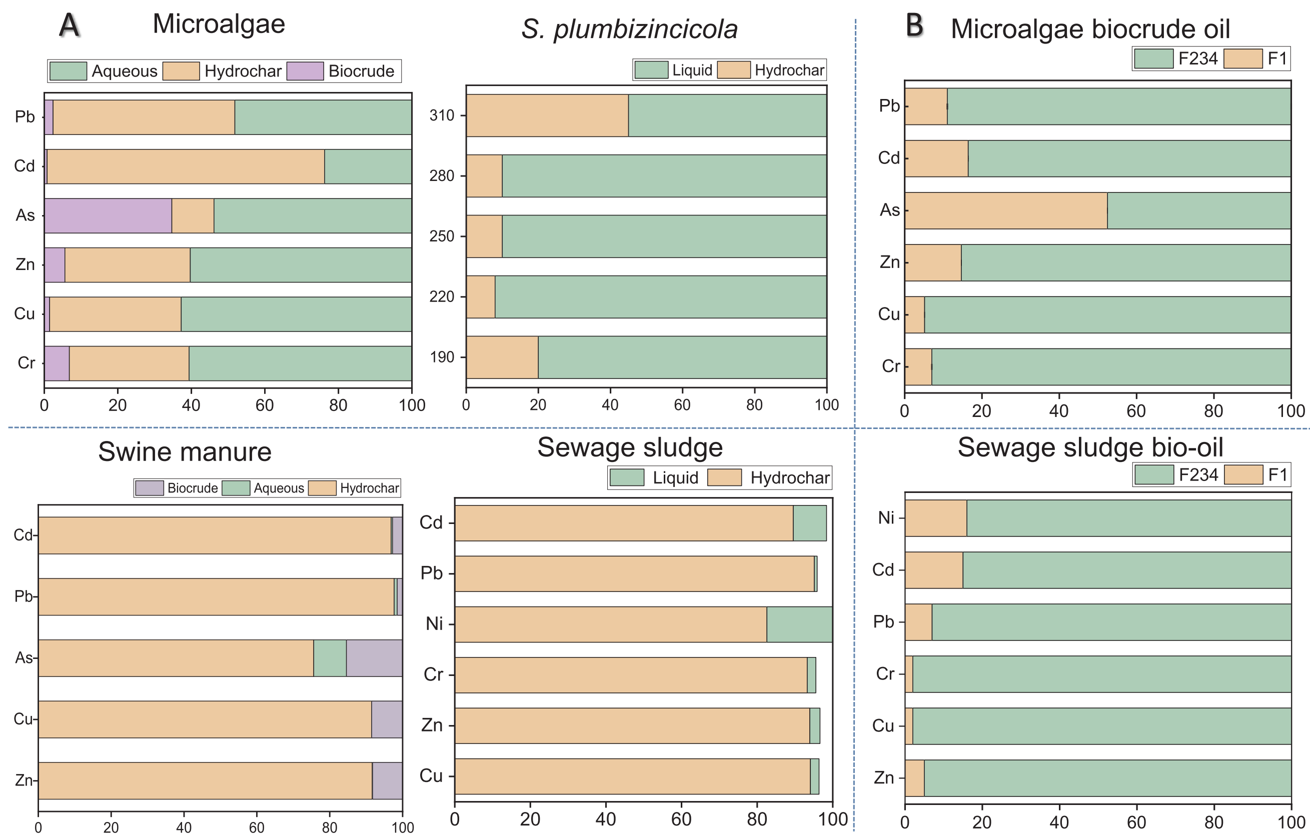

Fig. 4. The migration of heavy metals during the HTL of microalgae (A, unpublished data), *Sedum plumbizincicola,* swine manure, and sewage sludge (Leng et al., 2018; Li et al., 2018a, b, c; Lu et al., 2018; Qian et al., 2018; Wang et al., 2016). The *Sedum plumbizincicola* data was only available for Zn. The heavy metals speciation of biocrude oil (microalgae) and bio-oil (sewage sludge) was obtained through hydrothermal treatment. The continuous HTL of anaerobic digestate effluent-fed microalgae (unpublished data) was conducted at 300 °C, 20% total solid load, and a 40 mL/min feed delivery rate.

Subsequently, the metal ions then reacted with Fe, Mn and other inorganic ions to achieve a more stable speciation state through ion exchange and complexation (F3/F4) (Qian et al., 2016). Microalgae are able to adsorb heavy metals through biological metabolism. It was inferred that the main speciation of heavy metals included bioavailable fractions, which were easily released into the liquid phase under hot pressured water. Oxidizable and organic Fe/Mn fractions were primarily formed which was attributed to the content of Fe and Mn in microalgae (Li et al., 2018a, b, c). Ion exchange, complexation, and reduction reactions promoted the transformation of these metal species from unstable state to relatively stable state. In particular, the predominant fraction of arsenic in microalgae was arsenic (V), which constituted up to 99% of the total arsenic in the cytosolic fractions (Duncan et al., 2015; Wang et al., 2013). A large amount of arsenic was also previously reported to migrate into the aqueous and oil products, which was consistent with the general distribution trends of As for anaerobic digestate-fed *Chlorella sp.* during HTL (Fig. 4A).

3.2.2. Biomass and metal types

The migration behavior of heavy metal species also varies with the type of biomass and specific metal. One study investigated the effect of temperature and metal selection on the HTL of *S. plumbizincicola* (the concentration of Zn was 1335 ppm) (Qian et al., 2018). Nearly 60% of the metals in *S. plumbizincicola* were classified into the acid exchangeable fraction. A reaction medium with a low pH obviously affected heavy metal release via ion exchange during HTL. In addition, heavy metal polluted materials must be pre-treated, due to the fact that the unstable speciation of heavy metals is associated with a higher risk to the environment. A different trend of heavy metal migration was reported in another study (Li et al., 2018a, b, c). This study found that over 91% of heavy metals (Cu, Zn, Cd, and Pb) in fresh swine manure was released into the solid products during HTL. 15.4% of As in the feedstock migrated into the biocrude oil due to the existence of acetone-dissolvable roxarsone (Li et al., 2018a, b, c). Furthermore, the main speciation of Zn in the hydrochar obtained from the HTL of swine manure and the hazardous hyperaccumulators was obviously different. The speciation and transformation of different heavy metals during HTL of swine manure showed that the unstable fraction (F1, F2, and F3) of Zn, Cu, Pb, and Cd in the feedstock decreased significantly; however, the stable fraction (F5) of hydrochar obviously increased compared with the feedstock during HTL (Li et al., 2018a, b, c). Shi et al. demonstrated that the heavy metals in sewage sludge could migrate from the unstable fractions (F1, F2) into more stable fractions (F3, F4) due to a complex mechanism involving adsorption, precipitation and complexation which was reported to occur during hydrothermal treatment (Shi et al., 2013). Cu, Cr and Pb in the hydrochar derived from sewage sludge was primarily classified into the stable fraction (Wang et al., 2016a,b). In conclusion, the transformation behavior of metals varied depending on the specific metal. The difference between the heavy metal transformation behaviors among different microalgae species and organic wastes was attributed to the distinctive speciation of heavy metals in the feedstock.

3.2.3. pH

The pH plays a critical role in metal precipitation reactions. Each metal precipitate has a characteristic solubility that depends on the pH value. The solubility of metal carbonate, hydroxide, and sulfur varies with the pH value. The formation of solid components of heavy metals under hot pressured water can be influenced by the concentration of OH^- ions during thermochemical reactions. The speciation of heavy metals also varied when exposed to different pH conditions. Further research needs to be investigated on the effect of pH on the migration, chemical speciation, and transformation of heavy metals during hydrothermal treatment.

4. Challenges and outlook for a proposed integrated system coupling algal wastewater treatment, heavy metal recovery and hydrothermal biofuel generation

4.1. An improved integration system for achieving the environment-enhancing energy paradigm

The environment-enhancing energy paradigm was primarily aimed at producing biofuels and valuable bio-products from biowaste, simultaneously achieving nutrients recovery and maximizing environmental sustainability (Zhou et al., 2013). However, several issues limit the synergistic promise of combining wastewater treatment and biofuel production, including the low lipid accumulation in algae cultivation, the high energy input, the high growth inhibition effect caused by contaminated post-HTL wastewater, and the low nutrient recycle efficiency associated with this paradigm. There is a critical need for developing other technologies to alleviate the disadvantages of the environment-enhancing energy paradigm. Wastewater-grown microalgae generally contains a high ash content (Chen et al., 2017; Roberts et al., 2013). It has been reported that the ash content of biomass contributed very little to the accumulation of biocrude oil (Cheng et al., 2017; Li et al., 2018a, b, c). Ash mainly consisted of mineral compounds, including a certain amount of heavy metal salts. Recently, heavy metals have drawn increased attentions due to their impact on public health and the environment. Heavy metal issues should be taken into accounted in the combined environment-enhancing energy paradigm. In this study, a novel system was proposed, that integrates wastewater treatment, algae cultivation and biocrude oil/hydrochar production, achieving valuable metal recovery, detoxification of heavy metal wastewater, and synergistically obtaining valuable bio-products. Such integrated system is more efficient for providing environment-enhancing energy while simultaneously eliminating contamination associated with heavy metal accumulation. In this system, the heavy metals in contaminated wastewater were recovered through two pathways: biological adsorption through microalgae and physical/chemical absorption via hydrochar. Previous studies revealed that the hydrochar from microalgae exhibited an excellent capability to remove copper due to the oxygen-containing functional groups on the hydrochar surface (Saber et al., 2018). Furthermore, KOH modification of hydrochar enhanced the heavy metal absorption capability by increasing the aromatic and oxygen-containing groups, such as the carboxyl groups (Sun et al., 2015). On top of these, the combined system is able to enhance the bioremediation efficiency of toxic metals as well as reduce their environmental risk by converting unstable fractions into relatively stable fractions.

The integrated utilization of microalgae for biofuel generation and wastewater treatment has been reported (Zhou et al., 2014). In addition, the mechanism of heavy metal uptake and release by microalgae for wastewater remediation has been systematically studied (Hwang et al., 2016). However, the speciation and distribution of heavy metals in downstream products (bio-oil and hydrochar) are still unclear. Recently there have been some reports on heavy metal issues while dealing with the treatment of livestock manure, sludge, and other biowaste. However, these studies primarily focused on the solid products. A previous study utilizing BCR sequence extraction method revealed that the unstable heavy metals were immobilized in the solid products through hydrothermal treatment (Li et al., 2018a, b, c; Shi et al., 2013). In conclusion, the unstable heavy metals in feedstocks were mainly transferred to the hydrochar and mainly existed in a relatively stable fraction. HTL treatment has dual benefits of reducing metals concentration and stabilization metal fractions. The transformation fate of heavy metals from the feedstock to biocrude oil is still unclear. In terms of practical application, a couple of points need to be addressed to reduce the content of heavy metals for wastewater-derived biofuel, such as treatment efficiency, cost, and the capability of achieving large-scale biocrude oil production.

4.2. Fundamental issues

Wastewater treatment and green energy production are the main challenges facing the environment-enhancing paradigm at the present. Microalgae have proven to be resilient to toxic contaminants and can serve as sustainable feedstocks for biofuel production. The economic advantage and environmental benefit of using microalgae for wastewater treatment and biofuel generation are the driving force to achieve the utilization of such integrated technology.

Microalgae has been predominantly utilized as a biofuel production feedstock due to its high content of lipids, proteins and carbohydrates. Heavy metals should be sequestered due to safety and environmental concerns associated with their existence in bio-oil, bio-fuel and valuable bio-products. Currently, there are two basic routes to remove heavy metals: pre-treatment and post-treatment. The pre-treatment approach mainly refers to the traditional methods used for wastewater treatment (ion exchange, precipitation, and physical treatment), which are energy inefficient, can lead to a decrease in the biocrude oil yield, and it can lead to the production of additional biosolid (e.g., precipitate) after treatment processes that is in need of subsequent treatment. Both physical and chemical treatment methods decrease the content of organic compounds (lipids, carbohydrates, and proteins), and these methods are not beneficial if a biofuel refinery is the desired outcome. Additionally, this treatment approach could potentially lead to an increased treatment volume, cause water pollution, increase the difficulty and cost associated with the separation process of reactant/additive material and microalgae, as well as reduce the processing efficiency in low concentration conditions.

In comparison, the post-treatment approach of heavy metals could obviously reduce the volume, mass, and simultaneously produce valuable energy and by-products. Previous results demonstrated less than 10% of the original heavy metals except arsenic in the raw microalgae migrated into the biocrude oil (Fig. 4). Nearly 5% of the initial heavy metals were transferred into the biocrude oil from municipal sewage sludge during hydrothermal treatment (Huang et al., 2018). Thus, the treated volume of the heavy metal matrix was greatly reduced. Furthermore, the bioavailability of heavy metals in bio-oil decreased through HTL. Therefore, this thermochemical technique is proven to be an effective process to immobilize heavy metals (Li et al., 2018a, b, c). In addition, a preceding study demonstrated that hydrochar (HTL) and biochar (pyrolysis) had very similar properties including surface area, pore size distribution and ion-exchange capacity (Liu et al., 2017; Xiong et al., 2016). Biochar has been reported to be an excellent adsorbent (Ahmad et al., 2014). Therefore, hydrochar from hydrothermal treatment of microalgae can be considered to be a potential absorbent for contaminant management in wastewater. The downstream distillation of biocrude oil is suitable for blending with transportation fuels (Chen et al., 2018). It is believed that the majority of the heavy metals were released in the solid residue during the distillation process accounting for the low volatility of metal compounds. Overall, post-treatment has proven to be beneficial for reducing and stabilizing heavy metals during the algae biofuel generation process combined with wastewater treatment.

4.3. Engineering and economic issues

The fundamental challenges facing the industrialization and commercialization of the integrated system are the high cost of the system for scale-up and operation. In addition, the development of a large-scale, high-efficiency, continuous HTL reactor system still remains a critical technical problem. The selection and cultivation of microalgae with a high growth rate and high resistance to polluted wastewater is still the key for the integrated system. Industrial wastewater usually contains a high concentration of COD, total nitrogen, total phosphorus, and other toxic compounds, so it cannot be directly used for microalgae cultivation. The selection and optimization of wastewater pre-treatment methods for microalgae cultivation still needs to overcome technical barriers. The optimization of the HTL parameters plays an important role in the feasibility of yielding high-value products in the combined system. The multiple use of post-HTL wastewater as a means of producing value-added products (such as pesticides, high valued chemical materials) should be further investigated. In summary, there are many technical problems that need to be further identified and resolved in the future.

In this study, a modified integrated system for wastewater treatment, biofuel production and heavy metal removal using microalgae was designed and demonstrated. Currently, the economic analysis for products profits in the integrated system mainly focused on nitrogen and phosphorus, which were ultimately converted to energetic products (upgraded biofuel and fuel gas) and ammonium sulfate-based fertilizer (Li et al., 2018a, b, c). The economic valuation of the products was based on the total value of the upgraded biofuel, fuel gas, and fertilizer. Some valuable metals recovered in the combined system could also add additional value to the whole system. The cost of traditional treatment of toxic wastewater was very high. The multiple treatment process including biological adsorption and physicochemical adsorption by treated hydrochar improved the treatment efficiency of wastewater. The main challenge is the feasibility of recovering the stable fraction of heavy metals as well as obtaining a high capability of adsorption. Additionally, the potential reduction of cost associated with nutrient recovery for microalgae cultivation can further boost the economic feasibility and environmental benefits of the proposed integrated system.

5. Conclusion

This review systematically discussed the distribution and transformation of heavy metals during the hydrothermal treatment of microalgae and biowaste. A modified system coupling wastewater treatment, heavy metal recovery and biocrude generation was proposed. Several technical bottlenecks need to be settled in order for this new paradigm to reach the level of a commercialized technology. In particular, high metal resistant microalgae species, cost-effective facilities, and optimized integration parameters need to be investigated. It is recommended that subsequent studies place emphasis on the use of distillation as a post-treatment technology of separating heavy metals from biocrude oil.

Declaration of Competing Interest

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

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