論　文　の　要　旨

題　目　Efficient Removal of Arsenic and Chromium from Water by Polymer Hydrogel Adsorbents
（高分子ゲル吸着剤を使用した水からのヒ素とクロムの効率的除去）

氏　名　　宋　玉

Heavy metal ions, especially arsenic (As) and chromium (Cr), pose a substantial threat to human health and ecosystem. To deal with this issue, various techniques for removing heavy metal ions from wastewater have been developed, including chemical precipitation, ion exchange, membrane separation, and notably, adsorption technologies. Adsorption stands out for its operational simplicity, cost-effectiveness, and the potential for using low-cost, high-efficiency, and easily regenerable adsorbent materials.

Among the adsorbents, hydrogels are particularly notable. Hydrogels boast high water content, adjustable swelling properties, superior mechanical performance, and the ease of modification. Their primary roles in water treatment include: (1) Maintain structural integrity like solid substances, (2) providing nanoscale channels for the unhindered diffusion of small, water-soluble molecules, and (3) offering additional active sites through hydrogen bonding, enhancing the interaction with water-soluble molecules. Therefore, This research focuses on the development of cost-effective and highly efficient removal methods and change the existence state of adsorbates in the aqueous environment for heavy metal ions removal.

This research addresses several critical concerns: (1) Trivalent arsenic predominantly exists as arsenous acid molecules in acidic and neutral water environments, posing challenges for its removal, in contrast to pentavalent arsenic, which primarily exists in anionic form above pH 2, rendering it more amenable to extraction; (2) Hexavalent chromium, apart from being highly toxic, is susceptible to remobilization under varying physicochemical conditions, thus exhibiting pronounced mobility, unlike trivalent chromium, whose toxicity is a mere fraction (one percent) of its hexavalent counterpart and which is more readily immobilized; (3) Although the toxicity levels of pentavalent arsenic and trivalent chromium are markedly lower than those of trivalent arsenic and hexavalent chromium, their coexistence and the concurrent removal of anions and cations significantly challenge the efficacy of adsorbent materials. Therefore, Functionalizing hydrogels with suitable functional groups or modifying the state of the adsorbates to enhance the effective removal for heavy metal ion adsorption is the research purpose.

In response to the insights and issues from previous research and several critical concerns, the research is arranged as follows:

(1) Trivalent arsenic should be oxidized first, and hexavalent chromium reduced, to enhance the overall adsorption efficiency.

(2) To reduce costs, the processes of oxidation-reduction and adsorption should be integrated into a single step.

(3) The hydrogel needs to be functionalized to acquire capabilities it inherently lacks.

(4) In the simultaneous removal of both anionic and cationic harmful ions, we aim to significantly improve the overall adsorption efficiency by altering the state of the adsorbate, rather than by functionalizing the gel.

The research encompassed:

(1) **Efficient removal of As** via oxidation of As (III) to As (V): A cationic polymer gel, supported with oxidizing agents such as $KMnO_4$ or $K_2Cr_2O_7$, has been developed to effectively remove arsenic. This gel demonstrates the capability to adsorb both arsenite (III) and arsenate (V) through an ion exchange process, wherein the oxidizing agent converts As (III) to the more adsorbable As (V) form. Theoretically, the concentration of the oxidant within these gels can attain a significant level of up to 73.7Mol%. The D-Mn gel, embedded with MnO_4^{-}, and the D-Cr gel, containing $Cr_2O_7^{2-}$, exhibit impressive maximum adsorption capacities for As (III)—reaching up to 163 mg g^{-1} and 263 mg g^{-1}, respectively, better than that of many other adsorbent materials. Moreover, these gels consistently maintain an As (III) removal rate of over 85% in neutral and mildly acidic aquatic environments. The results of this study suggest that D-Mn and D-Cr gels are highly effective for adsorbing As (III), making them suitable for application in the removal of arsenic from industrial wastewater. This innovative approach combines the unique properties of the DMAPAA-Q gel with powerful oxidizing agents to offer a promising solution for mitigating arsenic pollution in aquatic environments. The oxidation of As (III) to As (V), to enhance the removal efficiency, is one of the removal methods that change the existence state of adsorbates in the aqueous environment.

(2) **Efficient removal of Cr** via reduction of Cr (VI) to Cr (III): a novel approach using ascorbic acid as a reducing agent supported by a copolymer hydrogel is introduced. Theoretically speaking, the maximum proportion of the reducing agent, ascorbic acid, in the gel can reach up to 49Mol%. This method effectively targets the removal of hexavalent chromium, Cr (VI) and could integrates the reduction and adsorption processes into a single step, streamlining the traditional chromium removal techniques while also reducing the costs. The process involves the adsorption of Cr (VI) through an ion exchange mechanism, and the removal of Cr (III), reduced from Cr (VI) by L-ascorbic acid (VC), through surface complexation and the formation of insoluble hydroxides [$Cr(OH)_3$] inside the gel. The study comprehensively investigates the influence of various parameters on the reduction and removal efficiency of the DA/DQ and DA/DQ/VC gels. These parameters include solution pH, initial Cr (VI) concentration, the presence of co-existing anions, contact time, and temperature. Notably, the gels exhibit high adsorption efficiency within a pH range of 3 to 6, due to the enhancement of the electrostatic interaction between the adsorption sites protonated by H^+ and chromium anionic species. Moreover, the adsorption capacities of gels can reach above 90 mg g^{-1} at initial concentration of 100 mg L^{-1}, with solution pH 3.This method, leveraging the unique properties of the synthesized gels, offers a promising solution for the effective removal of hexavalent chromium from heavily contaminated wastewater. The reduction of Cr (VI) to Cr (III) is also one of the removal methods that change the existence state of adsorbates in the aqueous environment.

(3) **Simultaneous removal of As and Cr** via formation of positively charged complex ions (PCCs): The development of functional materials with enhanced adsorption capabilities and recyclability is gaining sustained attentions, which often limits their practical applications. Addressing this challenge, this study introduces a novel approach using ionic hydrogels to efficiently adsorb both cations and anions simultaneously by converting them into a stable complex form. (P.S. The formation of positively charged complex ions is also one of the removal methods that change the existence state of adsorbates in the aqueous environment.) This method significantly simplifies the adsorption process while maintaining high adsorption efficiency. Our research delved into the adsorption mechanisms of these ionic hydrogels, with a specific focus on the complex formation between arsenic and chromium in diverse environmental conditions. We conducted a thorough investigation into how various physicochemical factors influence the gel's adsorption capacities. One of the key findings was

the formation of a positively charged complex in aqueous mixtures of arsenic and chromium, demonstrating a remarkable capacity for simultaneous adsorption in the binary system. The study methodically analyzed the adsorption behavior of the gels, applying various adsorption isotherms and two kinetic models to fit the experimental data. This analysis revealed that the binary systems exhibited significantly higher adsorption capacities compared to the single systems. Additionally, we observed that changes in the pH of the environment affected the stability of the As-Cr complex, subsequently influencing the gel's adsorption capacity. An intriguing outcome of our research was the discovery that the presence of other co-existing anions or cations could impact arsenic and chromium removal. It was noted that other metal ions could form positively charged complexes, occupying the adsorption sites initially intended for the As-Cr complex. This finding opens new possibilities for the removal of a broader range of contaminants using the corresponding gel materials.