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TOXICITY OF MOLYBDENUM AND MICROBIAL APPLICATION IN MOLYBDENUM REDUCTION FOR BIOREMEDIATION: A MINI REVIEW

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Abstract

Molybdenum (Mo) is one the most widely used trace element in many industries and exhibit an important role in humans, animals and plant. Large quantities of hazardous Mo waste released by anthropogenic activities from industrialisation and advancement of technology tremendously increase the burden on the aquatic and soil environments. High accumulation or prolonged exposure of heavy metal such as Mo can cause deleterious health effects on ruminants and aquatic biota as its low toxicity towards human. However, the toxicity of Mo has been reported in spermatogenesis and embryo of mice and fish respectively. Its pollution from several hundreds to thousands of part per million has been documented in water and soils worldwide. Increased level of Mo can pollute the river and bring severe damage to the ecosystem. Bioremediation of heavy metals by microbes in removing the pollutants became more crucial in addressing worldwide environmental pollutions. The mini review summarises the applications of microorganisms in Mo reduction that would be beneficial to future studies on environmental reduction of Mo.

INTRODUCTION

Heavy metals including copper, arsenic, cadmium and mercury that causing pollution has been extensively studied worldwide; however, very few reported on Mo. Historically, in southern Norway, Knaben mine was the first Mo mine known opened in 1885 [1]. As a refractory metallic element, Mo is mainly used as an alloying agent, fertiliser and in body it acting as essential nutrient for metabolic functions. In addition, mining lead to toxic effects to the environment and even in animals due to the accumulation of high concentration of Mo in the system. This heavy metal can enter the animal, plant and human via inhalation, diet, drinking water and oceanic currents polluting the environment [1, 2].

Bioremediation is a popular environmental friendly technology that uses microbial strains for reducing waste pollutants. According to Fuentes et al. [3], this is more efficient than conventional methods as bioremediation is being used solely on the pollutant site without relocating contaminants using biological materials. Bioremediation of heavy metals has been investigated using bacterial, algal species and fungal species. Microorganisms remove heavy metals from solutions via percipitation, cell surface biosorption, intra- and extra-cellular accumulation and complexation facilitated microorganisms [4].

Molybdenum

Molybdenum was identified by the Swedish scientist, Carl Wilhelm Scheele in the 1778 by the forming Mo trioxide via heating of decomposed molybdenite in the air. The name Mo was originated from Greek, "molybdos" meaning lead-like. The oxide was then reduced with the carbon to yield a dark metallic powder known as Mo by Peter Jacob Hjelm in 1782 using carbon and linseed oil. French Schneider Electric Company produced its first Mo-steel armour plates in 1894 and was widely used during the World War I and II. During the war, manganese steel plating was used and found ineffective, therefore replaced with Mo for a better protection as it allows higher manoeuvrability even though thin [1, 5]. Major sources of Mo are mining commonly found in the United States of America, Canada, Mexico, Chile, and Peru. China is the main producer followed by the USA and Chile where the Mo is usually obtained from ores such as wulfenite (PbMoO4), molybdenite (MoS2) and ferrimolybdate (FeMoO3.xH2O). Molybdenum is essentially required as micronutrient for humans, plants, animals and microorganisms [6].

Molybdenum exists as an atomic weight transition metal of 42 and 95.94 g/mol. In the Periodic Table, it is located as the fourth member of second transition series in Group VIB. Molybdenum metal appears as silvery-grey in pure form that is malleable and resistant to corrosion. It has a lower melting point of 2623℃ compared to other naturally occurring elements, tantalum, tungsten, carbon and rhenium. Chemically, Mo is more similar to tungsten and vanadium compared to chromium [1, 7]. Among the commercially used metals, Mo possesses lower ability to resists tension applied on it, which known as thermal expansion.

Molybdenum is widely distributed in nature and found in molybdenite (MoS2), the main Mo ore, wulfenite, powellite, and ferrimolybdate minerals. About 50 inorganic Mo forms such as lead molybdate, insoluble metallic Mo and molybdenum disulphide (MoS2) have been identified. It is known that ammonium molybdate, calcium molybdate, molybdic oxide, sodium molybdate and molybdene trioxide are soluble molybdene compounds. Besides, Song et al. [8] stated that Mo is also obtained as a primary by-product of copper production. Transition metal does not react visibly at room temperature with oxygen or water as it exists with Pauling-based electronegativity. Very high temperatures such as 600℃ may results in molybdenum trioxide (MoO3). All Mo compounds generally have oxidation states from -2 to +6. Molybdenum forms compounds in inter-convertible oxidation states readily that ranging from -2 to +6 due to its extreme versatility. Oxidation states of +3 and +6 have the ability to create complexes with halogens, nitrogen-donor and oxygen donor ligands, whereas sulphur-donor ligands are most commonly complexed with arsenic and phosphorus-donor ligands [9]. **Figure 1** displays an example of polymolybdate anion incorporated with other ions to form polyoxometalates. The phosphorus-containing heteropolymolybdate P[Mo12O40]3 appears in dark blue commonly utilise in the spectroscopic detection of phosphorus [10].

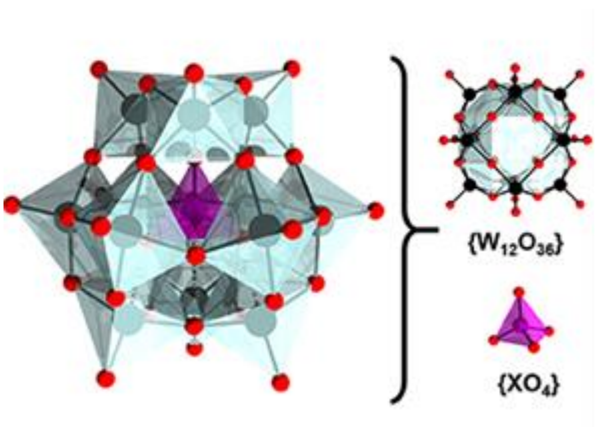

Figure 1. An example of polyoxometalate showing Keggin structure of the phosphomolybdate anion (P[Mo12O40]3-) [10].

Applications of molybdenum

Properties of Mo provide many development opportunities and new commercialised applications by the exploitation of its chemistry. Many materials made from molybdate are alloys, oxidation catalysts, lubricants, pigments, inhibits corrosion, smoke suppressants, ceramics, surface coatings and paints [11]. Molybdenum is extensively used as alloying agent in steel and iron by 75%, which can be found in automobile, aeronautical and defence industries for withstanding high temperatures and preventing corrosion [12]. As a catalyst, MoS2 is important in hydrodesulphurisation (HDS) of petroleum, petrochemicals and coal-derived liquids containing nitrogen, sulphur and oxygen. Molybdenum catalysts are resistant to sulphur poisoning and efficient in economical fuel refining with harmless release of sulphur to the environment [13].

Small amounts of sulphur from molybdenum sulphide are available to react with iron and provide a sulphide layer compatible with MoS2 to maintain the lubrication between the metal layers [14]. Corrosion inhibition and stable colour formation are the properties used in molybdate-based pigments such as lead molybdate or wulfenite which provide bright orange pigmentation. Light and heat stable pigments with colours ranging from bright red-orange to red-yellow were used in plants, inks, plastics, rubber products and ceramics. Zinc molybdate is the basis of pigment inhibiting white corrosion in paint primers. Sodium molybdates inhibit steel corrosion in different pH ranges such as water-based hydraulic systems and automotive anti-freeze motors. PVC containing ammonium octamolybdate is used to reduce the formation of smoke as wire or cable insulation in electronic technology. Molybdenum is required as an essential trace element in the enzyme nitrogenase, which catalyzes the conversion of atmospheric nitrogen to ammonia and is used in plants as a fertiliser [15].

Biological role of molybdenum in humans

Molybdenum is an essential mineral found in the body when it presents in soil of plant and is transferred into the body and animals that feed on those plants. Many foods such as legumes, grains, green leafy vegetables and meats contains Mo, the body only requires it in trace amounts; thus, deficiency is very rare. Recommended dietary allowance (RDA) is 45 µg of Mo daily intake for an adult. The chemical reaction of sulphur and nitrogen compounds in toxin metabolism aids is needed in enzymes as a cofactor. Four essential enzymes include sulphite oxidase, xanthine oxide reductase, aldehyde oxidase and amidoxime reductase with mitochondrial [16]. Human body contains 0.07 mg of Mo/kg of body weight and deficiency might be due to poor functioning of sulphite oxidase leading to toxic reactions to sulphites available in foods [17]. Furthermore, production of uric acid regulated by xanthine oxidase, deficiency or absence can allow the formation of kidney stones and renal failure. It ensures the uric acid excreted by the conversion of hypoxanthine to xanthine. Approximately 60% of ingested Mo is excreted through urine due to low Mo intake, however with high Mo intake will cause over 90% of it is excreted in the urine [18]. Metabolism of vitamin A, synthesis of steroid hormones, maintenance of lung function and circulation of blood require oxidase of aldehyde.

Biological role of molybdenum in animals

Molybdenum compounds enter the body via ingestion, inhalation and drinking. Cows with scouring and deaths occurring at 20 to 50 mg Mo/kg of body weight have been reported due to Mo pollution. In ruminants, high concentration of Mo will prevent the plasma proteins from binding to copper that involve the formation of a thiomolybdate complex and excrete urine high in copper [19]. Molybdenosis is a condition that develops symptoms such as diarrhoea, stunted growth and anaemia was observed however, these can be alleviated by copper supplements. It is also developed worldwide since Mo contamination by anthropogenic activity from a coal mine [20] and uranium-bearing lignites [21].

In certain animals Mo is essential for oxygen transferring reactions of sulphite oxidase, xanthine oxidase and aldehyde oxidase where it bounds to a pterin [22].

Biological role of molybdenum in plants

Plant growth requires Mo as components of enzyme nitrate reductase and nitrogenase. Nitrate reductase is a flavoprotein enzyme incorporated with Mo that reduce nitrate to nitrite. Molybdenum cofactor comprised with a pterin ligand of an oxomolybdenum sulphur species that acts as a reduced FAD enzyme electron acceptor [23]. Grass, corn or other legumes need more Mo than other crops due to the presence of symbiotic bacteria living in the root nodules of legumes that involved in atmospheric nitrogen fixation. Plant growth will be retarded when the Mo is insufficient. Rhizobium sp. is the symbiotic microorganism that fixes nitrogen while, Aztobacter sp. and Clostridium sp. are free-living asymbiotic microorganisms involved in the mechanism of nitrogen fixation [24].

Molybdenum pollution

There has been a rise in pollution and concerning health due to heavy metal contamination involving Mo that is widely used in many industries. However, Mo effluent is discharged into the environment mainly from the extensive use of Mo in industries [25]. Many heavy metals pollution widely reported worldwide however, very few on Mo. First Mo pollution was reported in Tyrol, Austria caused by industrial waste polluting a large pasture area affecting ruminants that grazed in the field. Evidence showed that a Mo mining company near Red River, New Mexico contributed to pollution and another case reported in Silesian Upland, Poland [26].

In 2017, Finley [27] reported that streams or creeks flowing into a water treatment plant in Colorado, USA has been polluted by Mo released from nearby Climax Mine, would cost up to $600 million to remove high levels of Mo pollution up to 2,500 ppb. According to World Health Organisation (WHO), the permitted safe limit of Mo content is 0.07 mg/L [28]. However, no general rules have been established for the safe level of Mo in Malaysia for the water system.

Molybdenum toxicity

Toxicity of Mo compounds can be assessed into acute and chronic toxicity. Uncontrollable anthropogenic activities leading to Mo and other heavy metals discharged into soil and aquatic environment have long-lasting effect on the environment [29]. Even at low concentration, it is cytotoxic, carcinogenic and mutagenic to animals, plants and human health. Limited studies have been reported on the toxicity of Mo to humans. The people in Armenia consumed high-volume Mo-containing foods ranging from 10 to 15 mg Mo/day, which led to increased activity of xanthine dehydrogenase and blood uric acid levels. Gout was also found associated with higher uric acid levels identified in the blood. Further, another case reported at a molybdenite roasting plant, which the workers suffer from fatigue, headache and weakness after exposure to 10 mg Mo/day via dust. Highest permitted concentration of Mo air is 5 mg Mo/m3 in 8 hours period according to the American Industrial Hygiene Association [30].

Molybdenosis in animals mainly affects the ruminants. According to Helaly et al. [31], regular doses of MoO3 ranging from 1200 to 6000 mg Mo/kg may be fatal, while low doses of 120 to 600 mg can decrease deaths in guinea pigs and rats. An experiment on farm animals with approximately 20 to 100 mg Mo/ kg body weight sodium molybdate showed that cows has low tolerance of extreme scoring at 20 to 50 mg Mo/ kg body weight compared to horses because they could tolerate high levels of Mo [32]. Several health effects visible in cows include osteoporosis, hypocupraemia and bone fractures. Low sulfate and copper diets increase Mo toxicity. A high intake of Mo also reduces livestock and swine intake for feeding, whereas Mo levels in the serum, scalp, ribs, internal organs and brain reflect a noticeable intake of the element [33]. A study recently reported molybdenum's toxic effects on trace elements in Shaoxing duck's digestive organs, Anas platyrhyncha. Molybdenum was seen accumulated primarily in its oesophagus and may interferes with homeostasis of other trace elements in the digestive organs [34].

Furthermore, with concentrations of ≤0.06 μg/L of Mo in freshwater systems has been shown to inhibit primary production due to deficiency [35]. In the aquatic environments, Mo can naturally mobilised into aquatic environments by weathering of bedrock, formation of shale due to anthropogenic from mining, fertilisers as well as wastewater discharges causing to increase highly soluble molybdate anions (Mo42-) [36]. The most sensitive acute toxicity of LC50 in freshwater oligochaete, Tubifex tubifex with concentration of 2782 mg/L was reported by Lucas et al. [37].

Bioremediation of molybdenum using microorganisms

Bioremediation is indeed a treatment which uses micro-organisms like fungi, bacteria, yeast or algae that breakdown or degrade toxic substances into less or non-toxic substances. This term is categorized into two aspects, "bios" relates to living organisms and "to remediate" implies to resolve a problem. Thus, it refers to the use of certain biological organisms to minimise or resolve an environmental dispute such as heavy metals contamination in soil or groundwater [38].

Microorganisms degrade the organic or inorganic contaminants into a harmless product such as carbon dioxide and water. In most cases, it involves redox reaction. The chemicals that loss electrons are oxidized and vice versa, whereas the electron recipient acts as electron acceptor and the contaminant as electron donor. Organic contaminants serve as carbon source for building blocks of new cell constituents and electrons to obtain energy by microorganisms [39].

There are two types of bioremediation, in-situ and ex-situ. *In situ* is the most desirable and cost-effective technique not requiring contaminants to be transported or excavated but limited to certain soil depth. Meanwhile, ex situ requires removal or excavation of contaminants from ground [40]. Bioremediation is one of most cost efficient for removal or disposal of hazardous substances from the environment without causing any harm to human health and surroundings. It is, however, limited to biodegradable and highly specific compounds that require a long period. Bioremediation manipulates microbe capacity to remove heavy metals that involve mechanisms including bioreduction, chelation, sequestration, biosorption, and bioaccumulation. The interactions of microorganisms with heavy metal ions are partially dependent on type of cell, because the prokaryotes are less sensitive to metal toxicity eukaryotes [41, 42].

Bacteria reduce metal ions such as Mo by bioremediation mechanisms. The molybdate reduction has been previously reported long ago in bacteria, *Escherichia coli* by Capaldi and Proskauer [43] and proceeded by *E. coli* K12 in 1985 [44]. Other bacteria reported by Sugio in 1988, such as *Thiobacillus ferroxidants*, following *Enterobacter cloacae* strain 48 [45], *Serratia marcescens* strain DRY6 [46], *Pseudomonas* sp. strain DRY1 [47], *Klebsiella oxytoca* strain DRY14 [48], *Bacillus* sp. strain A.rzi [49], *Bacillus* sp. strain Khayat [50], *Klebsiella oxytoca* strain Saw-5 [51], *Burkholderia* sp. strain Neni-11 [52], *Enterobacter* sp. strain Saw-1 [53], *Enterobacter* sp. strain Saw-2.[54], *Bacillus* sp. strain Neni-10 [55], *Burkholderia vietnamiensis* strain AQ5-12 [56], *Burkholderia* sp. strain AQ5-13 [56] and *Serratia* sp. strain HMY1 [57]. These bacterial-based Mo remediation decrease molybdate into precipitate form, Mo-blue. Firstly reported bioremediation was performed in Tyrol, Austria on agricultural soil exposed to high toxicity of Mo, by using phytoremediation and mixture of microbes isolated from the soil to immobilise the molybdate into non-soluble form [26].

Several aspects are taken into account such as the reduction of Mo to Mo-blue that requires an optimal temperature of 10℃ to 20℃ for psychrotolerant microorganisms in polar and temperate regions, glucose as the most suitable source of electrons and carbon, ammonium sulphate as a source of nitrogen and molybdate concentration that may varies from 20 mM [58], 50 mM [59] and high as 80 mM [44]. Meanwhile, most of the bacteria exhibited inhibition for phosphate concentration of more than 5 mM which can prevent the Mo reduction.

Microbes could eliminate toxic metals from wastewater in their cell walls via functional groups including ketones, aldehydes and carboxylic groups as well as generate fewer chemical sludge [60]. The use of algae as biosorbents does not produce toxic substances, unlike other microorganisms such as bacteria or fungi [4]. Based on previous studies, Mo was degraded by various bacterial species; however, none were reported on using algae to remediate Mo. The use of algae is known as algal bioremediation or phytoremediation to remove pollutants from the environment. Hlihor et al. [61] stated that algae are photosynthetic eukaryotic organism found primarily in the aquatic region ranging from unicellular and multicellular. In the case of pollution, they toxic heavy metals or other organic pollutants can be degraded or bioaccumulated.

Algae and bacteria play a major role in changing the environment through various contaminants from its original state. Microbes can degrade the pollutants in a short time by understanding the genes that coded for the enzymes involved [62]. Biosorption and bioaccumulation are two main mechanisms of microorganism bioremediation, due to the ability to acquire, regenerate and reuse the biomass from industrial waste in many cycles, a passive adsorption mechanism known as biosorption is a reversible, fast and inexpensive technique. In the bioremediation process, either living or dead biomass can be used in biosorption, but bioaccumulation involves only living biomass which could not be reused and is therefore costly [63]. Heavy metals biosorption in the solution can affect different environmental conditions such as pH, ionic strength, the concentration of biomass, temperature, particle size, and the presence of other ions. Several study results have also shown that numerous metals including Pb, Cu, Cd, Co, Hg, Zn, Mg, Ni and Ti are sequestered into polyphosphate algae bodies, stored and detoxified metals as shown in **Figure 2** [64].

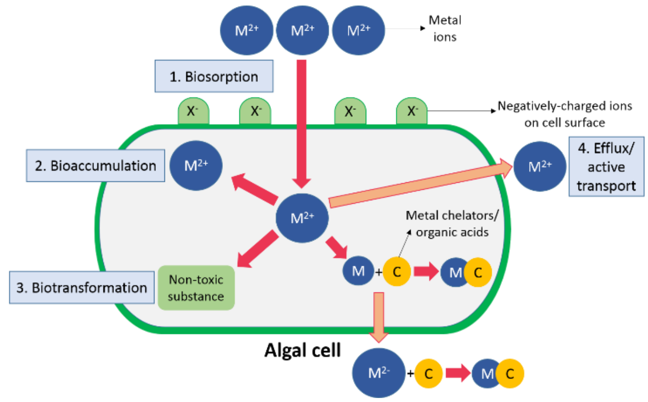

Figure 2. Biosorption and bioaccumulation of heavy metals by algae cell [64].

Mechanism of molybdenum

Molybdenum with a 6+ (Mo^{6+}) oxidation state does not exist as a solution for molybdate ions $(MoO_4)^{2-}$. This molybdate ion would form polyions by using ascorbic acid as reducing agents to yield isopolymolybdenum blue. This molybdate ion would form polyions that reduced to yield isopolymolybdenum blue by using ascorbic acid as reducing agents. Heteroatoms such as phosphate, tungsten, sulphate and arsenate that form heteropolymolybdates are reduced into intense blue known as heteropolymolybdenum blue [63]. For instance, a combination of molybdate and silicate forms silicomolybdate while phosphate will form phosphomolybdate [7]. In a series of redox mechanisms, two electrons from reducing agent, dithione are received to convert heteropolymolybdenum to Mo-blue as shown in **Figure 3** [66]. Mo-blue has a valence of +5 or +6 mixture when observed under 17O nuclear magnetic resonance (NMR) spectroscopy as it appears in very mobile condition [67]. Varies scanning spectra reading may be obtained from different reduced heteropolymolybdates.

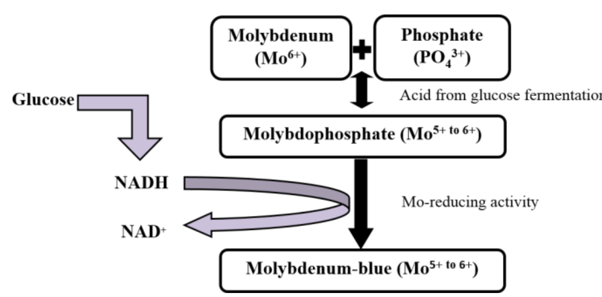

Figure 3. Mechanism of molybdate reduction to Mo-blue [66]

CONCLUSION

Heavy metals such as Mo are known to be naturally occurring compounds, but due to anthropogenic activities which introduced them in large quantities in different environmental compartments. This leads to a significant decrease in the ability of the environment to foster life as human, animal, and plant health are threatened, due to bioaccumulation in the food chains. This review provides an opportunity to reveal the biochemistry of Mo and its toxicity to the environment by understanding the role of microorganisms and their mechanisms towards remediation of heavy metals and environmental research. Therefore, bioremediation is a cost-effective and a green technology that has advantages, especially in the context of environmental protection.

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