The Bio-Removal of Heavy Metals from Wastewaters a Green Approach

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Abstract

Most heavy metals are well-known toxic and carcinogenic agents and when discharged into the wastewater represent a serious threat to the human population and the fauna and flora of the receiving water bodies. Cultivation of microalgae has been suggested as a green approach for a sustainable wastewater treatment especially heavy metal bioremediation. This study investigated the bio-removal of lead, nickel, cadmium, manganese and cobalt from wastewater using microalgae, *N. oculata*. The results revealed high removal efficiency of Mn > Co > Ni> Pb > Cd, after 5 days of the culture compared to control. Mn were successfully removed at the highest efficiencies up to 87.8%, Ni was up to 80% and reduction of metal concentration from 2.45 to 0.66 µg/l. Pb was reduced from 3.49 µg /l to 1.75 µg /l. The Cd was reduced from 0.98 µg /l to 0.74 µg /l which is equivalent to 22.1%. Meanwhile, Co reduced from 3.04 ppm to 0.53 ppm (87.8%) under indoor culture condition. Overall, the bio removal and recovery efficiency in wastewater was promising removed toxic metals elements was successfully performed. More broadly, further investigation is also needed to determine the influence of the application of outdoor culture condition on the bio-removal of metal ions coupled with potential precious biomass production.

Keywords: Wastewater, *N. oculata*, bio removal, heavy metals..

Introduction

Water is the key element responsible for life in the world is becoming more valuable due to the increased consumption and demand. In order to provide a locally controlled water supply, wastewater recycling offers great environmental advantages. Recycling of water can corporate in decreasing the consumption of water from sensitive ecosystem, reducing the environmental pollution, and even preventing accumulation of pollutants in our ecosystem. Wastewater treatment is applied in many countries to compensate for freshwater shortages. Various conventional methods are used to achieve that goal, but they are costly, a bit harmful and not economic. The Biological wastewater treatments using microalgae were widely accepted as eco-friendly, effective and low cost conventional treatment techniques [1]. These techniques were considered the best solutions to solve the high pollution rates, nutrient enrichment and the dissolved oxygen depletion in addition to producing energy from the algal biomass. Also, microalgae provide a pathway to remove the vital nutrients (nitrogen and phosphorus), carbon dioxide, heavy metals from the different types of wastewaters as they are necessary for the algal growth [2]. The bioremediation processes are depending on the ability of microalgae to convert solar energy into useful biomasses by consuming nutrients as phosphorus and nitrogen in the process of photosynthesis [3]. In current decades there has been an increasing attentiveness in heavy metals and metalloids, not only because they pose a danger to humans, animals, plants, and other living organisms, but also because they cannot be removed from contaminated soils or water effectively. Metals and metalloids occur naturally in the environment with an array of oxidation and this diversity is related to their toxicity [4]. Literature indicates that certain species of algae uptake heavy metals such as copper, cadmium, chromium, lead, and nickel. The uptake of metals by algae in aqueous solutions occurs when algae release a protein called metallothioneins. When metallothioneins are released, the alga begins to chemically bind the metal to itself as a defense mechanism to remove the metal from its regular cellular activity [4]. The accumulation of metals and metalloids by algae may occur by any or an amalgamation of the following processes: active transport along the cell membrane, entrapment by cellular components adsorption, cation exchange or complexation [5]. Bioaccumulation is an increase in the concentration of a chemical in a microorganism over time, compared to the chemical's concentration in the environment [5]. During this process of active transport, energy is required; proteins help molecules migrate to the plasma membrane. Matsuto et al. [6] found that within the cell membrane compounds are moved against their concentration gradient and migrated through the membrane by carrier and transport proteins. The complex chemical makeup of cell walls of certain species of algae has a high affinity for metal ions and carries a net negative charge. This is mainly due to carboxylic, phosphoric and sulfhydryl groups. Biosorption is an energy-independent process, which causes metal ions to bind along the cell wall of the algae [4,5&6]. This process entails the use of either living or dead cells and includes the mechanisms of adsorption and cation exchange.

Rapid population growth and industrial development are expected to contribute extremely to the generation of waste, especially wastewater. Increasing in population normally will be accounted to the production of wastewater which is highly contaminated and harmful to the environment. Similarly, the booming industry is becoming one of the leading contributors of wastewater that pollutes the receiving water bodies. Both domestic and industry wastewaters contained a high amount of organic and inorganic nutrients which are suitable for growth of microalgae [7]. The growing microalgae can then be used to carry out the phycoremediation process [8]. However, these wastewaters contained not only nutrients but also harmful heavy metals that threaten the aquatic life and public health. Conventional techniques to remove heavy metal are often ineffective and very expensive. In addition, these methods are used to reduce heavy metal contaminations at low concentrations. In fact, most of the conventional techniques provided incomplete metals removal, require high energy and used a significant amount of reagent, and had limited tolerance to pH changes [9]. Hence, the green approach has been introduced to address these problems. What is meant by green approach is to apply the cultivation technology of microalgae using wastewater and simultaneously reduce the concentration of hazardous metals indirectly [10]. This approach has a promising potential to contribute to achieving this goal in an environmentally friendly manner. Moreover, green technologies comprise low-cost, high-efficiency technique for heavy metals bio-removal from wastewaters [9,10]. However, the effectiveness of metal removal using this approach depends on microalgal species, environmental factors and microalgae concentrations [11].

There has been few information exist on the potential of microalgae, *Nannochloropsis* sp. in the removal of heavy metals from wastewater. Previously, Onalo et al. [12] grew the microalgae, Botryococcus sp. in heavy metal contaminated wastewater for the potential Cr, Cu, As and Cd bio-removal. They found that Botryococcus sp. effectively reduce Cr, Cu, As and Cd up to 45%, 9% and 2%, respectively. Soeprobowati and Hariyati [13] reported using *Chaetoceros calcitrans* to remove Pb, Cd, Cu and Cr from wastewater. while Worku and Sahu [14] also used wastewater to phytoremediate the Cr, Ni, Fe and Hg using microalgae, *Synechocystis salina*. In 2012, Krustok and Nehrenheim [15] had demonstrated the cultivation of microalgae (species not specify) for the reduction of heavy metals present in wastewater. Accordingly, the objective of the present work is to investigate the capability of *Nannochloropsis oculata* in bio-removal of selected heavy metal present in wastewater with different time under indoor culture condition. In the bio removal processes, microalgae uptake high amount of metals. The harvested algal biomass can be potentially used as an energy source.

2 Materials and Methods

2.1 Experimental design

Nannochloropsis oculata was used for bio removal of heavy metal from wastewater. The predominant species of marine microalgae, *N. oculata* was cultivated in 15 L glass tank filled with 29 ppt seawater containing f/2 medium for 9 days [16]. The cultured was stored at room temperature (20–24ºC) with continuous illumination in laboratory. The aeration was supplied by bubbling air at constant pressure. This was followed by cell observation and cell concentration count using Neubauer haemocytometer chamber.

Indoor culture condition was employed in the current study. The contact time on adsorption of Lead, Nickel, Cadmium, Manganese and Cobalt was determined at varying periods of incubation time (24 hrs. 48 hrs. and 96 hrs.) with effluent. After incubation for specific contact time, the supernatant was then analyzed for residual metal concentration in the solution. The wastewater samples were filtered using a membrane filter (Whatman) with a 0.45 μm pore size to remove suspended solids before commencing the experiments. Erlenmeyer flasks (500 mL) were filled with 350 mL of prepared waste water were used in this study. Each treatment represents initial concentrations of microalgae at the beginning of the experiment. The culture flasks were exposed to controlled indoor condition. The flasks were covered and continues aeration to ensure homogenised cells in the wastewaters. Total removal efficiencies calculated following to Equation. Removal Efficiency (%) = (Initial concentration − Final concentration) / (Initial concentration) x 100

2.2 Metal determination procedure using AAS

Heavy metal concentrations of Nickle (Ni), Lead (Pb), Cadmium (Cd), Manganese (Mn) and Cobalt (Co) were measured with Atomic Absorption Spectrophotometer- AA-7000 Shimadzu. The stability of the device was checked by reading a standard every tenth sample. A blank solution was used to determine the analytical solution and probable contamination. All of the analysis were repeated three times.

2.3 Data analysis

For comparing and maintaining the uniformity and homogeneity, all the data were transformed into the same units and the results were expressed as standard deviation (SD). Efficiency of metal recovery was expressed as percentage.

3. Results and Discussion

This experiment was conduct to study the removal of lead (Pb), nickel (Ni), cadmium (Cd) manganese (Mn) and cobalt using the microalgae, *N. oculata* in the wastewater with different periodicity. There was a significant effect on the bio-removal of Pb, Ni, Cd, Mn and Co under indoor culture condition. The highest removal of Pb from wastewater was 63.48% and 54.35%, after 48 and 96 hours respectively. Accordingly, Pb had been reduced from 3.49 µg /l to 1.75 µg/l from the initial period to 96 hours respectively (Figure 1). However, the recovery efficiency of Ni was up to 80% and 39.9 % and reduction of metal concentration from 2.45 to 0.66 µg/l; while the Mn was able to recovery about 87.8 % at the period to 96 hrs. Reduced metal concentration from 3.47 µg/l to 0.24 µg/l. The Cd was reduced from 0.98 µg /l to 0.74 µg/l which is equivalent to 22.1%. Meanwhile, Co was reduced from 3.04 ppm to 0.53 ppm (87.8%) under indoor culture condition.

Most of the sorption occurred during the first twenty-four hour of the experiment as indicated in Figure 1. The data also indicated increases in recovery efficiency with time. The present study, however, makes several noteworthy contributions to the application of green approach in the removal of metals in wastewater using microalgae, *N. oculata* is highly influenced by the different metal concentration employed. Obviously, each metal element study required a different period of to perform the bioremoval process effectively. These phenomena may be due to the difference of metals and also affected by the metal concentration itself in wastewater [17]. Concerning the efficiencies and, the best uptake was Manganese 82.5%. The second most efficient removal was of cobalt. The culture was able to take up (67.42) percentage of the initial concentration. (Figure 2). The efficiency of removal of Ni and Pb was 80.0 and 63.48 %. The least amount of concentration uptake by the algal biomass was of Cadmium 22.1 %. Overall, the recovery efficiency in wastewater was promising and simultaneously remove some toxic metal elements (Pb, Ni, Cd, Mn and Co) was successfully performed. Previously, El-Sheekh et al. [18] found that the microalgae *Chlorella vulgaris* was able to remove Zn, Mn, and Fe concentration in sewage water up to 64.96%. While *Chlorella salina* successfully reduced about 15.6- 28.5%, after 10 days of treatment. The present study *N. oculata* was able to remove 14.73 - 87.8 % in 4 days of treatment. In another Study, *Chlorella vulgaris* also successfully reduced the concentration of Zn, Fe, and Mn up to 80.1% from domestic secondary effluent [19]. In 2014, Onalo et al. [12] investigated the removal of Cd in wastewater using *Botryococcus* sp. only up to 2%. Meanwhile, Chan et al. [20] reported that *Chlorella vulgaris* and *Spirulina maxima* capable of reducing Zn concentration up to 96.3% and 94.9%, respectively. Hamouda et al. [19] studied removal of heavy metals in industrial wastewater using green microalgae and found that *Scenedesmus obliquus* was able to reduce Cd by 7 % in the light and dark culture condition. Therefore, heavy metals removal efficiency in wastewater mostly depending on the species of microalgae used because of their different accumulation affinities towards the tested elements. Moreover, it is also relying on the nature and charge of the cell wall polysaccharides of microalgae [18]. In fact, green microalgae cells cultivated in wastewater with high metal contents also reduced higher metal concentration. In other words, the metal accumulate was independent on the external metal concentration [18].

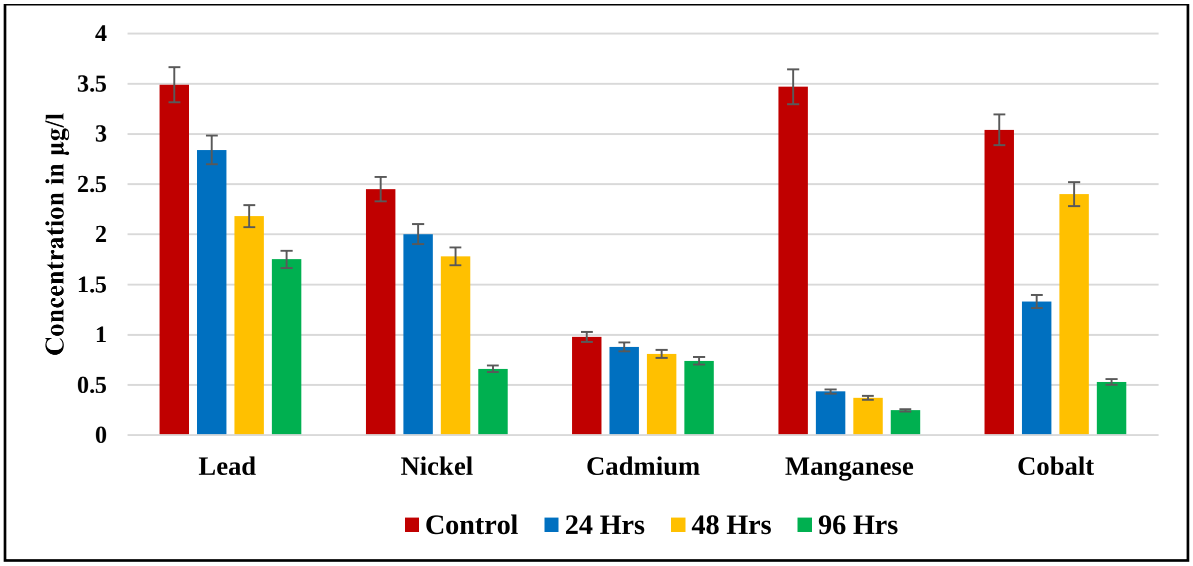

Figure 1: Average & SD concentration of metals in wastewater in µg/l after different period

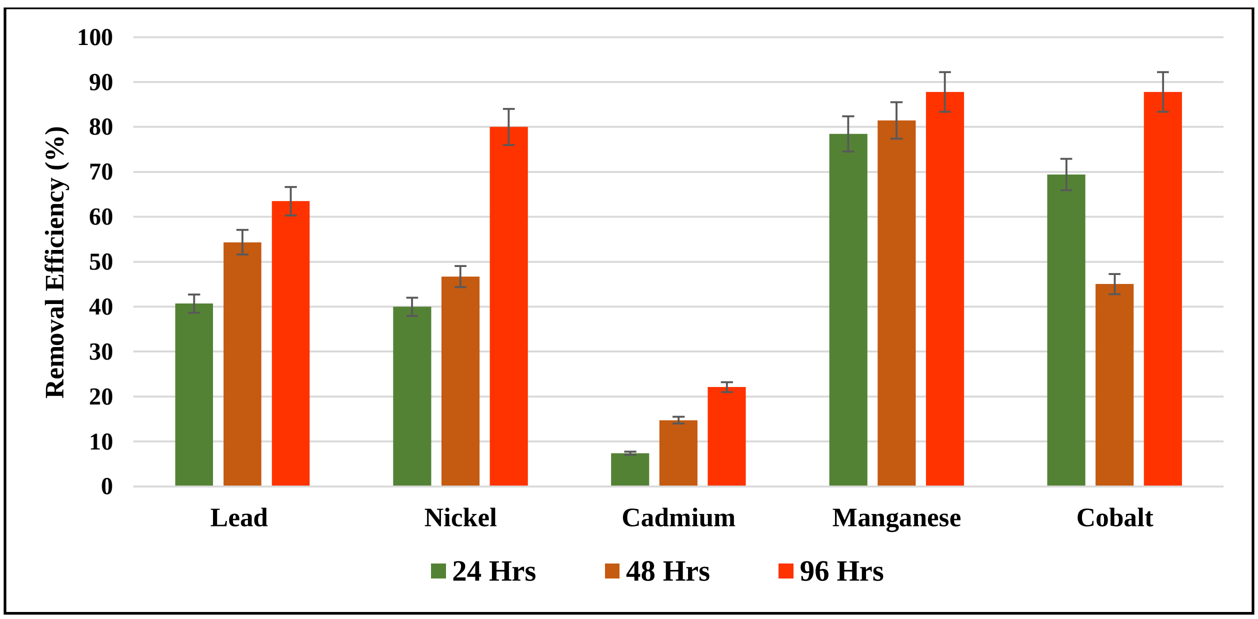

Fig 2: Removal efficiency in % of *N. occulata* cells, different metal concentration with the effect of experimental hours, data are mean values of replicates, error bars indicates standard deviation

4. Conclusions

The purpose of the present study was to investigate the effect of the microalgae; *N. oculata* on the bio-removal of heavy metal from wastewater under indoor culture condition. The capability of *N. oculata* in metals removal is clearly supported by the current findings. However, removal efficiencies are highly depending on the microalgae and the time period applied. The use of algae for removal of metal from water or wastewater is an attractive treatment alternative. This study indicates the potential of the use of algae for metal removal. A bio removal technology in which living biomass is used to accumulate heavy metals is a method that can replace conventional processes for remediating metal pollution in waste waters. The results demonstrated that *N. oculata* stands out as a good accumulator of heavy metals. The establishment of a more efficient, natural, and economic based system is also required with the aim of making optimal conditions for the removal of metals from contaminated water. It was understood that bio removal is an effective procedure to increase removal capability. It can be used in a full-scale biosorption facility. This study led to the conclusion that *N. oculata* has rapid adsorption rate and made them well suited for the removal of metals in wastewater. More broadly, the investigation is also needed to determine the influence of the application of outdoor culture condition on the bio-removal of metal ions coupled with potential precious biomass production.

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Conflicts of Interest

The authors declare no conflict of interest.

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