

学 位 論 文 題 名

Development of a System Based on Copper-Palladium Bimetallic Catalyst for Remediation of Nitrate Polluted Groundwater

(硝酸汚染地下水の浄化システムの構築)

学位論文内容の要旨

The pollution of groundwater, especially with nitrate ions, has recently become serious worldwide problem. Nitrate can cause blue-baby syndrome when ingested by infants and are responsible for some cancers and diabetes. Conventional physicochemical methods and biological de-nitrification process due to high cost and secondary pollution limit the application of these processes. Catalytic de-nitrification using solid catalysts as a new and alternate technology for removal of nitrates from groundwater is being focused. Many studies had been carried out on the catalytic reduction of nitrate in water using Cu-Pd bimetal catalyst, since the discovery of Cu-Pd/ Al_2O_3 as an active and selective catalyst by Vorlop and colleagues. However, the selectivity for N_2 was insufficient even for the Cu-Pd/Active carbon and thus the concentration of ammonia formed exceeded allowable level for drinking water. Therefore, at presents there is no simple process in catalytic reduction of nitrate that can meet the demands of the concentration of nitrate, nitrite, and ammonia simultaneously in real groundwater purification. In this study, with a view to profitable and practical use of solid catalyst, purification system for groundwater polluted with nitrate was developed. In this system, development of the catalyst showing high activity and selectivity for the reduction of nitrate is a key technology, by combining these technologies, a system for purification of groundwater contaminated with nitrate, consisting of pretreatment with ozone oxidation, catalytic reduction with Cu-Pd/Active carbon and post-treatment by ion-exchange technology using zeolite is proposed and demonstrated.

Type of active carbon and Cu/Pd ratio in the Cu-Pd/Active carbon were systematically examined in order to develop a highly active, selective and stable catalyst. The result showed an active carbon derived from coconut shell was the most suitable for Cu-Pd/Active carbon with high activity and high selectivity for N_2 ($+\text{N}_2\text{O}$), and the Cu/Pd ratio significantly affected the catalytic performance, at the same time, the selectivity for NH_3 was suppressed to meet the allowable level of NH_3 for drinking water (0.5 ppm) under low H_2 partial pressure (0.05 atm) with neutral pH. The Cu-Pd/Active carbon catalyst showed constant conversion and selectivity.

Cu-Pd/Active carbon catalyst was applied for the practical groundwater polluted with nitrate, the result showed activity was decreased and selectivity for NH_3 was increased for the purification of groundwater, comparing with that in distilled water over the Cu-Pd/Active carbon. The influence of groundwater including coexistence matter on adsorption and reduction over Cu-Pd/Active carbon was systematically investigated. When chloride anion was present in water, the performance

of Cu-Pd/Active carbon was decreased due to the competitive adsorption; the presences of SO_4^{2-} and cation had no effect on nitrate reduction over Cu-Pd/Active carbon; the organic matters contained in the groundwater decreased the activity and selectivity. In addition, ozone pretreatment of groundwater suppressed catalyst deactivation.

The formation of NH_3 is serious problem in the purification of groundwater containing some coexistence matter. Ion-exchange adsorption using synthetic zeolite as a high adsorption capacity was researched. The author found that Na-form mordenite was an efficient cation-exchanger for removal of low-concentration NH_3 in water in comparison with Na-ferrierite, Na-ZSM-5, Na- β , and Na-Y, as well as K- and H-form mordenite. Coexistent K^+ and Na^+ in water had little influence on ammonia uptake with Na-mordenite. In contrast, coexistent Ca^{2+} and Mg^{2+} significantly lowered ammonia uptake. However, Na-mordenite can remove low concentration NH_3 even in the presence of excess Ca^{2+} and Mg^{2+} .

By using a three-stage system consisting of ozone oxidization, catalytic reduction on the Cu-Pd/Active carbon catalyst, and ion-exchange with Na-mordenite for purification of real groundwater polluted with nitrate, groundwater was successfully purified to meet the standards of drinking water.

学位論文審査の要旨

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(硝酸汚染地下水の浄化システムの構築)

硝酸イオン (NO_3^-) による地下水の汚染が顕在化している。固体触媒法による NO_3^- の還元浄化が有望視されているが、 NH_3 の副生が問題となっており実用に至っていない。本研究では、 NH_3 の副生を極めて低レベルに抑制しうる高性能触媒を開発し、これを礎とした硝酸汚染地下水浄化システムの構築を目的とした。

担体となる活性炭の種類ならびに触媒成分の銅とパラジウムの組成を系統的に調べた結果、椰子殻原料の活性炭に銅とパラジウムを組成比が3となるよう調製した触媒が、触媒活性ならびに選択性に優れることを見いだした。さらに、水素分圧、反応温度、水素と硝酸イオンの流速比等の反応条件の影響を調べたところ、水素分圧を低くするほど NH_3 の副生を抑制できることが分かった。蒸留水に硝酸イオンを溶解させた模擬水の浄化において、最適触媒および最適反応条件で NH_3 の生成を 0.5 ppm に抑制しつつ硝酸イオンを還元浄化できた。

硝酸イオンで汚染された実際の地下水の浄化を試みたところ、模擬水での反応と比べて、触媒活性の低下と副生 NH_3 量の増加が観測された。また実地下水の浄化では、触媒の顕著な不可逆劣化が見られた。これらの原因を解明するべく、地下水に含まれる各種イオンならびに有機物が触媒反応に与える影響を調べたところ、塩化物イオンと有機物が触媒性能を低下させる原因物質であることを突き止めた。

地下水中の有機物の分解には、オゾン酸化処理が有効であった。触媒反応器で副生した NH_3 は、ナトリウム型ゼオライトを充填した吸着塔に触媒反応器出口水を通すことで完全に除去することができた。これらの結果を踏まえ構築した、オゾン酸化塔－触媒反応器－ NH_3 吸着塔から構成されるシステムにより、硝酸イオンで汚染された

地下水の浄化に成功した。

以上、本研究は水中の硝酸イオンを還元浄化する高性能触媒を開発し、これを礎とする浄化システムが硝酸イオンで汚染された地下水を浄化できることを実証したものである。審査委員一同は、これらの成果を高く評価し、また研究者として誠実かつ熱心であり、大学院博士課程における研鑽や修得単位などもあわせ、申請者が博士（環境科学）の学位を受けるのに十分な資格を有するものと判定した。