Cellulose-based adsorbent for arsenite removal as a waste-free operation

Keisuke Nakakubo[1*], Koki Yunoshita[1], Foni B. Biswas[1,2], Masaru Endo[1,3], Tsuyoshi Taniguchi[1], Tatsuya Nishimura[1], Katsuhiro Maeda[1], Asami S. Mashio[1], Hiroshi Hasegawa[1*]

1: Kanazawa University, Kakuma, Kanazawa 920-1192, Japan

2: Department of Chemistry, University of Chittagong, Chittagong 4331, Bangladesh

3: Daicel Corporation, 1239 Shinzaike, Aboshi-ku, Himeji-Shi, Hyogo 671-1283, Japan

*corresponding author: k-nakakubo@stu.kanazawa-u.ac.jp

Keywords: volume reduction, sludge-free operation, cellulose, adsorption, arsenic

INTRODUCTION

Arsenic, a toxic metalloid, has been causing serious pollution. The toxicity depends on its chemical forms, for instance, arsenite (As^{III}) is more toxic than arsenate (As^{V}). As^{III} is the predominant species in groundwater that is often used as drinking water in developing countries. To remove arsenic from aqueous media, the coagulation/flocculation with inorganic coagulants is widely used. However, this method does not remove all of As^{III}, and multiple operations are required. Besides, large amounts of inorganic sludge containing arsenic must be treated ahead of disposal and can overload landfill sites. Therefore, there is a great need for a method that can effectively remove As^{III} with less waste. Adsorption can solve such problems because of its cost-effective, easy, rapid, and sludge-free operations. In addition, the use of green materials is getting more important than ever before. In this work, we synthesized a dithiocarbamate (DTC) modified cellulose for the purpose of developing a low-cost and effective adsorbent to As^{III}.

MATERIALS AND METHODS

Synthesis of the adsorbent

The adsorbent named DMC was fabricated according to Nakakubo K., Hasegawa H. et al., 2019.

Adsorption experiments

Adsorption studies were carried out in centrifuging tubes containing 10 mg of the adsorbent and 10 mL of metal-containing solutions by agitating them for 20 minutes at 200 rpm and 25 °C. By following this procedure, the effect of solution pH, and selectivity were investigated. The concentrations of metal ions were quantified by inductively coupled plasma atomic emission spectroscopy (ICP-AES; iCAP 6300, Thermo Fisher Scientific, MA, USA).

Volume reduction process

The adsorbent was incinerated at 500 °C for a certain time to reduce its volume for disposal. The volume and weight were measured, and pictures were taken every 15 minutes.

RESULTS AND DISCUSSION

Adsorption behavior of As^{III}

The effect of pH on inorganic arsenic species was investigated. The adsorbent quantitatively extracted As^{III} over a pH range of 2–8, but poor adsorption was observed at pH 9 and 10. On the other hand, the extracted

As^{V} was around 8% at pH 2, and 0% at the other pHs. At pH 2, about 40% of As^{V} is negatively charged, and some hydroxyl groups (–OH) in cellulose, which were not substituted by DTC groups, are protonated ($–OH^{+}$), hence electrostatic interaction between As^{V} and $–OH^{+}$.

The selectivity of DMC to various elements was examined at pH 3 (**Fig. 1**). The extracted elements (>95%) were Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, and Pb^{II}, so-called hazardous heavy metals, and Pd^{II}, Ag^{I}, Ir^{III}, Pt^{IV}, and Au^{III}, namely precious metals. In addition, one of the oxyanions (Se^{IV}) was also quantitatively adsorbed. However, the alkali and alkaline earth metals were not extracted. According to the HSAB theory, the sulfur atom in DTC groups is a soft base, and the unextracted metals are defined as hard acids, resulting in little adsorption.

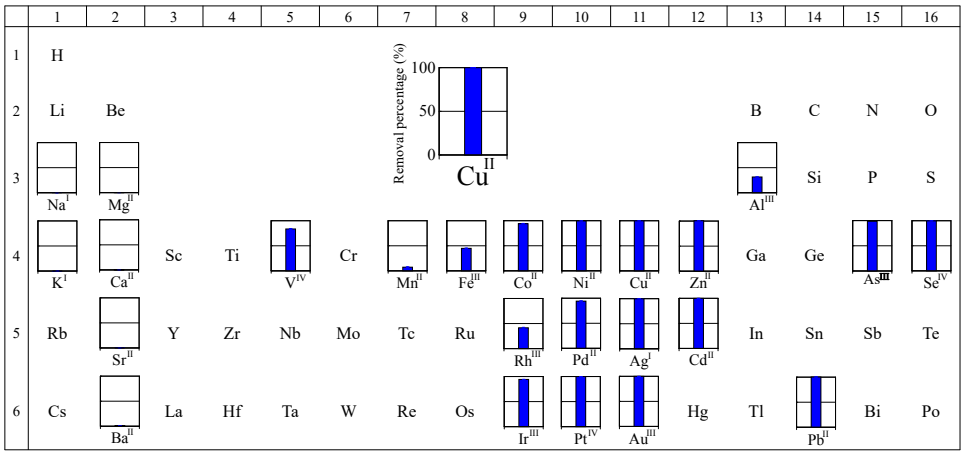

Fig. 1. The selectivity of DMC to various elements

Volume reduction

Even after incineration for 15 minutes at 500 °C, the weight decreased by about 99%, and the material has disappeared in 30 minutes. During the combustion, some harmful gases like As_2O_3, SO_x, and NO_x, resulting from DTC groups, would be released. By using conventional absorbents, As_2O_3 gases can be safely removed. Therefore, unlike the coagulation/flocculation, DMC can be significantly reduced in volume, which can minimize landfill waste.

CONCLUSION

This study examined the adsorption performance of the synthesized adsorbent and revealed that the material was very selective to As^{III} over a wide pH range. Moreover, toxic heavy metals including Pb^{II} and Cd^{II} as well as precious metals (Ag^{I}, Au^{III}, Pd^{II}, and Pt^{IV}) were extracted, but alkali and alkaline earth metals were not adsorbed. The adsorbent was incinerated and reduced by 99% in volume. Therefore, DMC can contribute not only to removing As^{III} but also to reducing landfill waste.

ACKNOWLEDGEMENT

The research was supported by Grants-in-Aid for Scientific Research (18H03399) from the Japan Society for the Promotion of Science.

REFERENCES

Nakakubo, K., Hasegawa, H., et al., Dithiocarbamate-modified cellulose resins: A novel adsorbent for selective removal of arsenite from aqueous media. J. Hazard. Mater. 380, 120816, 2019.