Molybdenum to Molybdenum Blue

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Contributor: Mohd. Yunus Abd. Shukor

Molybdenum (Mo) microbial bioreduction is a phenomenon that is beginning to be recognized globally as a tool for the remediation of molybdenum toxicity.

Keywords: molybdenum ; bioremediation ; molybdenum-reducing bacterium ; molybdenum blue ; inhibition kinetics ; enzyme purification

1. Introduction

Human activities are endangering the environment. Due to the growth of the population, intensive industrialization, in addition to urbanization and agriculture, has caused significant damage to the environment. The overexploitation of natural resources and ignorance of the laws of nature have exacerbated these problems. Pollution caused by hydrocarbons and metal ions has increased in recent years [1][2], representing a significant global problem.

Toxicity cases ranging from acute to chronic, within occupational and environmental high-exposure settings, have been identified to be caused by toxic agents from metals and their compounds. Typically, heavy metals naturally exist in the environment. Since the pre-industrial period, the level of heavy metals has significantly increased due to anthropogenic activities [3][4][5]. A considerable and indiscriminate release of pollutants into the environment has occurred in parallel with the growing population and intensity of industrialization [6][7]. Harmful effects on human health and biota can be exerted when heavy metals reach levels above the critical load [8][9][10][11]. In their elemental forms and different combinations, metals such arsenic, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, nickel, silver, and zinc are known to be toxic [12][13][14], and they are also non-degradable [15]. Thus, the accumulation of metals within the food chain can lead to a serious threat to the ecosystem [16] due to their carcinogenic and mutagenic properties [17]. Pollution caused by heavy metals has become a global public health concern. Hence, their removal from the environment is vital.

Molybdenum (Mo) is an important trace element that acts as a micronutrient that is necessary as a co-factor for more than 50 enzymes [18][19]. Within animal and plant physiology, for example, it helps to promote cellular function by catalyzing a variety of hydroxylation and redox transfer reactions [20]. Due to the heavy usage of molybdenum in the industrial manufacturing of ceramics, glass, contact lens solutions, metallurgical processes, lubricants, pigments, catalysts, electronic products, and color additives in cosmetics, the risks towards humans exposed to its toxicity have also arisen [18][20]. Increments up to 0.5 mg/L in the level of molybdenum have been discovered in the groundwater around mining areas, which is above the World Health Organization's (WHO's) recommended limit of 0.07 mg/L in drinking water [21]. Animals that have been in direct contact with molybdenum taken via the drinking of water or the foraging for plants are likely to portray symptoms of hypocuprosis or suffer from molybdenosis over a long exposure period [18].

For over a century, the microbial molybdate reduction to Mo-blue has not been understood. This phenomenon has been proven to be enzymatic rather than abiotic [22]. Previously, the focus of bacterial molybdate reduction research was on isolating molybdenum-reducers with higher Mo-blue production capacities. However, because most polluted sites contained mixed contaminants from organic and inorganic origins, effective remediation has thus become a complex task. During the past five years, attention has shifted towards isolating microorganisms with multi-reduction and/or degrading potential that could be used to remediate co-contaminated areas. Recently, several molybdenum-reducing bacteria with the potential to degrade other organic contaminants have been isolated. Therefore, a further understanding of the reduction mechanism and kinetics of Mo-reducing enzymes through various optimization processes will help in understanding the phenomenon of molybdate reduction to Mo-blue. In turn, this would be an important step towards the effective translation of laboratory findings to field practice.

2. Molybdenum (Mo)

Molybdenum is located in group VI, period V, of the transition series as a metallic element. The atomic number for this element is 42, and it has a relative atomic mass of 95.94 g/mol, with melting and boiling points of 2623 and 4639 °C, respectively. Because molybdenum metal does not freely exist in nature, it typically presents either as molybdenite (molybdenum disulfide: MoS_2), wulfenite (lead molybdate), or powellite (calcium molybdate). The direct mining of molybdenite, which is commonly undertaken, enables the metal to be obtained. Furthermore, the metal can also be recovered as a byproduct of copper mining [23][24][25]. Molybdenum is commonly used in the industrial manufacturing of non-ferrous alloys, special steels, electrical contacts, X-ray tubes, spark plugs, tungsten production, glass-to-metal seals, and pigments. Due to several unique properties, molybdenum disulfide can be used as a lubricant additive, and molybdenum compounds are used in fertilizers or directly on seeds to mitigate molybdenum deficiency in crops [26][27].

Pure molybdenum naturally exists as a silvery-white metal with variable oxidation states between 2 and 6, the most stable of which are Mo^{4+} and Mo^{6+} [28]. Because molybdenum primarily exists as molybdate anions (MoO_4^{2-}) in nature, it can be combined to form an assortment of polymolybdate compounds [26][29][30]. Examples of these compounds that are soluble in an aqueous medium at room temperature are sodium molybdate (Na_2MoO_4), ammonium molybdate ($(NH_4)_2MoO_4$), and ammonium paramolybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$). By comparison, molybdenum trioxide (MoO_3) is sparingly soluble, and other compounds such as molybdenite (MoS_2), calcium molybdate ($CaMoO_4$), molybdenum chloride ($MoCl_5$), and metallic molybdenum (Mo) are completely insoluble in an aqueous medium [26][28]. Molybdenum is one of the important trace elements needed by most living organisms in daily life processes [7]. Molybdenum is commonly present at the active site and plays a role as a cofactor to more than 50 enzymes involved in sulfur, nitrogen. and carbon cycles [18][19]; these enzymes include aldehyde oxidase, nitrogenase, sulfite oxidase, and xanthine oxidase. In addition, molybdenum acts as an agent in electron transport [19][28].

2. Identification of the Mo-Reducing Enzyme

The optimization of Mo-blue reduction for the purpose of bioremediation offers a method for the removal of molybdenum pollutants in addition to physical and chemical methods. Presently, molybdenum pollutants are chemically treated as a remediation technique [31]. Microbial-based molybdenum bioremediation offers several advantages over chemical-based remediation. First, Mo-blue is colloidal and forms a precipitate with bacterial biomasses [32]. This is suitable for bioremediation via entrapment with membranes, in which cells are either enclosed or immobilized. The main challenge in the elucidation of the mechanism of reduction is the identification of the enzyme. Though the enzyme has been purified and characterized in one bacterium [33], the sequencing of the enzyme was not successful.

3. Conclusions

This review aimed to provide an update on the current knowledge regarding the molybdenum-reducing bacteria that have been isolated to date. This review also provided an update on the ability of some molybdenum-reducers to degrade other xenobiotics, which is a feature that needs to be studied and optimized in the future. A number of these xenobiotics, such as amides, can be used as electron donors for molybdenum reduction, and the ability of other xenobiotics to act as electron donors should be studied in the future. The inhibitory effect on the molybdenum reduction of cationic heavy metals, such as mercury, copper, and silver, is also seen in other anionic reductions, such as chromate and arsenate microbial reductions. Thus, means to combat this issue need to be studied for real remediation applications in the future. The true identity of the molybdenum-reducing enzyme is currently unknown, and the future sequencing of the purified enzyme could reveal the underlying mechanism behind the reduction process. Inhibition kinetics studies have shown that molybdate is toxic at high concentrations. Thus, the limits of the capability of bacteria to remediate sites highly contaminated by molybdenum, in addition to molybdenum-rich effluent from mine tailings, should be studied. The activation energy for molybdenum reduction also needs to be explored in future studies to distinguish molybdenum from other anionic metal reductions and other xenobiotic degradation processes.

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