

Sustainable Remediation Materials for Toxic-Metal Removal: Insights into Arsenic and Chromium Detoxification Mechanisms

Heavy metal remediation is achieved using an environmentally sustainable approach that involves thiol-functionalized black carbon and thermoacidophilic Cyanidiales.

The remediation of toxic metals, such as chromium (Cr) and arsenic (As), is vital for public health and ecological balance. The 2024 studies at the NSRRC explores the advanced materials and biological pathways for hexavalent Cr(VI) and arsenite [As(III)] removal. Utilizing synchrotron-based techniques, the research highlights thiol-functionalized black carbon for Cr(VI) remediation and thermoacidophilic Cyanidiales for As(III) detoxification, offering effective and sustainable solutions through materials science and bioremediation advancements.

Thiol-Functionalized Black Carbon as Effective and Economical Materials for Cr(VI) Removal:

Hazardous Cr(VI) continues to raise critical environmental and public health concerns, necessitating the development of effective remediation methods. Yu-Ting Liu (National Chung Hsing University) and her collaborators recently discovered the removal mechanisms of Cr(VI) by modifying black carbon (BC), which is synthesized from rice straw residue and contains thiol groups. This is the first study that alters BC with thiol groups to target Cr(VI) removal. Here, the designated samples were evaluated: i) BC and ii) thiol-functionalized black carbon (S-BC) with BC/thioglycolic acid ratios (g mL^{-1}) of 1:20 (S-BC20), 1:30 (S-BC30), and 1:40 (S-BC40).

The research team conducted X-ray absorption spectroscopy (XAS) at TLS 17C1 and TPS 44A to determine the related Cr speciation on solid samples.

The results revealed that Cr species on solid samples primarily transformed from Cr(VI) to Cr(III), as shown in Fig. 1. At pH 3.5, over 86.2% of Cr(VI) was reduced to Cr(III), with S-BC retaining only 4.1–6.8% Cr(VI) compared to 13.8% for BC. At pH 5.5, all Cr(VI) was converted to Cr(III) on both materials. Finally, at pH 7.5, S-BC retained no Cr(VI), while BC retained 13.2% Cr(VI).

Sorption isotherms confirmed that S-BC40 demonstrated high Cr(VI) sorption capacities—201.2, 145.8, and 106.6 mg g^{-1} at pH 3.5, 5.5, and 7.5—exceeding BC sorption capacities by 2.0–2.3 times. Notably, S-BC40 converted all sorbed Cr into Cr(III) at $\text{pH} \geq 5.5$, forming $\text{Cr}(\text{OH})_3$ and organic Cr(III) complexes. These findings highlight thiol functionalization as a promising strategy for effective Cr(VI) remediation and waste reutilization.

Accumulation and Bio-Oxidation of Arsenite Mediated by Thermoacidophilic Cyanidiales:

As contamination from geogenic and anthropogenic sources poses a critical

environmental and public health threat due to the high toxicity and mobility of As(III). Liu and her team unveiled the molecular mechanisms of As(III) removal by thermoacidophilic microalga Cyanidiales. This red alga, thriving in acidic, metal-rich environments, exhibits unique detoxification characteristics ideal for As remediation. This pioneering study evaluated As(III) removal by *Cyanidium caldarium* (Cc) and *Galdieria partita* (Gp) across a pH range of 2.0–7.0.

The team employed transmission X-ray microscopy (TXM) at TLS 01B1 to reveal the related As distribution on Cyanidiales, as shown in Fig. 2 (see next page). 3D tomography revealed that As present on Cc was distributed both near their surface and internally, particularly at pH 5.0, which suggests intracellular tolerance mechanisms. In contrast, Gp relied on surface-level As immobilization. These findings indicate that Cc is more resilient to As stress, particularly at $\text{pH} \leq 5.0$ due to its superior intracellular detoxification capacity.

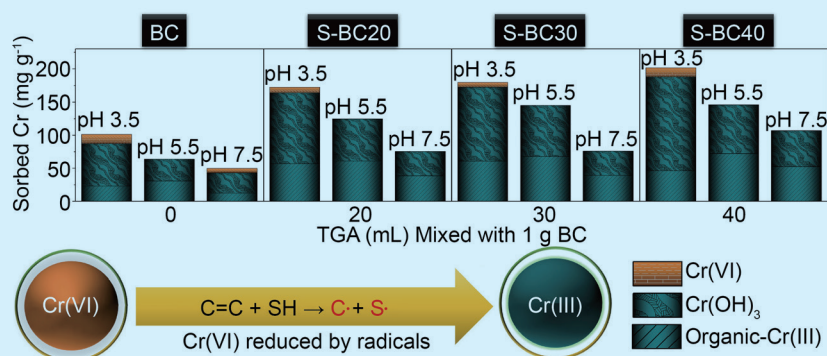


Fig. 1: Proposed removal mechanisms for Cr(VI) by thiol-functionalized black carbon. [Reproduced from Ref. 1]

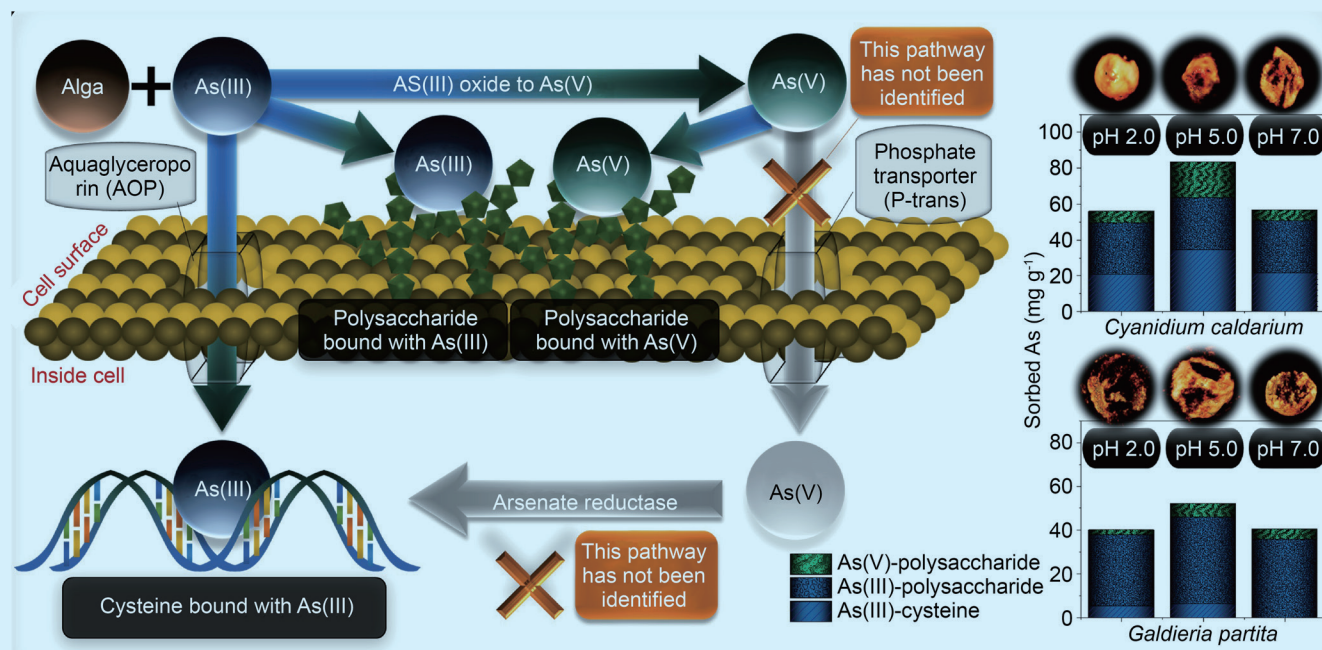


Fig. 2: Proposed mechanisms for As(III) removal by Cyanidiales. [Reproduced from Ref. 2]

The team conducted XAS analysis at **TLS 17C1** and **TPS 44A** to determine the related As speciation on Cyanidiales. As species were identified as arsenate [As(V)]-polysaccharide, As(III)-polysaccharide, and As(III)-cysteine, as illustrated in Fig. 2. At pH 5.0, Cc showed the highest sorption capacity that was dominated by As(III)-cysteine, while Gp retained mainly As(III)-polysaccharide. At pH 2.0 and 7.0, Cc exhibited balanced As(III)-polysaccharide and As(III)-cysteine with minimal As(V). These results highlight Cyanidiales' reliance on surface complexation and intracellular sequestration, with Cc exhibiting superior detoxification capacity.

To study As interactions in Cyanidiales, the team conducted synchrotron-based Fourier transform infrared spectroscopy at **TLS 14A1** to examine the changes in functional groups and protein secondary structures under As(III) exposure. The results show that α -helix/ β -strand ratios correlated with sorbed As levels. However, Gp exhibited a negative correlation between α -helix/ β -strand ratios and sorbed As levels, indicating structural fragility. In contrast, Cc displayed positive correlations at pH $\leq$ 5.0, reflecting strong protein

adaptation. Notably, Cc exhibited fewer unordered structures, suggesting intracellular protein proliferation as a key response to As toxicity, further highlighting its superior resilience.

Cc demonstrated superior sorption capacity, achieving 83.2 mg g⁻¹ at pH 5.0. Cc outperformed Gp across all tested conditions, driven by mechanisms such as As(III) oxidation, surface complexation with polysaccharides, and intracellular formation of As(III)-cysteine complexes, as shown in Fig. 2. These findings highlight Cyanidiales' ability to transform and immobilize As, paving the way for innovative and effective detoxification strategies.

In summary, this report showcases two sustainable approaches for heavy-metal remediation: i) thiol-functionalized BC for Cr(VI) removal and ii) thermoacidophilic Cyanidiales for As(III) removal. Leveraging NSRRC's synchrotron-based techniques, both methods demonstrated high levels of toxic-metal removal, offering promising solutions to environmental contamination. (Reported by Yen-Lin Cho, National Sun Yat-sen University, and Kamonchanok Huangmee, National Chung Hsing University)

This report features the work of Yu-Ting Liu and her collaborators published in *J. Environ. Manage.* **360**, 121074 (2024) and *Bioresource Technol.* **406**, 130912 (2024).

TPS 44A Quick-scanning X-ray Absorption Spectroscopy
TLS 01B1 X-ray Microscopy
TLS 14A1 IR Microscopy
TLS 17C1 EXAFS

- TXM, FT-IR, EXAFS, XAS
- Environmental and Earth Sciences, Biological Science, Chemistry

References

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2. Y.-L. Cho, Y.-M. Tzou, A. Assakinah, N.A.T. Than, H. S. Yoon, S.I. Park, C.-C. Wang, Y.-C. Lee, L.-C. Hsu, P.-Y. Huang, S.-L. Liu, Y.-T. Liu, *Bioresource Technol.* **406**, 130912 (2024).