論文の内容の要旨
Abstract of Dissertation

論文題目　**Microbiological transformation of arsenic in a drinking water treatment process in Bangladesh**

(バングラデシュの浄水装置における微生物によるヒ素の溶出に関する研究)

氏　　名　コンドカール　マフブブ　ハサン

（本文）**(Abstract)**

Arsenic, one of the world's most hazardous chemicals is found to exist within the shallow zones of groundwater of many countries like Argentina, Bangladesh, Cambodia, Canada, Chile, China, Germany, Hungary, India, Mexico, Mongolia, Myanmar, Nepal, Pakistan, Romania, Thailand, USA, Vietnam, etc. in various concentrations. Arsenic contamination in water has posed severe health problems around the world. Considering the lethal impact of arsenic on human health, environmental authorities have taken a more stringent attitude towards the presence of arsenic in water. As the diagnosis and medication of the arsenic related diseases are difficult, the treatment of contaminated water as a preventive measure appears to be an effective alternative to combat arsenic poisoning. Based on the established biological iron oxidation from groundwater, arsenic removal by adsorption and co-precipitation onto the flocs of iron hydroxides and subsequent sand filtration has become a very popular technique. Adopting this technique, a large number of arsenic and iron removal units (AIRU) were installed in various levels of household, community and municipality in many regions.

Organic matter greatly influences the mobility of arsenic in aqueous environments through both chemical and biological processes. The ligand exchange surface complexation mechanism for organic matter sorption to metal hydroxides is similar to that proposed for the sorption of arsenic. Therefore, organic matter tends to compete with arsenic for adsorption to the solid surfaces. Moreover, the aqueous organic-metal complexes may, in turn, associate strongly with dissolved arsenic anions, presumably by metal-bridging mechanisms, diminishing the tendencies of such anions to form surface complexes. Because organic matter is not only potentially reactive toward arsenic but also ubiquitous in natural waters, its potential influence on arsenic sorption and mobility is great. Nevertheless, microbial activity can greatly affect the mobilization of arsenic under anaerobic conditions by either an indirect or a direct mechanism. The former is the reductive dissolution of iron hydroxide minerals, leading to the release of associated arsenic into solution. The latter is the direct reduction of arsenate associated with a solid phase to the less

adsorptive arsenite. This biotransformation reaction is energetically favorable when coupled with the oxidation of organic matter, because the As(V)/As(III) oxidation/reduction potential is +135 mV. Organic matter, present in groundwater and from unsanitary operation and maintenance of the treatment unit, is a potential source to influence the arsenic removal process. In this study, the effect of organic matter on the arsenic and iron removal performances in the AIRU treatment process has been elucidated.

The specific objectives of this study were to (1) elucidate the influence of organic matter on the sorption process of arsenic onto iron hydroxide solid phase in the AIRU treatment process; (2) investigate the bioleaching potentials of arsenic from the pre-sorbed surface complexes in the accumulated sludge in filter bed; (3) model development on the removal and bioleaching of arsenic in response to organic contamination; and (4) look into the biofilm structure related to the oxygen penetration as well as the bioleaching of arsenic and iron from the settled sludge in the AIRU.

In order to presume the level of organic matter contamination and the treatment performance in field AIRUs, a pilot experiment was carried out in arsenic contaminated groundwater areas of Jessore district in Bangladesh. The influent raw groundwater in four AIRUs, out of six, was found to have high concentrations of total organic carbon (TOC), 15.8 ~ 23.8 mg/L. In these cases, the arsenic removal efficiency was found to be significantly less and the effluent arsenic concentrations, greater than 50 μg/L, beyond the acceptable limit of drinking water standards in Bangladesh. A precise and large-scale spatial survey was required to represent the real field situation of the above aspect. Considering the requirements of resources and time related to the precise field survey and the potential human health-risk related to the organic contamination in AIRUs, laboratory experiments were carried out using artificial contaminated groundwater in the simulated AIRU. Laboratory-scale AIRU was developed and tested under variable environmental conditions. The AIRU was operated in both the "continuous flow" and the "intermittent flow" modes, as per usual practice at the field level.

In the continuous flow mode of the AIRU, it was observed that the arsenic removal efficiency was negatively impacted even in the presence of a low concentration of organic matter, 5 mg/L as TOC, and gradually deteriorated with higher concentrations. In comparison to the humic acid, the simulated wastewater organic matter was found to be more worsening to the arsenic removal process. However, the effluent iron concentration was found to be higher in case of the humic acid contamination. The autoclaved examination showed similar results. Thus, the organic matter contamination in the AIRU impeded the sorption capacity of arsenic onto iron hydroxides solid phase and consequently a high concentration of arsenic was observed with the effluent water.

In course of the biodegradation process of organic matter, in the intermittent flow mode of the AIRU and under the nonoperational stagnant condition, an anaerobic condition was noticed within the accumulated sludge in the filter bed. In anaerobic condition, high concentration of effluent arsenic, over 100 μg/L, was observed due to microbial activity. However, the effluent iron concentration was not worth mentioning and found to be less than 0.15 mg/L. While collecting the effluents from the AIRU, the aqueous ferrous iron, reduced in the bioleaching process, re-oxidized to insoluble ferric form due to the intrusion of supernatant aerobic water within the sand filter bed and hence caused the re-adsorption of As(V) to some extent. Thus, the decomposition of organic matter due to the microbial action led to an anaerobic condition within the accumulated sludge in the AIRU and hence caused the bioleaching of arsenic.

Mathematical models were developed addressing the chemical and biological consequences of the organic matter contamination on the AIRU treatment process. A modified Langmuir-like model was employed for the competitive binary adsorption of arsenic and organic matter in the AIRU treatment process. The model for the bioleaching of arsenic was developed using the kinetic reactions for sequential terminal electron acceptors in the biodegradation of organic matter. Calibrations of the models were performed using batch experiments and finally the results obtained from the laboratory experiments were used to test the performance of the developed models.

Special biofilm study was carried out related to the oxygen penetration and hence the bioleaching of arsenic from the settled sludge in the AIRU. Oxygen penetration was found to vary with the structure of the biofilm and an anaerobic condition was noticed at the bottom part, which caused the bioleaching of both As(V) and As(III) in the associated bulk liquid phase. The iron concentration in the bulk liquid was found to be less than 0.2 mg/L throughout the whole observation period. Thus, the biofilm structure related to the oxygen penetration, which is critical to the oxidation/reduction reactions of aerobic respiration, had significant influence on the bioleaching of arsenic from the settled sludge in the AIRU.

The geochemical and the biological importance of organic matter interactions for the arsenic sorption and mobility are great. This study revealed several consistent phenomena regarding the consequence of organic matter contamination on the arsenic and iron removal performances in AIRU treatment process. Nevertheless, these basic observations suggest that organic matter would have a sufficiently important influence on arsenic mobility to warrant its consideration in designing safe remediation strategies in the context of arsenic and iron removal process for drinking water.