

Assessment of Arsenic Concentration, Speciation and Bonding Mode by Oxalate Extraction

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INTRODUCTION

Chemical extraction is an important tool for understanding arsenic (As) mobilization potential and speciation in soils, as well as for assessment and management of arsenic-contaminated sites. A commonly used extractant for assessment of arsenic is pH 3.0 ammonium oxalate (in the dark), which has been used to assess soil arsenic. In spite of its wide use, questions remain regarding the factors impacting results by this method. The objectives of this study were to evaluate (i) the influences of reaction time, light, pH, and the presence of CaCO₃ on As^{III} and As^V desorption by ammonium oxalate, and (ii) the desorption behavior of As from crystalline and amorphous Fe oxide and from soils.

METHODS AND MATERIALS

Goethite and 2-line ferrihydrite were synthesized by the methods outlined by Schwertmann and Cornell (1991). The soils utilized in the current study were 472 soils collected from 1-15 cm depth from *boro* rice paddies from Brahmanbaria, Faridpur, Paba, Senbag and Tala *thanas* in Bangladesh.

Desorption envelopes of Fe oxides were conducted by first adsorbing As^{III} or As^V to ferrihydrite (0.02 As: Fe molar ratio) or goethite (0.001 As:Fe molar ratio) in bulk at pH 7.0. Desorption was accomplished in batch by adding 0.2 M NH₄-oxalate or 0.1M Na-oxalate (final concentration) preadjusted to the desired pH between 1 and 9. Desorption envelopes were performed in light and dark conditions to determine the influence of light on As extraction and speciation. Samples were extracted for times ranging from 15 min to 48 h to evaluate reaction kinetics. Following the desired reaction time, samples were centrifuged and filtered through μ -pore filters (0.2 μ m) and pH of the filtrate was determined.

As^{III} and total As concentrations of extracts were determined by pH-selective hydride-generation flame-atomic-absorption spectroscopy (HG-AAS). Total soil As was determined following open-vessel digestion with HNO₃/HF. Total free Fe-oxide and poorly crystalline Fe-oxide contents of soils were determined by pH 3.0, 0.2 M ammonium-oxalate (in the dark) extraction (AOE) and citrate-dithionite extraction (CDE), respectively (Loeppert and Inskeep, 1996).

RESULTS AND DISCUSSION

Extraction of Arsenic from Fe Oxides

Extractions of As^{III} and As^V from ferrihydrite approached quantitative levels at pH 3.0 in the dark with 2 h extractions (Fig. 1A), but desorption decreased with increasing pH. Dissolution of Fe at pH 3.0 also approached quantitative levels, indicating that release of As at pH 3.0 was attributable to the dissolution of ferrihydrite at pH 3.0. In the dark, there was no appreciable transformation of As^{III} to As^V, compared to the extraction under laboratory light in which oxidation of As^{III} to As^V was appreciable. The transformation of As^{III} to As^V is attributable to the photocatalyzed oxidation of As^{III} in the presence of oxalate. There was no evidence of a photocatalyzed reduction of As^V to As^{III}. These results indicate that extraction in the dark, but not in the light, might be suitable for speciation of inorganic As^{III} / As^V,

There was no appreciable desorption (< 6 %) of As^V from goethite across the entire experimental pH range of pH 2 to 9 in the dark; at pH ≥ 5, desorption of As^V was negligible (Figure 1B). As^{III} exhibited a very different desorption behavior under similar conditions, i.e., As^{III} desorption approached quantitative levels at pH 2-3 and decreased to negligible values at pH ≥ 6 (Figure 1B). In all cases, Fe dissolution was negligible, indicating that in the dark, As was released by a ligand-exchange reaction rather than by a ligand-enhanced dissolution reaction. In the light, dissolution of goethite and release of As^V was appreciable, indicating a photocatalyzed ligand-enhanced dissolution reaction. The relative ease of release of As^{III} compared to As^V at pH 3 from goethite in the dark indicates different predominant adsorption mechanisms for As^{III} versus As^V. With As^V, there was an initial rapid rate of As release that is attributable to either a small proportion of loosely adsorbed As^{III} that was readily released from goethite or a trace of ferrihydrite in the sample from which As^{III} was readily released. This initial reaction was followed by a relatively slow rate of release of As^V that is attributable to tightly bound As^V on goethite.

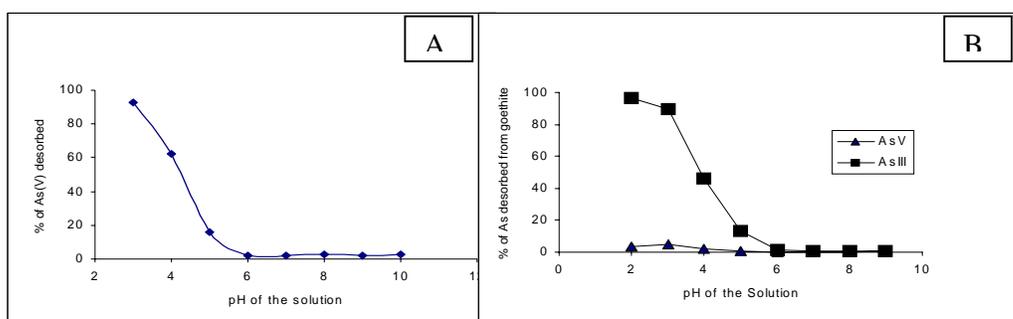


Fig. 1. Desorption envelopes for (A) As^V on ferrihydrite, and (B) As^V and As^{III} on goethite by pH 3, 0.2M ammonium oxalate, at Fe concentration of 0.5 g L⁻¹ and As concentration of 15 mg L⁻¹ for ferrihydrite and 1.5 mg L⁻¹ for goethite.

Assessment of As in Bangladesh Soils

Of the 472 soils of the Bangladesh rice-paddy soils, ammonium-oxalate extractable Fe represented a median of 28 % of the Fe-oxide Fe, which indicates that a significant proportion of the Fe oxide of these soils was poorly crystalline. In these air-dried rice paddy soils, the ammonium-oxalate extract contained predominantly As^V; only traces of As^{III} were detected. The oxalate-extractable As represented a median of 62 % of the total soil arsenic, which indicates the importance of poorly crystalline Fe oxide versus well crystalline Fe oxide in retention of arsenic by the Bangladesh paddy soils.

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