



# Cadmium removal from simulated groundwater using alumina nanoparticles: behaviors and mechanisms<sup>☆</sup>



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## ABSTRACT

Cadmium (Cd), one of the most toxic contaminants in groundwater, can cause a severe threat to human health and ecological systems. In this study, alumina nanoparticles were synthesized and tested for high-efficiency Cd removal from simulated groundwater. Furthermore, the synthesized alumina nanoparticles were successfully modified using negatively charged glycerol, to alleviate the challenge of its low mobility in groundwater for the Cd removal. The maximum removal efficiency of both synthesized and glycerol-modified alumina nanoparticles were more than 99%. The sorption isotherm and kinetic data of both synthesized and glycerol-modified alumina nanoparticles were best fitted to the Freundlich model and the pseudo-second-order model, respectively, indicating that the sorption of Cd ions occurs on heterogeneous surfaces of both alumina nanoparticles via the chemisorption mechanism. X-ray photoelectron spectroscopy and energy dispersive X-ray analysis revealed the presence of Cd peak in both sorbents after contact with Cd. In addition, the FTIR analyses demonstrated that hydroxyl group participated in the sorption of Cd on both synthesized and glycerol-modified alumina nanoparticles, while other glycerol associated groups contributed to the removal of Cd ions by the glycerol-modified alumina nanoparticles. It was concluded that Cd removal by synthesized and glycerol-modified alumina nanoparticles were mainly due to ion exchange and electrostatic attraction, respectively. Desorption experiment suggested that both alumina nanoparticles are effective and practically significant sorbents to remediate Cd from contaminated groundwater. However, the stronger bond between Cd and glycerol-modified alumina, plus its potential of higher mobility due to the negative charge on the surface, warrant glycerol-modified alumina nanoparticles a better performance in remediating Cd contaminated groundwater than that of the synthesized alumina nanoparticles.

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## 1. Introduction

Cadmium (Cd), one of the most toxic environmental contaminants, exposes a great threat to human health and ecosystems due to its tendency for bioaccumulation and relative mobility in the environment (Rao et al., 2010). It has been identified as one of the 10 most dangerous chemicals for public health and has also been categorized as a group 'A' human carcinogenic agent (Harbison and Johnson, 1997). Cd is widely used in electroplating, pigments, stabilizer, and batteries (Zhang et al., 2010), which are the main

sources contributing to Cd contamination in groundwater. In addition, the irrigation of Cd-contaminated water, unmanaged dumping sites, and the unsystematic use of phosphorous fertilizers are anthropogenic sources of Cd in groundwater (Hutton and Symon, 1986). Cd has been widely detected in groundwater at a broad concentration range of 13–120 µg/L (Buragohain et al., 2010; Stamatis et al., 2001), exceeding the World Health Organization (WHO) permissible limit (i.e., 3 µg/L) (WHO, 2004).

Cd can neither be degraded nor reduced. Precipitation, sorption, membrane separation, ion exchange, coagulation, floatation, and solvent extraction processes are commonly applied physico-chemical treatment techniques that have been used to remove Cd from aqueous solutions (Khairy et al., 2014; Rao et al., 2010). Among them, sorption has been found to be one of the best methods to

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remediate heavy metals from water due to its easy operation, low cost, and high efficiency (Afkhami et al., 2010; Mahdavi et al., 2015). A variety of sorbent materials have been commonly used in the sorption process to remove Cd from aqueous solutions, such as activated carbon (Mohan and Singh, 2002), agricultural wastes (Yadanaparathi et al., 2009), and zeolites (Allawzi and Al-Asheh, 2010). However, these materials require more or less complex processing steps to increase their sorption capacity. The selectivity and the low concentration sensitivity are their major challenges in Cd removal applications in groundwater remediation (Afkhami et al., 2010; Khairy et al., 2014). Therefore, researchers are seeking effective, economically viable, and environmentally friendly sorbents to remove heavy metals from aqueous solutions, especially from groundwater, which poses a challenge for the sorbent delivery in the subsurface.

Recently, using nanoparticles in the sorption process has become more attractive to many scientists because of their unique properties (Rahmani et al., 2010). Alumina nanoparticles are some of the widely studied metal oxides that can remove heavy metal ions from aqueous solutions due to their large surface area, high sorption capacity, and mechanical strength (Zhang et al., 2008a). However, previous researches on the removal of heavy metals using nano-alumina showed very low removal efficiency from aqueous solutions, e.g., less than 30% (Mahdavi et al., 2013; Poursani et al., 2015). Researchers used modifiers such as 2,4-dinitrophenylhydrazine (Afkhami et al., 2010), sodium dodecyl sulfate (SDS) (Afkhami et al., 2011), and 1,5-diphenyl carbazon (Mahdavi et al., 2015) to modify nano-alumina to remediate heavy metals, including Cd ions, from aqueous solutions. Although they increased the sorption capacity to some extent, most of the modifiers are harmful, mutagenic, and carcinogenic agents (Khan and Zareen, 2006), which significantly limit the use of modified nano-alumina in groundwater. Therefore, it is important to develop an alumina nanoparticle that not only has a high sorption capacity for Cd but also is eco-friendly.

For the first time, we explored the removal efficiency of Cd ions from simulated groundwater by the synthesized  $\gamma$ -alumina nanoparticles, following the synthesis process of nano-alumina developed by Manivasakan et al. (2009). In general, there are two key criteria for the evaluation of nanoparticle applications in the remediation of Cd contaminated groundwater: Cd removal efficiency and nanoparticle mobility in groundwater. Zhang et al. (2008b) concluded that many metal oxide nanoparticles and other inorganic nanoparticles rapidly aggregate in water, which presents a challenge for environmental engineers to implement nanoparticles in the subsurface to remediate heavy metals and other contaminants. This suggests that the mobility of synthesized alumina nanoparticles might impede their applications in groundwater remediation. Hence, to increase the mobility of alumina particles, we explored the applicability of different eco-friendly, negatively charged modifiers, such as carboxymethyl cellulose (CMC), glycerol, and humic acid, because negatively charged molecules are generally considered to be the most mobile in aquifers due to electrostatic repulsion, as most aquifer materials have a negative surface charge (Domenico and Schwartz, 1990). As glycerol-modified alumina nanoparticles provided the best Cd removal efficiency in preliminary tests, it was selected for further detailed study.

The objectives of this research are (1) to study the efficiency of both synthesized  $\gamma$ -alumina and glycerol-modified alumina nanoparticles to remediate Cd from aqueous solutions under different experimental conditions of pH, sorbent dose, contact time, and initial concentration (2) to investigate the Cd removal mechanism of both synthesized and glycerol-modified alumina nanoparticles based on sorption kinetics, isotherm, desorption experiment,

characterization of both sorbent before and after contact with Cd, and the relationship between pH of working solution and zero-point charge ( $\text{pH}_{\text{zpc}}$ ) of sorbents.

## 2. Experimental methods

### 2.1. Materials, chemicals, and analytical methods

Synthesized alumina nanoparticles was prepared in the laboratory using low cost natural bauxite and analytical grade sodium hydroxide by the sol gel technique as described by Manivasakan et al. (2009). Qi et al. (2009) reported natural bauxite as an inexpensive and environmental friendly mineral. Further, Manivasakan et al. (2009) and Poursani et al. (2015) reported that sol-gel technique is a fast, simple, convenient and low-cost technique than other techniques such as hydrothermal, microwave, and micro emulsions for the synthesis of nano-metal oxides. Further, the synthesized alumina nanoparticles were modified with negatively charged eco-friendly modifiers: CMC, humic acid, and glycerol separately in three-neck flasks with a volume of 500 mL as described by Jiemvarangkul et al. (2011). The center neck of the flask hosted a mechanical stirrer set at 60 rpm. While modifying, the weight ratio of synthesized nano-alumina to two modifiers (CMC and humic acid) was 1 to 0.1. For the modification by glycerol, 20 mL glycerol was added to a mixture consisting of 1 g synthesized alumina nanoparticles and 100 mL deionized (DI) water (resistivity  $\rho > 18.2 \text{ M}\Omega\text{cm}$ ), and was then stirred for 6 h at pH 9.5–10. The mixture was evaporated using an oven set at 50 °C and the leftovers were washed with DI water, followed by air-drying, and was stored in a sampling bag for subsequent uses. The modifiers were of analytical grade and purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China) and Aladdin Industrial Corporation (Shanghai, China), respectively.

The Cd stock solution was prepared by dissolving analytical grade  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Tingxin Chemical Factory, Shanghai, China) with DI water. Solutions of 0.1 M  $\text{HNO}_3$  and 0.1 M NaOH were used for pH adjustment. A dilute mineral salt nutrient solution (MSNS), as modified by Murphy et al. (1997), representing the dilute groundwater chemistry, was used to mimic the field conditions more closely (Song and Seagren, 2008), so as to select the efficient sorbents and to study the desorption rate. The MSNS was prepared in DI water, adding macro and trace nutrients. Macronutrients contained 0.1 mg/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 2 mg/L  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 3 mg/L  $\text{NH}_4\text{Cl}$ , and 0.6 mg/L  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ . The trace nutrients contained 5  $\mu\text{g}/\text{L}$  each of  $\text{MnCl}_2$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . The simulated Cd-contaminated groundwater was prepared using appropriate volumes of macronutrients, trace nutrients, and 200  $\mu\text{g}/\text{L}$  Cd. The solution was mixed vigorously, and the pH was maintained within a range of 6.8–7.0. All the reagents were of analytical grade, with the exception of  $\text{HNO}_3$ , which was guaranteed grade.

Cd concentrations were determined using a graphite furnace atomic absorption spectrophotometer (GFAAS) (Varian spectra AA 220Z, Varian, Palo Alto, California, USA). A pH meter (Mettler-Toledo, Ayer Rajah Crescent, Singapore) was used for pH measurements. Gas Chromatograph (Agilent 6890A, USA) was used to analyze the presence of glycerol in water solution after the sorption process.

### 2.2. Selection of sorbent

Cd removal efficiency of four different sorbents (synthesized alumina nanoparticle, CMC-modified alumina nanoparticle, humic-acid-modified alumina nanoparticle, and glycerol-modified alumina nanoparticle) were studied varying the dosage of sorbents from 0.1 to 0.7 g/L in 200  $\mu\text{g}/\text{L}$  of simulated Cd-contaminated

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