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nZVI@TiO_2 Hetero-interface Activity for NO_3^- Removal as Water Remediation Application

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Abstract: *Interface has a synergetic effect in catalytic reactions. Nano particle zero Valent iron (nZVI) is high active (Oxidant, Reductant) of almost contaminants of wastewater such like nitrate through reduction as part of water remediation. nZVI agglomeration lead to severely decreasing in surface area then hence drop in its activity. There were some additives served as anti-agglomeration such like polymers, bi-metals and stabilizers. However, metal oxide nanostructure could prohibit nZVI agglomeration furthermore create an interface with higher activity. TiO_2 as a photocatalytic material has same function after excitation with suitable energy. Electrons play main role for reduction while holes are for oxidation, and hence its efficiency depend on mainly in time recombination of electrons and holes. nZVI@TiO_2 successfully synthesized and demonstrated synergetic reduction removal activity for NO_3^-. SEM have been used to analysis new composite structure, furthermore several batch experiments have been performed to suggest reduction possible scenario including future plan.*

Keywords: Interface activity, water remediation, nZVI, Nitrate removal, TiO_2

1. INTRODUCTION

nZVI is active (Oxidant, Reductant) of almost contaminants in water such like nitrate as part of water remediation and products are non-toxic/ or less toxic [1]. nZVI has a problem of agglomeration lead to decreasing in its surface Area and hence its activity. Nitrate is one of poplar contaminant in wastewater as a result form agriculture fertilizers. That contaminant has hazardous effect in drinking water for humans and animals as well. [2] Some process uses to remove it such like reverse osmosis and ion exchange as well as catalytic denitrification [3]. There are some trials to enhance nZVI performance by using some additives to prohibit agglomeration such like polymers [4], bi-metals [2,5] and stabilizers [6], however TiO_2 nanowires could serve as anti-agglomeration structure, in additional to an interface of synergetic effect for nitrate removal. Heterogeneous photocatalytic plays an important role worthy enough to be a major discipline as it combines different fields together. [7] TiO_2 matrix via sol gel has enhanced nZVI reduction performance by prohibiting them oxidation [8,9].

In this study, it would discuss the activity removal of nitrate as part of water remediation by using nZVI@TiO_2 nanowires. Batch experiments of nitrite removal would suggest the mechanism scenario as well. This would first step to study and analysis the mechanism itself in future work.

2. Materials and Methods:

2.1 Chemical reagents:

Sodium hydroxide (>97%, Wako Co., Japan) and Titanium (IV) Oxide, Rutile form Wako Co., Japan), All solutions were prepared using deionized water.

nZVI Synthesis: Ferric chloride ($FeCl_3 \cdot 6H_2O$, Junsei Chemical Co., Japan, purity>99.0%), sodium borohydride ($NaBH_4$ Sigma–Aldrich Inc., USA, purity >98.0%,) and ethanol (C_2H_5OH, Wako Co., Japan, purity =99.5%). Deionized water was bubbled by N_2 gas for 10 minutes for all solutions. No Further purification or special treatments for all chemicals were required.

Batch tests: 200 mg/l solution of Nitrate was prepared by dissolving Sodium nitrate ($NaNO_3$, Junsei Chemical Co, Japan, purity > 99.0%). 50 mg/l solution of Phosphorus was prepared by dissolving Potassium dihydrogen phosphate (KH_2PO_4, wako pure chemical industries, Ltd, Osaka, Japan, purity =99.0 %). Deionized water was bubbled by N_2 gas for 10 minutes for both of them.

2.1 Synthesis nZVI@ TiO_2:

Composite has successfully synthesized by with sodium borohydride $NaBH_4$. The amount of $NaBH_4$ and DI water are organized proportional according to the amount of $FeCl_3$. Wet-impregnation is the crucial step for interface fabrication and percentage control of TiO_2 with nZVI.

3. Results and discussion:

Figure (1) shows activity of composite of 0.25g cat/200 ml solution.

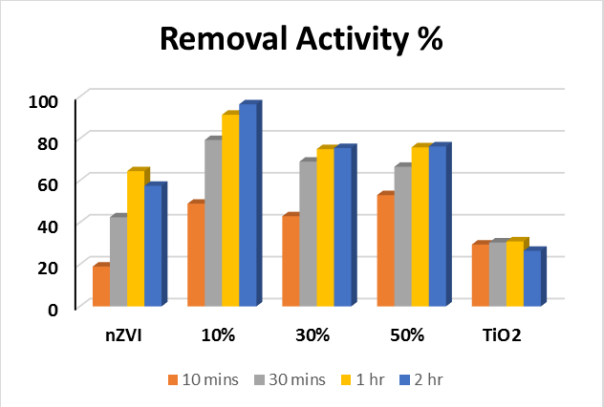

Fig. 1. Reduction removal activity of NO_3^- Batch. nZVI@10% TiO_2 composition is best removal activity overall.

Removal Activity is the percentage (%) NO_3^- removed amount from the solution comparing to its initial concentration. nZVI@10% TiO_2 composition has been found best removal activity overall. 10% TiO_2 composite activity higher 3.5 times from bare TiO_2 at 120 mins., While higher 2.5 time from bare nZVI at 10 mins.

SEM image for bare nZVI which agglomeration appear clearly in it as shown in Fig (2), That agglomeration decreased once usage small amount of TiO_2 nanostructure.

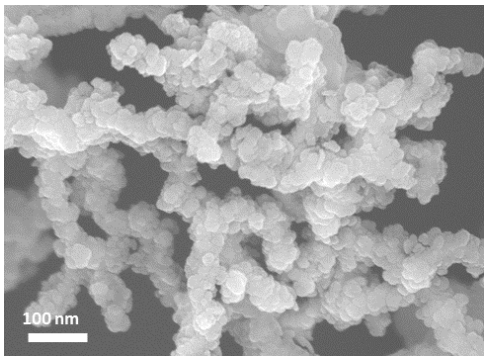

Fig. 2. SEM image for bare agglomerated nZVI

Further batch tests shown demonstrated that neither photocatalytic effect of TiO_2, nor surface area of nZVI played a role in higher activity but synergetic effect of interface of nZVI@TiO_2.

4. Conclusion:

In this study, a new Nano composite of nZVI@TiO_2 has been successfully synthesized and demonstrated synergetic effect for Nitrate (NO_3^-) removal as part of water remediation application. TiO_2 nanostructure can serve as anti-agglomeration of nZVI, furthermore interface of two materials could improve each other for better reduction reaction. Synthesis process started with three main steps: TiO_2 synthesis, Wet-impregnation of $FeCl_3$, then finally chemical reduction with $NaBH_4$. Wet impregnation is a crucial step to successful distribute of nano particles of Fe^0 along with TiO_2 nanowires, furthermore controlling the mass percentage (%) of total composition of composite. Final step is chemical reduction of $FeCl_3$ to zero valent iron then followed by washing during vacuum filtration. Several Batch experiments have been performed and demonstrated that only 10% of TiO_2 composite could increase activity higher 3.5 times from bare TiO_2 after 120 mins, while higher 2.5 times from bare nZVI after 10 mins. The enhanced activity is neither to photocatalytic nor surface area but due to synergetic effect of interface. SEM Structure analysis was included to emphasis on hetero-interface catalytic role.

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