ATLANTIS PRESS
Advances in Engineering Research, volume 123
2nd International Conference on Materials Science, Machinery and Energy Engineering (MSMEE 2017)

Size-dependent and shape-dependent algal toxicity of Aluminum oxide nanoparticles

Wenting Ren, Ruifeng Hou, Shuang Yin, Huan Yao, Xuesong Cao

[1]College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China

Keywords: Al_2O_3 nanoparticles, shape, size, toxicity, electrostatic interaction

Abstract: In this work, we investigated the toxicity of Al_2O_3 particles with different size and shape to algae (*Chlorella pyenoidosa*). It was indicated that the toxicity of Al_2O_3 nanoparticles (NPs) was the strongest and the toxicity caused by bulk particles (BPs) was weaker than that of Al_2O_3 NPs. Al_2O_3 Fiber exhibited weakest toxicity to algae. Electrostatic interaction-induced physical contact could be a major mechanism to explain the difference of the observed toxicity.

1. Introduction

Al_2O_3 nanoparticles (NPs) are widely used in commercial applications such as explosive combinations, ceramics, catalyst and composite materials [1]. With the rapid increases in production and application, Al_2O_3 NPs will be released into aquatic environment. Upon exposure, they will exhibit adverse impacts on organisms. Sadiq et al. (2011) reported that Al_2O_3 NPs can inhibit the growth of *Scenedesmus sp.* and *Chlorella sp.* The EC_{50} of *Scenedesmus sp.* is higher than that of *Chlorella sp.* and the entrapment ability of algal cells to Al_2O_3 played an important role[2]. Jacqueline et al. (2009) have used 0.7 μm Al_2O_3 and 1.6 μm SiO_2 to assess the cellular uptake and cellular toxicity of lunar dust particle analogs. According to the results, two type of cells showed minimal cytotoxicity exposure to Al_2O_3[3]. Wang et al. (2009) characterized the toxicity and behavior of nanoparticles and bulk metal oxide ZnO, Al_2O_3 and TiO_2 to *C.elegans* in an aqueous medium. The results indicated that Al_2O_3 NPs induced the weakest toxicity among the three type of metal NPs and the toxicity caused by Al_2O_3 NPs is stronger than that of bulk particles (BPs)[4]. In the natural environment, the morphologies of Al_2O_3 particles are various and may occur a series of interaction. Ren et al. (2014) reported that Al_2O_3 could heteroaggregate with graphene oxide, altering the environment fate and biovailability of graphene oxide[5]. Many articles had reported that the shape and size factors had a great effect on the toxicity of nanoparticles. Leanne et al. (2016) revealed that compared to CuO nanospheres, CuO nanosheet had higher surface reactivity and bacterial toxicity[6]. Pan et al. (2009) reported that 1-2 nm Au NPs reduced the most toxicity among all the 0.8-15nm Au NPs[7]. So, it is important to investigate the toxicity of Al_2O_3 with different morphologies on freshwater algae. Therefore, in the study, Al_2O_3 particles with different size and shape were chosen to research the toxicity on *Chlorella pyenoidosa.*

2. Materials and Method

2.1 Exposure Experiment. The three types of Al_2O_3 particles (Al_2O_3 NPs, Al_2O_3 BPs and Al_2O_3 Fiber) were purchased from Nanjing XFNANO (China). The *Chlorella pyrenoidesa* was purchased from the institute of Hydrobiology, Chinese Academy of Science, China. In our study, the modified SE medium (one-tenth SE medium) was used for algal cells culture medium, in which the nutrient was sufficient for algal growth. The pH of culture medium was adjusted to 7.0 by adding negligible amounts of NaOH or HCl. The algal cells were grown under the light intensity of 12000 lux (14: 10 light: dark cycle) in a light growth chamber (GXZ, China) at 24°C. For algal growth inhibition assay, algal cells (1×10^6 cells/mL) were cultured two days to achieve the exponential growth phase. Al_2O_3 were pre-suspended in algal medium and then added to exponentially growing algal cells to reach the final concentrations. The algal suspensions were shaken twice every day and the algal cells were counted under a light microscope (JNOEC, China) after two days.

2.2 Statistical Analysis. The inhibition rate of Al_2O_3 particles was calculated by the equation as follows:

Inhibition Rate (%) = $(1-A/A_0)$ *100% (1)

A: the algae cells concentration of treatment group

A_0: the algae cells concentration of control group

The median effective concentration (EC_{50}) was calculated by nonliear regression using the cumulative distribution function of SPSS Statistics. All data included three replicates and standard error was statistically analyzed ($p<0.05$).

3. Results and Discussion

3.1 Characterization of different types of Al_2O_3. Characterization of Al_2O_3 particles was analyzed by transmission electron microscopy (TEM, H-7650, Hitachi, Japan). The TEM images showed that the size of Al_2O_3 NPs was 8-12 nm (Fig. 1A). The size of Al_2O_3 BPs was 100-300 nm (Fig. 1B). The length of Al_2O_3 Fiber was 100-200 nm and the width was 8-10 nm (Fig. 1C). Different with Al_2O_3 BPs and Al_2O_3 Fiber, Al_2O_3 NPs formed the biggest homoaggregate. It was possibly attributed to the huge surface area of Al_2O_3 NPs.

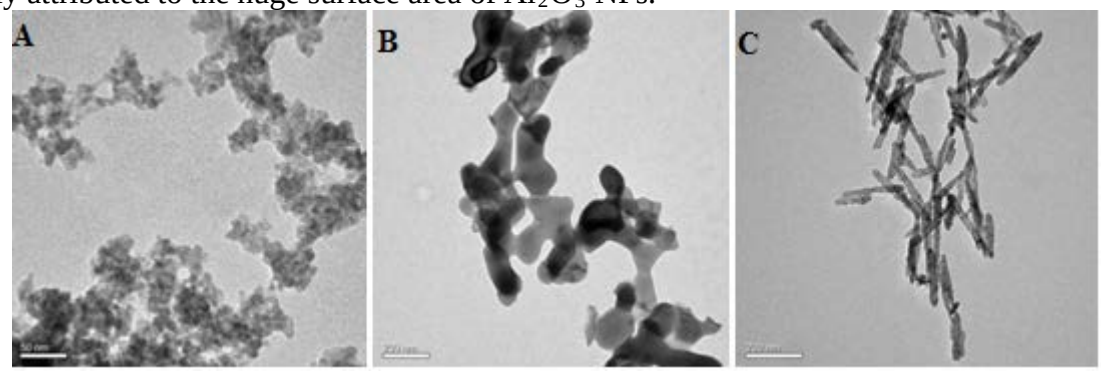

Fig. 1 TEM images of Al_2O_3 particles. (A) Al_2O_3 NPs, the ruler line is 50 nm; (B) Al_2O_3 BPs, the ruler line is 200 nm ; (C) Al_2O_3 Fiber, the ruler line is 200 nm.

At pH 7.0, the zeta potentials of Al_2O_3 and algae were measured by Zetasizer (Nano ZS90, Malvern, UK) and showed in Table 1. The zeta potentials of Al_2O_3 NPs, Al_2O_3 BPs and Al_2O_3 Fiber were 35.04 mV, 28.87 mV and 19.16 mV, respectively. However, algae cells were highly negatively charged.

Table 1 The zeta potential of Al_2O_3 particles and algae at pH 7.0

Type	Al_2O_3 NPs	Al_2O_3 BPs	Al_2O_3 Fiber	algae
Zeta potential (mV)	35.04±3.56	28.87±0.87	19.16±0.48	-33.43±0.65

3.2 The toxicity of Al_2O_3 particles. Fig. 2 showed the toxicity of Al_2O_3 particles on 48 h. Al_2O_3 NPs had the strongest toxicity among the three type of Al_2O_3 particles, while the toxicity of Al_2O_3 Fiber was weakest. The EC_{50} of Al_2O_3 NPs, Al_2O_3 BPs and Al_2O_3 Fiber were 64.57 mg/L, 95.50 mg/L, 147.91 mg/L, respectively. The order of toxicity was completely same with that of zeta potential. The three types of Al_2O_3 particles were both positive charged at pH 7.0, while algae was highly negatively charged. Zhao et al. (2015) reported that GO with negatively charged and goethite with positive charged could happen heteroaggregation[8]. Heteroaggregation may occur between Al_2O_3 and algae, too. So we assume heteroaggregation caused by electrostatic interaction may be a major reason to explain the toxicity of Al_2O_3 particles.

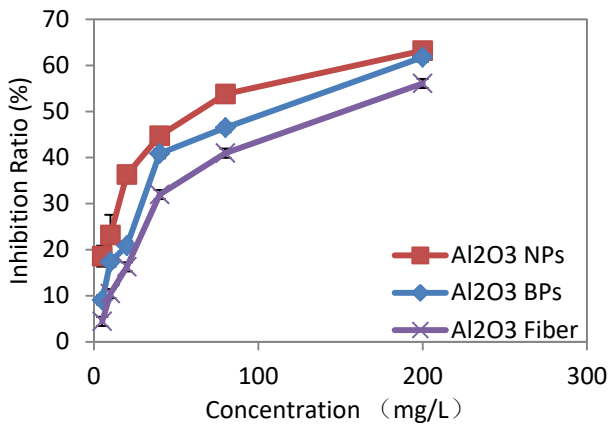

Fig. 2 The toxicity of Al_2O_3 particles to algal cells on 48 h. The red, blue and purple column indicated respectively the toxicity of Al_2O_3 NPs, Al_2O_3 BPs and Al_2O_3 Fiber. Error bars indicated one standard deviation of at least three measurements.

4. Conclusion

Al_2O_3 particles were toxic to algae. Among the three types of Al_2O_3 particles, Al_2O_3 NPs showed the strongest toxicity, while, the toxicity of Al_2O_3 Fiber was weakest. Electrostatic interaction-induced physical contact could be a major mechanism for the toxicity.

Acknowledgments

This research was supported by Natural science Foundation of China (41573092, 41530642).

References

[1] Pamela J, Kaste B. Novel energetic materials for the future force: The army pursues the next generation of propellants and explosives. The Amptiac Newsletter, 2004, 8(4): 85-89.
[2] Sadiq I M, Pakrashi S, Chandrasekaran N, et al. Studies on toxicity of aluminum oxide (Al_2O_3) nanoparticles to microalgae species: *Scenedesmus sp.* and *Chlorella sp.* Journal of Nanoparticle Research, 2011, 13(8): 3287-3299.
[3] Jordan J A, Verhoff A M, Morgan J E, et al. Assessing the in vitro toxicity of the lunar dust environment using respiratory cells exposed to Al_2O_3 or SiO_2 fine dust particles. In Vitro Cellular & Developmental Biology-Animal, 2009, 45(10): 602-613.
[4] Wang H, Wick R L, Xing B. Toxicity of nanoparticulate and bulk ZnO, Al_2O_3 and TiO_2 to the nematode Caenorhabditis elegans. Environmental Pollution, 2009, 157(4): 1171-1177.
[5] Ren X, Li J, Tan X, et al. Impact of Al_2O_3 on the aggregation and deposition of graphene oxide. Environmental science & technology, 2014, 48(10): 5493-5500.
[6] Gilbertson L M, Albalghiti E M, Fishman Z S, et al. Shape-dependent surface reactivity and antimicrobial activity of nano-cupric oxide. Environmental science & technology, 2016, 50(7): 3975-3984.
[7] Pan Y, Leifert A, Ruau D, et al. Gold nanoparticles of diameter 1.4 nm trigger necrosis by oxidative stress and mitochondrial damage. Small, 2009, 5(18): 2067-2076.
[8] Zhao J, Liu F, Wang Z, et al. Heteroaggregation of graphene oxide with minerals in aqueous phase. Environmental science & technology, 2015, 49(5): 2849-2857.