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Aquatic acute toxicity assessments of molybdenum (+VI) to *Daphnia magna*

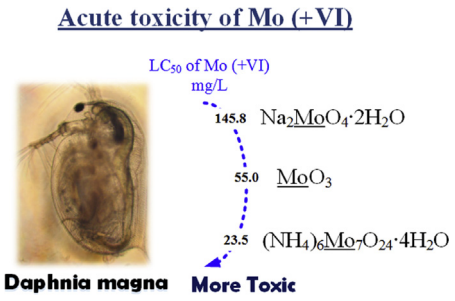
Chi-Wei Wang, Chenju Liang*, Hui-Ju Yeh

Department of Environmental Engineering, National Chung Hsing University, 250 Kuo-kuang Road, Taichung 402, Taiwan

HIGHLIGHTS

- Impact of Mo^{6+} in aquatic system via *D. magna* acute toxicity bioassay was studied.
- The acute toxicity increased in the order: $Na_2MoO_4{\cdot}2H_2O < MoO_3 < (NH_4)_6Mo_7O_{24}{\cdot}4H_2O$.
- The level of Mo toxicity is highly dependent on the form of molybdenum salts.
- LC_{50} determined for Mo can be used to establish toxicity values for Mo in aquatic systems.

GRAPHICAL ABSTRACT



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ABSTRACT

Generally, molybdenum (Mo) metals in the environment are very rare, but wastewater discharges from industrial processes may contain high concentrations of Mo, which has the potential to contaminate water or soil if not handled properly. In this study, the impact of three common compounds of hexavalent Mo (sodium molybdate ($Na_2MoO_4{\cdot}2H_2O$), ammonium molybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$) and molybdenum trioxide (MoO_3)) in an aquatic system were assessed based on 48-h exposure acute toxicity to *Daphnia magna (D. magna)*. The LC_{50} toxicities for associated conjugate ions including Na^+, Cl^-, SO_4^{2-}, and NH_4^+ were determined. Furthermore, the LC_{50} values for the three forms of hexavalent Mo were determined, and the acute toxicities of the Mo forms were found to follow the order: $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O > MoO_3 > Na_2MoO_4{\cdot}2H_2O$ in solution. $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ exhibited the lowest LC_{50} of 43.3 mg L^{-1} (corresponding to 23.5 mg Mo L^{-1}) among the three molybdenum salts. The research confirmed that the toxicity of molybdenum in the aquatic system is highly dependent on the form of molybdenum salts used, and is also associated with the influence of the background water quality.

1. Introduction

Molybdenum (Mo), with exceptional thermal conductivity and electrical conductivity, low thermal expansion coefficient, and good corrosion resistance, was gradually adopted as a replacement of the traditional toxic metals (such as hexavalent chromium) in many industrial processes (Shields, 2013; Heijerick et al., 2012). Mo is now used prevalently in the semiconductor and thin-film-transistor liquid-crystal display industries. Typically, the concentration of Mo in natural environments is very low, but discharges from industrial processes may contain high concentrations of Mo, which poses the potential to contaminate water or soil if releases to the environment occur. Mo has a wide range of oxidation states, i.e., −2 to +6; however, the most stable valences are +4 and + 6

* Corresponding author.
E-mail address: cliang@nchu.edu.tw (C. Liang).

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(Huang et al., 2012). Among them, molybdate (+VI), an oxyanion with hexavalent Mo, is the most soluble Mo salt compound.

In the organism, Mo is one of the essential dietary micronutrients (Atia, 2008; Smedley et al., 2014), but excessive ingestion of Mo could result in anemia, gastrointestinal disturbances, hypothyroidism, bone and joint deformities, sterility, liver and kidney abnormalities, etc. (Shields, 2013; Diamantino et al., 2000). In view of this, the World Health Organization recommends a limit of 70 μg L^{-1} Mo in drinking water (WHO, 2011). Moreover, Taiwan, a high-tech industry export-oriented country, formulated the current limit of 0.6 mg L^{-1} Mo for industrial effluents. Generally, the regulatory concentration or standard for any controlled substance would be low compared to the LC_{50} in order to ensure that the toxic substance produces no observed adverse effects to the organism when exposure occurs in the environment. It has been reported that the concentration of Mo is low in natural environments, e.g., around 5 nM in river waters (Martin and Meyback, 1979). However, Mo in industrial wastewater could be high as 4–145 mg L^{-1} (Shan et al., 2012).

However, even though a maximum concentration level was regulated, several different Mo ions and/or compounds (e.g., different valences and associated conjugate cations or anions) in water may present different biological toxicities. For example, the median lethal concentrations (LC_{50}) for hexavalent Mo, sodium molybdate and ammonium molybdate, were reported to be 800 mg L^{-1} (rainbow trout, 96 h exposure) (Sigma-Aldrich, 2015a, b, c) and 420 mg L^{-1} (rainbow trout, 96 h exposure) (Sigma-Aldrich, 2015a, b, c), respectively, which are equivalent to 373 and 228 mg L^{-1} Mo. It can be seen that with the same test toxicity organism, ammonium molybdate presents a higher toxicity with respect to Mo than that induced by sodium molybdate. Hence, the toxicity of Mo in aquatic systems is also dependent on the contribution of its associated conjugate cations.

Bioassays, which rely on measuring the response of organisms exposed to contaminants, relative to a control, are the most widely used test methods for the toxicity assessment of chemical compounds and effluents. *Daphnia magna* (*D. magna*) (Fig. 1) is one of the biological organisms allowed in Taiwan's biological acute toxicity testing for the Water Pollution Control Act. *D. magna* is sensitive enough to distinguish between the toxicity to the several different Mo compounds and is therefore a good test organism to predict the potential impact of new chemicals, or whole effluents, on the aquatic environment (Barmentlo et al., 2015; Stanley et al., 2013; Yim et al., 2006). This research was conducted to explore the impact of Mo (+VI) from different molybdate salts in aquatic system via *D. magna* acute toxicity bioassay. There are seven commercially available molybdenum salts, including ammonium molybdate, potassium molybdate, sodium molybdate, phosphor molybdic acid, molybdenum disulphide, molybdenum trioxide, and molybdic acid (Sajan overseas Ltd., 2015). Heijerick et al. (2012) indicated that the simple MoO_4^{2-} is most likely to be formed from different molybdenum containing substances under common environmental conditions. The predominating ionic species of Mo (+VI) reported to be present in solution at pH > 2, were $Mo_7O_{24}^{6+}$ (pH 2–7) and MoO_4^{2-} (pH > 4) (Xiong et al., 2011). Molybdenum trioxide (MoO_3) is produced on the largest scale of any molybdenum compound (US Research Nanomaterials Inc., 2015). Therefore, $Mo_7O_{24}^{6+}$, MoO_4^{2-} and MoO_3 were selected as reference test substances for the evaluation of Mo (+VI) compounds. As a first step, this study carried out a thorough LC_{50} evaluation of several aquatic impact factors including pH, conductivity, and background aquatic ions associated with Mo (+VI) salts. Thereafter, LC_{50} values for three different sources of molybdate (i.e., sodium molybdate (Na_2MoO_4), ammonium molybdate ($(NH_4)_6Mo_7O_{24}$), and molybdenum trioxide (MoO_3) were determined. Data from this study addresses the critical data gaps concerning the acute toxicity of Mo associated with releases to the environment from industrial processes.

2. Materials and methods

2.1. Chemicals

All reagents were of analytical grade and used without further purification. Sodium molybdate dihydrate ($Na_2MoO_4{\cdot}2H_2O$, min 99%), ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, min 99%), molybdenum trioxide (MoO_3, min 99%), sulfuric acid (H_2SO_4, min 95%), potassium chloride (KCl, min 99.5%), sodium bicarbonate ($NaHCO_3$, min 99.7%), sodium hydroxide (NaOH, min 99%), sodium chloride (NaCl, min 99.8%), nitric acid (HNO_3, min 65%), ammonium hydroxide solution (NH_4OH, min 28%), ammonium sulfate ($(NH_4)_2SO_4$, min 99%) and sodium sulfate (Na_2SO_4,

Fig. 1. (a) side view and (b) dorsal view of *D. magna*.