学 位 論 文 内 容 の 要 旨/Dissertation Abstract

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学 位 論 文 題 名/Title of Dissertation

Development of anion-exchange resin incorporating single metal particles for rapid removal and catalytic decomposition of nitrate in water toward groundwater purification

（地下水浄化に向けた水中硝酸イオンの迅速除去と触媒分解のための単一金属粒子を取り込んだ陰イオン交換樹脂の開発）

Groundwater is an indispensable freshwater resource, and its effective use is essential for developing a sustainable society. Recently, however, groundwater pollution with nitrate (NO_3^-) is becoming apparent in many parts of the world. The main course of groundwater pollution with NO_3^- is excess use of nitrogen fertilizer in the development of modern agriculture. In addition, unexpected discharge of domestic and industrial wastewater to the environment also causes groundwater pollution. Detrimental effects of NO_3^- in drinking water on human health have long been studied, and it was found that NO_3^- taken in human body can cause methemoglobinemia (blue baby syndrome) particularly for infants and fetuses. In view of this, removal of NO_3^- in groundwater is necessary and urgent.

So far, various methods have been investigated for purification of the polluted groundwater. Ion-exchange method using ion-exchangers including anion-exchange resin is one of the excellent ones for that purpose because of facile operation and rapid treatment. However, formation of the waste solution with high concentration NO_3^- is an unavoidable problem when the spent ion-exchangers are regenerated using brine, which is concentrated salt solution. To address the problem of the ion-exchange method, the integration of catalytic decomposition with anion-exchange removal using anion-exchange resins incorporating metal particles was proposed. The previous studies demonstrated that anion-exchange resins incorporating bimetallic particles including CuPd and SnPd captured NO_3^- in water through an anion-exchange reaction, and NO_3^- taken in the resin was decomposed by catalytic reduction with H_2 over the bimetallic particles. The advantage of the process installed with such metal particle-resin materials is that brine is unnecessary for regenerating the spent one. However, bimetal particles involve a considerably larger number of parameters in the catalyst preparation to determine their catalytic performances, which prevents rational design of catalysts to enhance the performances. Based on the background mentioned above, this study was conducted to develop an anion-exchange resin incorporating single metal particles that were highly active for decomposition of NO_3^- without compromising anion-exchange performance.

In Chapter 1, status of freshwater use and problems, situation of groundwater pollution with NO_3^- and detrimental effect of NO_3^- on humans are described. After comprehensive consideration of advantages and disadvantages of various methods usable for NO_3^- removal, ion exchange and catalytic methods are explained in detail. Finally, the purpose of this study mentioned above is clearly stated.

In Chapter 2, anion-exchange resins (Amberlite^{TM} IRA410(OH), Organo Co.) containing various metal particles (M@AER, M= Ru, Rh, Pd, Ir, Pt, and Au) were prepared, and ion-exchange and catalytic performances of M@AER for NO_3^- removal and decomposition were evaluated. It was demonstrated that the decomposition of NO_3^- proceeded even with single metal particles. Among the tested metals, Au was chosen as an active single metal introduced into the resin because $AuCl_4^-$, which was a precursor of the Au particle, in the resin was spontaneously reduced to form metal particles without additional reducing agent. The preparation conditions of Au@AER and the reaction conditions for NO_3^- decomposition were intensively investigated to improve the catalytic performance for NO_3^- decomposition. Au@AER prepared under the optimal conditions and optimum Au contents decomposed 0.38 mmol g^{-1} of NO_3^-, which corresponded to 41 % conversion of NO_3^-, mainly into N_2O at 80 °C for 5 h. The introduction of Au particles in the resin increased the ion exchange capacity by about 1.2 times, while ion exchange equilibrium constant was slightly decreased. Au@AER was reusable for ion-exchange removal of NO_3^- and its decomposition in H_2 at 80 °C up to five uses without any performance degradation.

In Chapter 3, the mechanism of NO_3^- decomposition in Au@AER was investigated especially focusing on the role of water, and it was suggested that presence of water promoted the diffusion of NO_3^- in the resin. Free NO_3^- in the resin and NO_3^- at the ion-exchange sites close to the Au particles were decomposed in the presence of water in the resin, but NO_3^- at the ion-exchange sites far from the Au particles were not done even in the presence of water. NO_3^- was decomposed on the surface of the Au particles and OH^- was generated. Then, the generated OH^- on the surface of the Au particles was exchanged with free NO_3^- in the resin or NO_3^- at ion-exchange sites adjacent to the Au particles. NO_3^- was decomposed in the resin by the repetition of these reactions.

In Chapter 4, preparation conditions of Ru@AER, which had the highest activity for NO_3^- decomposition among M@AER tested in Chapter 2, and reaction conditions for NO_3^- decomposition were systematically investigated. Hydrogen pressure, and treatment time and temperature in the reduction process of Ru precursor in the resin greatly affected the catalytic performance and the optimum conditions were 10 atm, 5 h and 120 °C, respectively, while increase of only one of temperature and pressure was ineffective to improve the catalytic performance. Ru@AER prepared with the optimum conditions decomposed 100 % of NO_3^- taken in the resin at 80 °C for 5 h. As with Au@AER, water in Ru@AER had a critical role for NO_3^- decomposition and it was essential that Ru@AER was wet to obtain 100 % conversion of NO_3^-. Ru@AER was reusable for the ion-exchange removal of NO_3^- and NO_3^- decomposition for up to five reuses without any loss of performance.

In Chapter 5, the conclusions and future perspective of the study are stated.

Through this study, the present author broke the common sense that single metal catalysts were ineffective for NO_3^- decomposition and demonstrated that anion exchange resin containing even single metal particles showed high activity for the reaction, which allowed complete regeneration of the spent anion-exchange resin without use of brine. The present author confident that this finding will lead to a rational design of the catalysts to develop higher performance catalysts with single metals, which promotes the large-scale application of this methodology contributing to the actual purification of the polluted groundwater.