



Adsorption of aromatic organoarsenic compounds by ferric and manganese binary oxide and description of the associated mechanism



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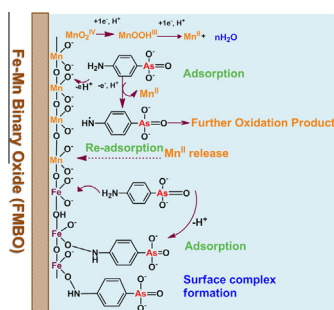
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HIGHLIGHTS

- FMBO shows higher removal capacity towards p-ASA and ROX than FeOOH and MnO₂.
- Adsorption of p-ASA and ROX onto FMBO, FeOOH, and MnO₂ is more favorable at pH 4.0.
- Heterogeneous oxidation involves in the adsorption of p-ASA onto FMBO and MnO₂.
- The synergism of Fe- and Mn-oxide dominates the high adsorption capacity of FMBO.

GRAPHICAL ABSTRACT



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ABSTRACT

The aromatic organoarsenic compounds including p-arsanilic acid (p-ASA) and roxarsone (ROX) used as feed additives in the poultry appear to be excreted with no chemical structural change, tending to environmental release of inorganic arsenic. Thus, effective removal and understanding the mechanism of organoarsenic compounds are of significant urgency. We herein investigated the interactions of organoarsenic compounds with ferric and manganese binary oxide (FMBO) to investigate their adsorption efficiency and mechanism, whereas ferric oxide (FeOOH), and manganese oxide (MnO₂) were also studied for the comparison. The maximum adsorption capacities (Q_{max}) of FMBO towards p-ASA and ROX were determined to be 0.52 and 0.25 mmol g⁻¹ (pH = 7.5). FeOOH and MnO₂ showed lower adsorption capability, the responsive Q_{max} , p-ASA were 0.40 and 0.33 mmol g⁻¹ and Q_{max} , ROX were 0.08 and 0.07 mmol g⁻¹, respectively. The elevated pH inhibited the adsorption onto the adsorbents owing to the increased repulsive forces; the Q_{max} , p-ASA and Q_{max} , ROX onto FMBO increased to 0.79 and 0.51 mmol g⁻¹ at pH 4.0. Based on results of UV–vis spectra, UPLC-ICP-MS, FTIR, and XPS, the synergistic effect of heterogeneous oxidation and adsorption was the core for efficient aqueous removal of p-ASA by FMBO. Manganese oxide showed significant oxidation of p-ASA, while adsorption process was observed in ferric oxide and this effect also involves in the adsorption of ROX. Results herein extended the knowledgebase on organoarsenic species adsorption to Fe/Mn oxides, are important for potential engineering treatment application and help us to understand reactions at the interfacial level.

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1. Introduction

Aromatic organoarsenic, e.g., 4-aminophenylarsonic acid (para-arsanilic acid, p-ASA) and 4-hydroxy-3-nitrophenylarsonic acid

(Roxarsone, ROX), are widely used as feed additives of broiler chickens to control coccidial intestinal parasites, improve feed efficiency, stimulate rapid growth, and improve pigmentation [1,2]. The arsenic content in poultry manure is as high as over 40 mg kg⁻¹ [3]. The use of poultry litter as organic fertilizer transfers from 'point' to 'non-point' source pollution, and increases the risk of organoarsenic contamination towards soils and groundwater accordingly [4]. Upon entering environments, organoarsenic tends to transform into more mobile toxic inorganic arsenite [As(III)] and arsenate [As(V)] by microbial activities [1,5,6]. The removal of organoarsenic prior to its entering environments is of crucial importance to control their environmental risk.

Adsorption exhibits the advantageous of simple operation, high efficiency, low cost, and is practically valuable for organoarsenic removal [7]. Many adsorbents have been developed for the removal of inorganic arsenic such as multi-wall carbon nanotubes (MWCNTs) [8], biosorbent (scales of *Cyprinus carpio*) [9], zeolitic imidazolate frameworks [10], copper impregnated natural mineral tufa [11], and ferrihydrite [12]. However, the adsorbents for organoarsenic removal are relatively rare. There have been reported several adsorbents, i.e., birnessite [13], mesoporous zeolitic imidazolate framework-8 [14], metal-organic frameworks [15], MWCNTs [16,17], chitosan-based copolymers [18], iron and aluminum oxides [19], and titanium oxides [20] for the removal of organoarsenic (Table S1). However, their practical application is limited due to the difficulty in large scale production. Previous studies in our research group using ferric and manganese binary oxide (FMBO), for arsenic(III) removal revealed interesting results and led to development of engineering applications [21]. This result inspired us the effectively converted the chemical structure of the organoarsenic was conducive to entire removal process. In FMBO, manganese (Mn) oxide shows oxidative and adsorptive capacities towards aromatic amines [22]. Then, the low cost iron oxides have been exhibited the good adsorption performances towards aromatic organoarsenic [23]. Thus, we speculated if the same synergistic effects of mixed Mn(IV)/Fe(III) oxide could provide similar adsorption capacity for organoarsenic species.

In this study, we selected two aromatic organoarsenic compounds of p-ASA and ROX with different reductive dissolution effect, investigated removal efficiency of FMBO, and adsorption mechanism. The macroscopic adsorption experiments such as adsorption kinetics, adsorption isotherms, and pH effects were conducted. After that, removal mechanisms of organoarsenic compound on the interfacial of FMBO were analyzed by UV-vis scan, UPLC-ICP-MS, and microscopic characterization techniques such as FTIR and X-ray photoelectron spectroscopy (XPS). Finally, the dominant interfacial reactions involved in the adsorption of p-ASA and ROX onto the adsorbents were proposed accordingly.

2. Experiments

2.1. Materials and analysis methods

The p-ASA (>98%) and ROX (>98%) were respectively purchased from TCI Chemicals Co. and Sinopharm Chemical Reagent Co. Table 1 illustrates their dominant physicochemical characteristics and their species distribution over a wide pH range. All other analytical grade chemicals were purchased from Beijing Chemical Co. The stock solutions of p-ASA and ROX (15 mmol L⁻¹) and working solutions of different concentrations were prepared using Milli-Q deionized water (18.2 MΩ-cm). FMBO with different Fe/Mn molar ratios were prepared at room temperature, among of which the ratio of 3:1 was the optimal one. The preparation of FMBO, FeOOH, and MnO₂ followed the methods as described in previous studies

[21,24,25], and the detailed procedures are illustrated in the supporting information (Text S1).

2.2. Adsorption experiments

Sodium perchlorate (NaClO₄·H₂O) at 0.01 M was used to maintain the background ionic strength. pH was adjusted during adsorption using 0.1 M NaOH and 0.1 M HNO₃ to achieve pH variation in the range of ±0.1. All the batch experiments were proceeded in triplicate at the same time. Blank control experiments without the addition of adsorbents confirmed that no adsorption occurred on the glass vial wall. Control experiments only adsorbents without p-ASA/ROX indicated that no loss of Fe and Mn from adsorbents.

In adsorption kinetic experiments, the initial concentrations of p-ASA ([p-ASA]₀) and ROX ([ROX]₀) were 0.15 mmol L⁻¹, and adsorbents doses were 0.2 g L⁻¹. Batch adsorption experiments were conducted in a beaker with magnetic stirrer (350 rev min⁻¹) at pH 7.5 ± 0.1 in room temperature. Aliquots (~5 mL) were taken from the suspension at different time intervals of 0.016, 0.08, 0.25, 0.5, 1.0, 1.5, 2.0, 3.0, 5.0, 8.0, 13.0, 23.0, 37.0, 55.0, and 79.0 h. The adsorbent capacity (q_t) was calculated according to Eq. (1) as follows:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where q_t is adsorption capacity in mmol g⁻¹, C₀ and C_t are the concentrations of p-ASA and ROX (mmol L⁻¹) before and after adsorption, m is the amount of the adsorbent used (g), and V is the volume of the initial solution (L).

The removal rate (%) was calculated according to Eq. (2):

$$\text{Removal \%} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where C₀ is the initial concentrations of the p-ASA and ROX and C_e are the final concentration of p-ASA and ROX, respectively.

In adsorption isotherms experiments, the concentrations of [p-ASA]₀ and [ROX]₀ were in the range from 0.02 to 1.0 mmol L⁻¹ with the adsorbents doses of 0.25 g L⁻¹. Adsorption experiments were conducted in 50 mL polypropylene tubes with 40 mL solution at pH 7.5 ± 0.1, and the tubes were kept on an end-over-end shaker set at 40 rpm for 24.0 h in room temperature to achieve equilibrium. To investigate the effects of pH on adsorption, similar procedures were used except that initial pH was adjusted to desired values from 4.0 to 9.0 prior to the addition of adsorbents.

The equilibrium uptake (q_e, mmol g⁻¹) of an adsorbent towards an adsorbate is calculated using Eq. (3).

$$q_e = \left[\frac{(C_0 - C_e)XV}{M} \right] \quad (3)$$

where C₀ is the initial concentration (M) of the adsorbate, C_e is the equilibrium concentration (M) of the adsorbate, V is the volume (L) of the adsorbate, and M (g) is dosage level of the adsorbent employed.

2.3. Characterization and analytical methods

The powder X-ray diffraction patterns (XRD) of FMBO, FeOOH, and MnO₂ were determined using an X'Pert 3040-PRO Powder diffractometer machine (PANalytical Co.). Data were collected at 40 keV using a graphite curved crystal monochromator between 10° and 90° 2θ in 0.02° steps. The specific surface area (S_{BET}), pore volume, and pore size distribution were measured by nitrogen adsorption method with a Micrometrics ASAP 2020 HD88 surface area analyzer (Micrometrics Co. USA). The morphology of the adsorbents was observed under scanning electron microscope

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