



# Roxarsone desorption from the surface of goethite by competitive anions, phosphate and hydroxide ions: Significance of the presence of metal ions



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## HIGHLIGHTS

- The presence of metal ions enhanced roxarsone adsorption on goethite surface. The effect from  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  was more pronounced.
- Based on the adsorption/desorption kinetics, phosphate displayed stronger replacement ability than hydroxide ion at any conditions has been confirmed.
- When surface was nearly completely covered, roxarsone had the highest tendency to desorb from the goethite surface.

## ARTICLE INFO

### Article history:

Received 27 November 2015

Received in revised form

15 February 2016

Accepted 27 February 2016

Available online 19 March 2016

Handling Editor: J. de Boer

### Keywords:

Roxarsone

Goethite

Adsorption

Desorption

Surface complex

## ABSTRACT

Aromatic organoarsenical roxarsone (ROX) is a common additive for livestock feed. This arsenic containing pollutant could be discharged into the environment through agricultural application of animal manure, and pose potential threats to both humans and the wider environment. In this study, the influence of pH, competing anions and metal ions on the adsorption and desorption of ROX on goethite were investigated in order to understand their mobility in the environment. Both hydroxide ions and phosphate are common substances in the environment, and both are potential competing anions for ROX. Our results showed the addition of phosphate desorbed more ROX than the addition of hydroxide ions. As pH increased, the effect of phosphate did not show much difference to that of hydroxide ion. The results indicate that the presence of phosphate will greatly increase the mobility of ROX at low pH. Six common metal ions, including  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ , were tested and all spiked metal ions enhanced the stability of ROX adsorption on the surface of goethite, and led to less desorption when phosphate was added. The results demonstrate that metal ions may form complex/surface precipitation with ROX to enhance its adsorption. The effect from  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  was more pronounced than other metal ions, which might result from the fact that these three metal ions tend to associate with hydroxide ions and decrease the pH. The results of this research may shed light on the environmental fate and transportation of aromatic organoarsenicals in soil.

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## 1. Introduction

Roxarsone, 4-hydroxy-3-nitrobenzenearsenic acid, is an organoarsenic compound that is industrially produced and is used as a feed additive in the poultry and swine industries. Roxarsone (ROX) has an arsenic acid moiety and a benzene ring in its chemical structure (Fig. S1), and therefore is called aromatic arsenic. It is used to improve feed efficiency and control coccidial intestinal parasites, and has been added to the feed eaten by broiler chickens for over

sixty years (Chapman and Johnson, 2002). The recommended ROX dosages are 25–50 ppm in poultry feed and 25–37.5 ppm in swine feed, according to the regulations regarding veterinary drugs in Taiwan. However, in the treatment of swine dysentery, up to 200 ppm of ROX is recommended for six straight days. Kerr et al. (1963) conducted a study to compare the differences between ROX treated animals and untreated ones. Although most ROX was excreted by animals through their waste, trace levels of the arsenic could still be found in the tissues. The results showed the arsenic concentration increased significantly in the liver and kidney in chicken, turkey and swine. Almost all ROX was excreted chemically unchanged in poultry waste when the birds were fed with tested

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dosages (Brown et al., 2005). The total arsenic concentration in poultry litter ranges from 15.65 mg/kg to 27 mg/kg (Pavkov and Goessler, 2001; Hancock et al., 2002; Garbarino et al., 2003; Jackson et al., 2003), implying that ROX is likely to be released into the environment when applying raw manure in agricultural fields.

During the process of composting, ROX can degrade into other arsenic species due to the actions of microorganisms or photolytic reactions. Several studies revealed that possible degradation products of ROX are arsenite ( $\text{AsO}_3^{3-}$ ), arsenate ( $\text{AsO}_4^{3-}$ ), methylarsonic acid (MMA), and dimethylarsinic acid (DMA) (Bednar et al., 2003; Garbarino et al., 2003). These arsenic species are very much water soluble, and thus the runoff from such agriculture areas may carry these pollutants throughout the land or aquatic environment. Inorganic arsenics have been recognized as environmental carcinogens (Jomova et al., 2011), and the European Union has banned arsenic additives in poultry feed since 1999 (99/29/1999). In addition, Pfizer voluntarily suspended the sale of ROX to the U.S. livestock industry (FDA Press Announcements). However, ROX has also been approved for wide use in many other countries around the world, including India, China as well as Taiwan. According to the Taiwan agricultural statistics yearbook, around 9 million pigs and 1.1 billion chickens are raised annually in Taiwan. After excretion, the animal litter and manure from the farms are often used as fertilizer due to their nutrient value. However, an increasing concentration of ROX in soil has been shown to reduce rice production significantly (Liu et al., 2009). It is also reported that arsenic accumulates in plant tissues, with the levels of arsenic following, from high to low, the order of root, stem, leaf, husk, and grain (Liu et al., 2009). ROX in rice or garden vegetables may pose a potential risk to human health by entering the food chain. Studies have shown that ROX can be leached easily from poultry litter to groundwater and rivers (Jackson and Miller, 1999; Rutherford et al., 2003). Brown et al. (2005) sampled the soil in the Shenandoah Valley of Virginia, USA, an area with dense poultry production, and the results of batch experiments indicated that ROX exhibited weak adsorption to the Ap horizon; in addition, it rapidly biotransformed to As(V) in this soil horizon, whereas strong adsorption of ROX was shown in the Bt horizon.

Iron oxides are very stable minerals and commonly exist in soil. Many studies report that iron oxides have a high affinity for arsenic species in water. Arsenic forms inner-sphere complexes with iron oxides, including monodentate, mononuclear bidentate and binuclear bidentate complexes (Hiemstra and Van Riemsdijk, 1996). Arsenate adsorbs mainly as the bidentate complex when a high surface loading is applied, while the binuclear bidentate complex is more stable than the mononuclear bidentate complex (Hiemstra and Van Riemsdijk, 1996). Arts et al. (2013) studied the surface interactions between ROX/p-arsanilic acid (ASA) and hematite nanoparticles with attenuated total internal reflectance spectroscopy (ATR-FTIR). The results showed that aromatic arsenics adsorbed slower than inorganic arsenic and the surface complexes between arsenic-containing compounds and iron oxides were more than one type. The adsorption of arsenate on the surface of iron oxide is influenced by several environmental factors, such as pH, ionic strength, competing ions, and charges to the iron oxide surface. Arsenate had high adsorption at a low pH of 4.6, and this decreased significantly at pH 7 to 11 (Raven et al., 1998). The same adsorption tendency was also observed in ROX and ASA (Chen and Huang, 2012). Arsenate has similar chemical properties as phosphate, and the pKa values of both anions are almost same. At high surface loading the main complexation forms of arsenate and phosphate are bidentate, because under this condition bidentate species load more charges at the surface than monodentate ones, allowing a lower electrostatic repulsion between the adsorbed

species in the 1-plane. Phosphate is thus a common competing ion for arsenic species on mineral surfaces. Chen and Huang (2012) studied the influence of phosphate on the adsorption behavior of ROX and p-arsanilic acid (ASA), and the results showed that the adsorption reactions of ROX and ASA on the surfaces of iron and aluminum oxide were significantly interfered by phosphate. Similar results were also observed by Antelo et al. (2005), which reported that phosphate can rapidly displace the adsorbed organoarsenic from metal oxides. Besides soil minerals, the adsorption of ROX on  $\text{TiO}_2$  was examined, and results showed the photocatalytic decomposition of ROX under UV/ $\text{TiO}_2$  could cause the cleavage of the As–C bond, and that inorganic arsenic was formed (Lu et al., 2014). With advances in nanotechnology, some studies on adsorption of ROX by carbon nanotubes have recently emerged (Hu et al., 2014). However, this technology is currently limited to wastewater treatment.

To date, most related studies mainly discuss the influence of anions on the surface interactions of ROX on iron oxides, because ROX is negatively charged. However, cations are abundant in the environment, and their effects on ROX's mobility have not been discussed. This study thus aims to investigate the influence of cations on the surface interactions of ROX on goethite. Few studies can be found that examine how the adsorption behaviors of ROX, as well as other arsenic compounds, are influenced by metal ions, such as  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ . In this study we investigated the adsorption reactions of ROX on goethite in the presence of metal ions, and the desorption reactions of competing anions. This study compared the desorption ability of competing anions, such as phosphate and hydroxide, which commonly exist in the environment, and investigated the influence of divalent metal ions on the surface interactions of ROX on goethite, in order to understand how ROX transports in the environment. It is anticipated that the results of this study can help develop methods for controlling and predicting the environmental mobility of ROX.

## 2. Materials and experimental set-up

### 2.1. Materials

Reagent grade water was prepared with Millipore Nanopure water-purification system. ROX was from Sigma-Aldrich with a purity of 98%, and other chemicals were obtained from Sigma-Aldrich and the J.T. Baker company. Metal chloride salts were used for the experiments to examine the effects of metal ions. Throughout the experiment, pH was adjusted by addition of NaOH or HCl. Goethite was the adsorbent in the adsorption and desorption experiments, and was synthesized in an acid system based on the procedure reported by Schwertmann and Cornell (2008). First, 56.6 g  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was dissolved in 70 mL 2 M  $\text{HNO}_3$ , and then diluted with Nanopure water to 280 mL with vigorous stirring. The stable solution was dark brown, and the yellow goethite started to precipitate on the bottom after 3 days. Goethite precipitates were dialyzed in cellulose tubing using Nanopure water changed twice daily until the resistance was greater than 18.2 M $\Omega$  cm. The surface specific area of the synthesized goethite was 92.3 m<sup>2</sup>/g, the mean pore diameter was 21.3 nm, and the total pore volume was 0.4927 cm<sup>3</sup>/g, as measured by  $\text{N}_2$  Brunauer-Emmett-Teller (BET) analysis. The zero-point-of-charge ( $\text{pH}_{\text{zpc}}$ ) of the prepared goethite was previously reported as pH 8.6 (Chen and Huang, 2012). The crystal structure analysis of the synthesized goethite was carried out using X-ray diffraction (XRD) on a Rigaku D/Max-IIIa diffractometer with Ni-filtered  $\text{CuK}\alpha$  radiation at 30 kV and 20 mA.

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