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Microalgae-based low-carbon heavy metals removal from wastewater and biomass utilization

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Abstract

Heavy metal pollution is a serious problem in the field of environmental protection at present. Microalgae as a bioremediation agent has been widely used in heavy metal wastewater treatment. This paper reviews the up-to-date heavy metals removal strategies by microalgae and potential utilization approaches of the generated microalgae biomass, together with the related analysis on the technology application potential and challenges. First, the paper describes the biosorption and biotransformation capabilities of microalgae and their effectiveness in removing various heavy metal ions from heavy metal wastewater. Second, the utilization pathways of microalgae biomass after treatment of heavy metals wastewater were discussed. Microalgae cells can incorporate heavy metals into intracellular organic matters through biotransformation, thus realizing the resourceful use of heavy metals in wastewater. Finally, prospect of microalgae-based heavy metals removal and utilization approaches of the generated microalgae biomass were provided. By selecting proper utilization approaches of microalgae biomass after remediation heavy metals from wastewater, it can achieve win-win from economic and environmental perspectives.

Keywords: *microalgae, heavy metal removal, wastewater, biomass utilization*

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I. INTRODUCTION

Environment pollution is an increasing problem due to rapid industrialization and urbanization. In particularly, population increase and unabated agricultural practices greatly enhanced the concentration of heavy metals in soil, groundwater and natural water bodies. The discharge of heavy metals into environment can cause unpredictable consequences to human beings[1]. The toxicity of heavy metals lies mainly in their potential for bioaccumulation, increasing their concentration in the food chain and impacting the upper trophic levels. It is also worth noting that exposure to heavy metals may also weaken people's immune system and increasing the risk of cancer development. Existence of heavy metals allows organic pollutants to remain in the environment for longer time and increase the negative impact[2]. Even at very low levels, heavy metals and their compounds are extremely toxic, carcinogenic, mutagenic and teratogenic. In humans, through direct exposure, inhalation and ingestion of heavy metals, they may cause mutations and genetic damage, as well as damage to the central nervous system[3]. Therefore, pre-treatment of heavy metals from wastewater prior to discharge is essential.

Heavy metals removal from wastewater mainly include physical, chemical and biological methods. Physical methods like adsorption has advantages of easy operation, but the adsorption effectiveness depends on the dosage and adsorption conditions of the adsorbent, which is easily affected by external factors like other competing pollutants[4]. Chemical methods to treat heavy metals like oxidation/reduction reactions and chemical precipitation can separate heavy metals into insoluble hydroxides, sulphides and carbonates, with removal rates of up to 97% in laboratory[5]. But the energy cost and carbon footprint are usually high. Together, the removal effectiveness of oxidation/reduction reactions or chemical precipitation are closely influenced by the heavy metals concentration and is not suitable for low concentration wastewater attributing to mass generation of hazardous sludge, limiting the application of these techniques. As complementary pathways, activated sludge has obvious effects on heavy metals removal, but the residual concentration in wastewater after activated sludge treatment is usually higher than discharge standard for the receiving water body[6]. In conclusion, traditional remediation techniques may require the addition of high energy or regents, which is contrary to low-carbon concept. It is necessary to find a method that is relevant to the theme of low-carbon heavy metals remediation with high efficiency.

Considering the urgency of finding innovative and green heavy metals treatment methods, the pathway of heavy metal bioremediation that utilize microalgae has gained popularity as an alternative approach due to environmentally friendly and low-carbon heavy metal removal[7]. Currently, microalgae-based bioremediation is chosen as the possible alternative to conventional remediation methods since microalgae can capture CO_2 at the same time and the produced microalgae biomass has a wide range of uses[8]. In addition, microalgae growth has long been used for remediation of municipal wastewater [9]. Among all microorganisms, microalgae are used for bioremediation of heavy metal from wastewater due to their high binding affinity, large number of available binding sites and large surface area[10].

In summary, microalgae-based heavy metals bioremediation is a feasible and environmentally friendly strategy. This paper reviews the bioremediation of heavy metal from wastewater by microalgae, focusing on the mechanism of adsorption and enhancement measures, as well as proposing what can be done on heavy metals adsorption by microalgae and how to convert the microalgae biomass after heavy metal remediation into clean energy or resources, which can be used to realize the recycling of heavy metals pollutants into resources.

II. TREATMENT OF HEAVY METALS FROM WASTEWATER BY MICROALGAE

2.1 Adsorption of heavy metal from wastewater by microalgae

It has been shown that microalgae can remove heavy metals from wastewater through adsorption in different wastewaters. The adsorption process of heavy metals by microalgae is considered as a process of biosorption, defined as the accumulation of heavy metals from wastewater by biological material [11]. One of the advantages of using biosorption to achieve the heavy metal removal is the green and sustainable characteristic. In addition, a significant advantage of using microalgae to remove heavy metals is that microalgae can remove heavy metal ions along with other ions such as K, P, and N, achieving multiple biological pollutants removals[12]. Yang and Xu et al.[13] found that microalgae can achieve over 90% removal of heavy metals in anaerobically digested wastewater, and it is noteworthy that the removal of N and P was also achieved along with the removal of heavy metals, and both removal rates were above 90%.

2.1.1 Microalgae adsorption mechanisms

The adsorption of heavy metals by microalgae is intricately linked to the function of the cell wall. Serving as the interface between the cytoplasm and the external environment, the cell wall is predominantly composed of proteins, lipids, and carbohydrates. These compositions provide platforms for relevant biochemical interactions, facilitating the heavy metals adsorption. Furthermore, the intricate arrangement of molecules within the cell wall offers binding sites that attract heavy metals, enabling their retention within the microalgae cell surface[14]. These substances can offer negatively charged functional groups, such as carboxyl groups (-COOH), hydroxyl groups (OH-), phosphate groups ($-PO_4$), amino groups ($-NH_2$), etc., which are crucial for adsorbing positively charged metal cations.

The removal of heavy metals by microalgae involves two primary mechanisms. Initially, heavy metals adhere to the surface of microalgae cells through electrostatic interactions, which is a process known as biosorption. In another word, the negatively charged functional groups on the microalgae cell wall attract positively charged heavy metal ions, binding them to the cell surface. This phase is followed by bioaccumulation, wherein heavy metal ons form complexes, crystals, or precipitates with substrates on the cell surface or binding enzymes on the cytoplasmic membrane. These compounds actively move into the cell interior, binding to intracellular proteins and peptides such as glutathione, metal transfer proteins, and phytochelatins[15]. Microalgae employs three main strategies to accumulate heavy metals on their surface: first, microalgal extracellular polysaccharides can establish covalent bonds with metal cations; second, heavy metal ions may exchange with cations on the cell wall; and third, heavy metal cations can adhere to negatively charged glyoxylates[16]. Notably, the adsorption of heavy metal ions onto microalgae is a rapid process, while bioaccumulation occurs more slowly over time.

2.1.2 Factors influencing the adsorption process

The adsorption mechanism is predominantly influenced by the chemical properties of impurities, particularly their hydrophobic characteristics. In contrast to hydrophilic compounds, pollutants carrying positive charges are more attractive to microalgae cells surface primarily due to electrostatic interactions, and the hydrophobicity may enhance the electrostatic interactions[17]. Nagappan et al.[18] emphasized that the cell wall of microalgae comprises polysaccharides, extracellular matrix, and sulfated carbohydrates, which contain various anionic functional groups exhibiting different affinities for positively charged heavy metals. The interactions between the negatively charged cell walls, secretions, and heavy metals of microalgae occur through passive, non-metabolic processes, as elaborated by Xiong in 2021[19].

It is worth noting that the commonly studied Chlorella vulgaris demonstrates remarkable capability in the removal of antibiotic metronidazole, achieving removal efficiencies of 100% from an initial concentration of 5 mM through bioadsorption [20]. Bioadsorption encompasses a range of mechanisms, including ion exchange, adsorption, surface complexation, precipitation, and chelation[15]. These intricate interactions emphasize the effectiveness of bioadsorption in capturing pollutants from the environment.

The process of bioadsorption is intricately influenced by a variety of physicochemical factors, including pH, temperature, and redox reactions. Notably, this process is not limited to live cells; both live and deceased cells can participate in bioabsorption. Research indicates that the cell surface receptors in microalgae retain their binding affinity for pollutants even after cell death. Utilizing deceased microalgae cells as bioadsorbents presents numerous advantages, including the absence of toxicity resulting from pollutants, the potential for reusing microalgal biomass following the desorption of adsorbed pollutants, and reduced operational costs due to the elimination of the need to maintain microalgae viability[7].

2.2 The impact of ions from heavy metal-contaminated wastewater on microalgae

2.2.1 Biomass

Research indicates that elevated levels of metal ions can impede the bioremediation capacity of microalgae, and in severe cases, result in their demise. For instance, Liu and Wu et al.[21] demonstrated that lead ions (Pb^{2+}) exerted varying degrees of inhibition on the growth of Chlorella, with inhibition rates reaching a maximum of 21.68% at higher concentrations of Pb^{2+}. Interestingly, within certain thresholds, the presence of heavy metal ions did not hinder microalgae growth but rather facilitated biomass accumulation. This phenomenon may be attributed to the suppressive effect of excessive heavy metal ions on microalgae cell division, thereby constraining overall growth[22].

2.2.2 Chlorophyll content

The concentration of chlorophyll within microalgae cells plays a pivotal role in their photosynthetic activity and subsequent growth. Chlorophyll-a (Chl-a) serves as the primary photosynthetic pigment, while chlorophyll-b (Chl-b) acts as a secondary pigment, aiding in the transmission of captured photons to Chl-a. Gao et al.[23] demonstrated that at low Cu^{2+} concentrations (≤1.5 mg/L), there was no significant inhibitory effect on chlorophyll. However, at higher Cu^{2+} concentrations (≥2 mg/L), a notable reduction in chlorophyll content was observed. Interestingly, prolonged exposure up to 96 hours resulted in a significant decrease in chlorophyll content across all groups except for those with a Cu^{2+} concentration of 0.5 mg/L, suggesting a time-dependent exacerbation of Cu^{2+} impact on photosynthesis. Li et al.[24] investigated the impact of varying concentrations of Cr(VI) on chlorophyll content in microalgae. Initially, as the concentration of Cr(VI) increased, there was a rise in chlorophyll content. However, beyond a certain threshold, high concentrations of Cr(VI) demonstrated an inhibitory effect on chlorophyll biosynthesis. This inhibition led to a decrease in photochemical conversion efficiency and the actual light energy capture efficiency of the photosynthetic system, thereby adversely affecting microalgae photosynthesis. Furthermore, the study also highlighted the influence of Zn^{2+} concentration on chlorophyll production in microalgae cells. When the Zn^{2+} concentration remained below 0.2 mg/L, the Fv/Fm values, indicative of photosynthetic efficiency, exhibited an increasing trend over time, suggesting that lower concentrations of Zn^{2+} did not impede chlorophyll production. However, when the Zn^{2+} concentration exceeded or equaled 0.2 mg/L, microalgae photosynthesis began to be hindered. Thus, it is evident that Zn^{2+} concentration plays a significant role in regulating chlorophyll content and consequently impacts microalgae photosynthetic activity.

2.2.3 Lipid accumulation

Dammak and Halima et al.[25] investigated the effect of mixing different heavy metal ions on lipid accumulation and showed that the maximum lipid content was reached when 66.6% Ni, 16.6% Cr, and 16.6% Co were present. Song and Liu et al. [26] explored the effect on lipid accumulation at different Cr(VI) concentrations, and the lipid content of microalgae increased when the Cr(VI) concentration was 0.5-2 mg/L, reaching a maximum of 131.79 mg/(L•d) when the Cr(VI) concentration was 2 mg/L. However, it's noteworthy that the lipid content doesn't consistently rise with increasing Cr(VI) concentrations. At excessively high levels of Cr(VI), there was an inhibitory effect on microalgal lipid production. Specifically, when the Cr(VI) concentration ranged from 10 to 40 mg/L, there was a notable decrease in lipid content within the microalgae. This decrease could be attributed to the detrimental effects of excessive Cr(VI) on intracellular structures, leading to inhibition of cell growth and relative enzyme activity.

III. SECONDARY USE OF HEAVY METAL MICROALGAE

3.1 Production of microalgae biodiesel

Biodiesel is developed from edible oils, non-edible oils and microalgae in the first, second and third generations. Algae biodiesel is a hydrocarbon fuel that absorbs all carbon dioxide during the growth of algae and ignition of fuel emissions. Therefore, this fuel is considered as a suitable and safe solution to adapt to the changing environment. The production process involves the transesterification reaction of excess methanol with triglycerides, yielding fatty acid methyl esters and glycerol as byproducts. This reaction progresses in three steps:

glycerol is initially converted into glycerol diesters, which further undergo conversion into glycerol monolipids, and ultimately into glycerol[27]. Microalgae represent a particularly promising source of biodiesel, potentially capable of fully replacing fossil diesel fuel. Studies have revealed that microalgae can yield 10-20 times more biodiesel compared to rapeseed biodiesel, highlighting its superior efficiency and potential as a sustainable energy source[28].

3.2 Bioethanol

Bioethanol is another unlimited biofuel that has been proposed as a viable alternative to fossil fuels. Unlike conventional bioethanol sources like corn, sugarcane, and sorghum, microalgae offer distinct advantages by mitigating CO_2 emissions through photosynthesis without encroaching upon agricultural resources. Additionally, microalgae boast a shorter harvest cycle, further enhancing their appeal as a bioethanol feedstock[29]. In a study conducted by Harun and Jason et al.[30], the production of biodiesel from alkaline-pretreated microalgae was investigated, yielding a maximum ethanol-to-microalgae ratio of 26.1 wt% and a minimum bioethanol yield of 10.66 wt%. These findings underscore the considerable potential of microalgae in bioethanol production, offering a promising avenue for sustainable energy generation.

3.3 Hydrogen production by pyrolysis

In light of challenges such as global warming and the dwindling reservoirs of fossil fuels, hydrogen emerges as a green and sustainable solution to the energy crisis. Algae organisms, renowned for their abundant carbohydrate content, have garnered significant interest in this regard. Hydrogen, serving as an efficient energy carrier, offers twice the energy output per unit mass compared to conventional fuels[31]. The production of hydrogen by microalgae can be realized through various methods, including direct or indirect photolysis, dark fermentation, and hydrothermal carbonation. This diversity of approaches underscores the versatility of microalgae in facilitating hydrogen generation, presenting a promising avenue for addressing energy shortages sustainably.

3.3.1 Photobiological hydrogen production

Microalgae can convert solar energy into chemical energy, $2H_2O + \text{light energy} \rightarrow 2H_2 + O_2$[32]. This pivotal process begins with the capture of light energy, facilitated by light capture complex (LHC) proteins categorized as LCH I or LCH II. Their classification hinges on their interaction with either photosystem I (PS I) or photosystem II (PS II). Direct biophotolysis represents a crucial transitional step characterized by its swift reaction time. During this process, PS I and PS II immobilize the captured light energy, which is subsequently electronically transferred to iron-oxygen-reducing proteins. These proteins then catalyze the reduction of H_2O to produce H_2. In the realm of photobiological hydrogen production, cyanobacteria emerge as promising feedstocks due to their minimal nutrient requirements and reliance solely on light energy. Moreover, their primary products comprise environmentally beneficial H_2 and O_2, aligning with the principles of environmental conservation[33].

3.3.2 Dark fermentation for hydrogen production

Because this feedstock is also the most abundant element in ionic form, microalgae producing biohydrogen through dark fermentation play a pivotal role in the field of renewable energy. The energy metabolism of microalgae during dark fermentation for hydrogen production does not require any specific energy to transport glucose into the cells, so dark fermentation requires less energy to produce biohydrogen from microalgal cell carbohydrate polymers[31].

3.4 Methane production

Anaerobic digestion usually occurs in the absence of emptying of biological waste and the gas produced is known as biogas, the main component of which is a mixture consisting of methane and carbon dioxide. Biogas is valuable as fuel and research indicates that algal biomass can be used as a biological feedstock for biogas [28].

IV. ECONOMIC BENEFITS AND ENVIRONMENTAL IMPACT

Heavy metals pose significant environmental and health risks, particularly when discharged directly into aquatic ecosystems, leading to adverse effects on aquatic organisms. However, these metals also hold considerable societal value, playing pivotal roles as catalysts in chemical processes, a subject of intense research. For instance, the combination of heavy metals with biochar has been explored in the study of activated persulfate for antibiotic degradation. When biochar was doped with copper (Cu^{2+}), the degradation efficiency of tetracycline significantly improved compared to undoped counterparts, from 61% to over 95%. Additionally, microalgae are increasingly recognized as a promising feedstock for biodiesel production, boasting advantages such as high lipid content, rapid growth, environmental resilience, and cost-effectiveness compared to other sources.

In industrial wastewater, the concentration of heavy metals, such as copper (Cu^{2+}) at 525ppm and zinc (Zn^{2+}) at 1755ppm, poses a significant threat to the environment upon direct discharge. This issue is compounded by the escalating usage of pharmaceuticals, which further exacerbates environmental degradation, particularly through antibiotic wastewater. However, there is a promising solution: the utilization of microalgae for the effective removal of copper and zinc ions from industrial effluents. Following the successful extraction of heavy metals, the microalgae can be transformed into a novel catalyst through pyrolysis in a tubular furnace. This method not only addresses the hazardous nature of heavy metal wastewater but also offers a sustainable approach to managing the toxicity associated with the captured heavy metals within the microalgae biomass. By converting toxic microalgae into biochar catalysts, this approach represents a significant advancement in environmental remediation strategies.

V. CHALLENGES AND PERSPECTIVES

Based on previous studies and future research prospects, the following suggestions emerge:

1) Investigations into the impact of pH on heavy metal removal by microalgae reveal that extreme pH levels significantly inhibit microalgae growth. Optimal removal rates of heavy metals by microalgae occur under acidic conditions, but excessively high or low pH levels hinder microalgae growth. Addressing this pH sensitivity in future research will substantially enhance heavy metal removal efficiency and increase the biomass energy utilization rate of microalgae.

2) Presently, microalgae face considerable toxicity from heavy metals, making survival challenging in high-concentration heavy metal wastewater, particularly in industrial settings. To enhance microalgae's resilience to heavy metals, future research should focus on domesticating microalgae through staged cultivation, thereby improving their adaptability to varying heavy metal concentrations.

3) Most current research on heavy metal removal by microalgae concentrates on treating single heavy metals. However, industrial heavy metal wastewater typically contains a variety of heavy metals. Future investigations should expand to explore microalgae's capability to treat diverse heavy metal wastewater types, thereby enhancing the feasibility of using microalgae for direct treatment of industrial heavy metal wastewater.

4) Microalgae have the propensity to accumulate heavy metals within their cellular structures during the process of heavy metal absorption. Consequently, this component of microalgae becomes highly toxic and presents challenges for effective recycling. However, subsequent research endeavors aim to mitigate the toxic impact of heavy metals on microalgae by exploring ways to harness the catalytic potential of both microalgae biomass and heavy metals themselves.

5) A promising avenue of investigation lies in the development of methods to encapsulate heavy metal-absorbing microalgae within heavy metal microalgae biochar for the activation of persulfate-based degradation of antibiotics. The utilization of heavy metal ions to activate persulfate has garnered significant attention in recent years. Nevertheless, the introduction of heavy metals into the environment can lead to secondary pollution, while the residual heavy metals in solution pose challenges for remediation. Leveraging the porous structure of biochar, which exhibits robust adsorption capabilities for antibiotics in solution and possesses inherent activation properties for persulfates, offers a viable solution for enhanced antibiotic removal.

6) In the realm of resource transformation, the utilization of heavy metal-laden microalgae as a fermentation substrate presents an avenue for resource conversion. While conventional microalgae have long served as a substrate for fermentation studies, the incorporation of heavy metals, within certain concentrations and under specific conditions, renders heavy metal microalgae suitable for fermentation. By harnessing the synergistic effects of heavy metal ions and microalgae biomass, the efficiency of energy output can be significantly enhanced. Laboratory and pilot-scale experiments are warranted to validate these findings and pave the way for practical applications in the future.

VI. CONCLUSION

The utilization of microalgae for treating heavy metal wastewater has garnered recognition as a sustainable and eco-friendly approach. In this symbiotic relationship, the presence of heavy metal ions in wastewater aids in the production of biomass rich in lipids and other valuable metabolites by the microalgae. This biomass can be harnessed for biofuel production while concurrently removing heavy metal pollutants from the water.Moreover, microalgae exhibit the capability to remove not only heavy metal ions but also nitrogen and phosphorus from wastewater. Their rapid growth rate further underscores their efficacy in wastewater treatment without causing environmental harm. Additionally, microalgae's ability to produce lipids presents a viable solution to the conventional oil scarcity issue. This study delves into the impact of microalgae on heavy metal wastewater treatment and explores strategies to enhance heavy metal ion adsorption, such as pH adjustment.It is crucial to highlight that heavy metal ions can influence microalgae metabolism during the adsorption process. This paper investigates how heavy metal ions affect lipid accumulation and chlorophyll content in microalgae cells. Results indicate that heavy metal ions exhibit a nuanced impact, promoting lipid accumulation within certain concentration thresholds but inhibiting it at higher concentrations. Furthermore, the study explores the secondary utilization of microalgae, which can serve as raw material for producing biodiesel, hydrogen, methane, and biochar. This offers valuable insights into deriving added-value products from algae in bioremediation efforts.

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