Comparison of Removing NO_3^- in the Polluted Groundwater of In-Situ Leaching of Uranium Mine with DNB and Fe^0

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***Abstract*—Removing NO_3^- in polluted groundwater of in-situ leaching uranium mine with iron powder (zero-valent iron, Fe^0), DNB, iron powder and DNB are studied. The condition of tests include different pH of solution, dosage of iron powder, and treating time. The experimental results show that over 93% of NO_3^- in unneutralized polluted groundwater (pH value about 1.46) can be removed with 16.5 g·L^{-1} iron powder in 4 days. NO_3^- in neutralized polluted groundwater (pH value about 7.62) can also be removed with 2 g·L^{-1} iron powder. The removing rate of NO_3^- is enhanced with time and the highest removing rate reaches 54% in 5 days. NO_3^- in neutralized polluted groundwater can also be removed with DNB in condition of ρ(COD)/ρ(NO_3^-) equal to 1.5, 35℃,pH 5-8. The removing rate of NO_3^- is over 90%in 5 days. In certain conditions, the removing rate of NO_3^- with DNB is 30% higher than that with iron powder. The removing rate is promoted with DNB adding iron powder. Comparing to DNB, the iron powder can be used in larger range of pH of the polluted groundwater.**

Keywords—DNB; zero-valent iron; in-situ leaching uranium ; polluted groundwater ; NO_3^-

I. INTRODUCTION

In-situ leaching technology of uranium has been the main way of exploitation of porous sandstone uranium deposit in China at present. SO_4^{2-}、NO_3^-、U(VI)、H^+ and heavy metal ions in groundwater are seriously exceeding standard when these in-situ leaching uranium mines are out of commission. Neutralizing the polluted water with calcareousness is the main way to dispose groundwater in in-situ leaching uranium mines now. But NO_3^- can't be removed from groundwater by neutralizing with calcareousness. NO_3^- is very stable and difficult being decomposed, and it does serious harm to of human and animals drinking water[1-4]. Now surface evaporation, electrodialysis, reverse osmosis, adsorption with ion exchange resin are the main technologies used by mine corporations in China to deal with polluted water containing NO_3^-.[5-8] But all the study results can't be applied in reality. And these ways always make second pollution. The cost is rather high too. Removing NO_3^- from the polluted groundwater in in-situ leaching uranium mines has been a difficult problem which must be solved urgently.

Because the polluted groundwater with nitrate can endanger people health directly or indirectly, the standard value of nitrate concentration in drinking water is defined by the countries all over the world. It is prescribed by World Health Organization that the nitrate concentration in drinking water must be no more than 50 mg·L^{-1} (NO_3^- measured, conversion to11.3 mg·L^{-1} NO_3-N), and nitrite concentration in drinking water must be no more than 3 mg·L^{-1} (conversion to 0.91 mg·L^{-1} NO_2-N). The nitrate nitrogen concentration in drinking water prescribed by Quality Standard of Drinking Water (GB5749-1985) implemented from the year 1986 in China should be less than 20 mg·L^{-1}. And it is improved in Quality Standard of Drinking Water (CJ94-1999) implemented from March 1, 2000. Now, the standard value is prescribed less than 10 mg·L^{-1}[7-11].

Denitrification is a process that nitrate and nitrite are deoxidized to gas nitrogen (mainly N_2) by heterotrophic denitrifying bacteria(DNB). DNB are a kind of bacterias having the function of denitrification. They are also a class of chemoheterotrophic and anaerobic microorganism. When in anoxic environment, DNB can make use of the nitrate and the nitride as the terminal electron acceptor, the organic compounds as carbon source and electron donor for energy. during this course, the nitrate and the nitride are gradually deoxidized to NO and N_2O, and finally to N_2[12-19], and no waste solution or secondary pollution in the process. so DNB can be used for the treatment of industrial wastewater, groundwater and domestic sewage polluted by NO_3^-.

Research shows that heavy metal ions, oxacid ion(NO_3^- for example) and organic pollutants in many kinds of wastewater can be effectively removed by zero-valent iron(Fe^0) in in-situ or in ex-situ[20-25].

It is up to 720 mg·L^{-1} that the concentration of NO_3^- in polluted groundwater of exploitation areas out of commission in some in-situ leaching uranium mines in Xinjiang. In this paper, removing NO_3^- in polluted groundwater of in-situ leaching uranium mine with iron powder in pH of solution, adding amount, reaction time and DNB in pH of solution, reaction time and adding Fe^0, and the comparison of the three treating conditions, are studied. It is the purpose of the research that NO_3^- in groundwater of decommissioned area in uranium mine can be removed or not by zero-valent iron（Fe^0）and DNB.

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II. EXPERIMENTS

A. Sources of DNB

There are various types of DNB in nature. And they exist widely in soil and water containing some organic compounds. The DNB in experiment is obtained from native sludge of some in-situ leaching uranium mine in Xinjiang. Firstly, removing the solid substances such as stone and undecomposed leaves, then using tap water to dilute, and taking the clean supernatant, then inoculating it to culture medium (see Table Ⅰ) by 10% (V/V) DNB solution, culturing it in bio-reactor under anaerobic conditions at 35℃. the concentration of NO_3^- in solution is analyzed every other day. When the removing rate of NO_3^- reaches 90%, the bacteria solution is used as a new mather bacteria. The inoculum amount is also 10%, same as the first time. The acclimation cultures are repeated many times later. When the concentration of NO_3^- in the solution drop from 1.0 $g \cdot L^{-1}$ to below 20 $mg \cdot L^{-1}$ within 3 to 5 days, the bacteria breeding work is finished. And the bacteria strain will be used for experiments.

TABLE I. COMPONENTS OF THE CULTURE MEDIUM OF DNB

Composition	CH_3OH	$NaNO_3$	KH_2PO_4	$MgSO_4 \cdot 7H_2O$	water
Mass/g	2	1.4	0.5	0.2	1000

Note: conditions for breeding $\rho(COD)/\rho(NO_3^-)$: 3:1; $\rho(NO_3^-)$: 1 $g \cdot L^{-1}$

B. Instruments and equipments

refrigerator, pH meter of pHS-3-type, incubator of constant temperature climate, shaking incubator, electronic balance, sterilization pot of high-pressure steam, shaker etc.

C. Water samples of tests

The polluted groundwater from decommissioned areas is used as test water sample 1. The neutralized contaminated groundwater is used as test water sample 2. Main chemical components are shown in Table 2.

TABLE II. CHEMICAL COMPONENTS OF GROUNDWATER BEFORE AND AFTER NEUTRALIZATION, MG·L-1(EXCEPT PH)

	before and after neutralization	U	NO_3^-	Ca^{2+}	Mg^{2+}	SO_4^{2-}	pH
test water sample 1	Concentration before neutralization	0.62	740	660	210	18850	1.46
test water sample 2	Concentration after neutralization	＜0.5	720	580	210	3650	7.62

D. Main analysis methods

Nitrate-spectrophotometry.

E. Test methods

Test water sample are added to a conical flask of appropriate volume (or test water samples and bacteria are added to the flask at a certain proportion), if necessary, a appropriate amount of iron powder can be added to the flask, then put it in the shaker for shaking treatment. A period of time later, the pH value and the concentration of NO3– in the test water sample are analyzed.

III. RESULTS AND DISCUSSIONS

A. The test of using different amounts of iron powder to remove NO_3^- in the test water sample 1

0.33、0.66、1.65、3.30、16.50、33.00 $g \cdot L^{-1}$ of iron powder are respectively added to the test water sample 1, then put them in the shaker for shaking treatment for 4 days and investigates the case of using different amounts of iron powder to deal with the polluted groundwater, and the experiment results are shown in Figure 1.

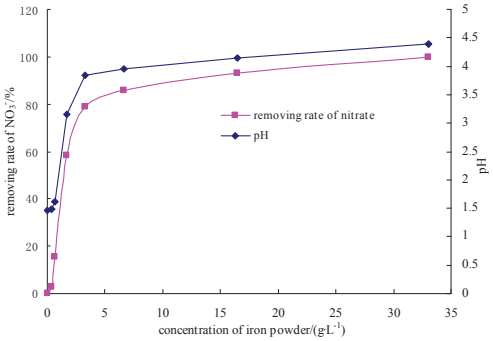

Figure 1. The NO_3^- removal rate and the pH value in the test water sample 1 with different amounts of iron powder

Figure1. shows that the dosage has a great effect on removing of NO_3^- with iron powder and increased the pH value of the wastewater remarkably. Over 93% of NO_3^- in the test water sample 1 can be removed with 16.5 $g \cdot L^{-1}$ iron powder in 4 days. And the pH value of solution is increased to 4.

B. The test of removing NO_3^- in the test water sample 2 with iron powder at different test time

2.0$g \cdot L^{-1}$ iron powder is added into the test water sample 2 of the neutralized contaminated groundwater, then the case of removing of NO_3^- is investigated at different time. The results of the experiment are shown in Figure 2.

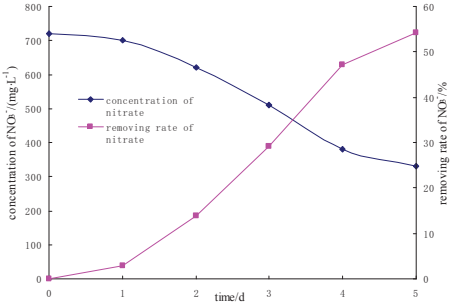

Figure 2. The change of NO_3^- in the test water sample 2 with iron powder at different test time

Figure 2 shows that, under the condition of adding iron powder of 2.0$g \cdot L^{-1}$, the NO_3^- concentration in test water sample 2 is decreased with the extending of treatment time and the removing rate of NO_3^- is increased gradually. The highest removing rate of NO_3^- reaches 54% in 5 days.

C. Test of removing NO_3^- in test water sample 2 with DNB

Test water sample 2 is inoculated with 10%DNB, carbinol used as carbon source, ρ(COD)/ρ(NO_3^-) equal to 1.5, 35℃, then for denitrification treatment, and the test results are shown in Figure 3.

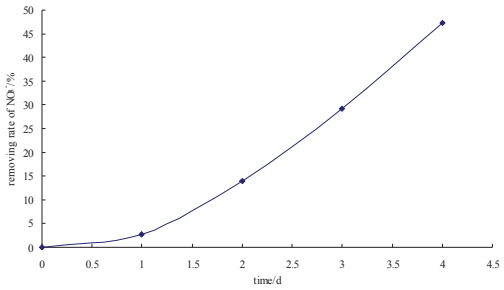

Figure 3. Result of removing NO_3^- in test water sample 2 with DNB in different time

Figure 3 shows that, under the action of the DNB, the NO_3^- concentration in test water sample 2 is decreased with the extending of treatment time and the removing rate increased gradually. What's more, the removing rate is over 90% in 5 days.

D. Effect of pH value on removing NO_3^- in test water sample 2 with DNB

As for DNB, pH value is an important factor affecting the activity of it. After test water sample 2 is inoculated with 10% DNB, the initial pH value of the solution adjusted to 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 respectively, carbinol used as carbon source, 35℃, then the effect of pH value on removing NO_3^- with DNB is studied. And the experiment results are shown in Figure 4.

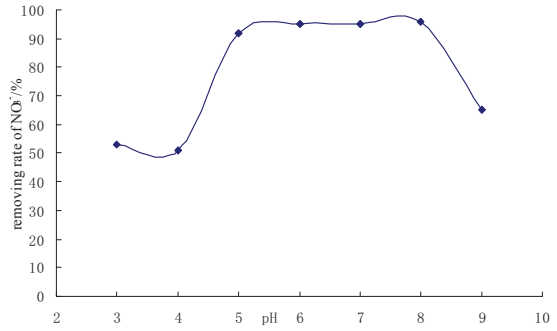

Figure 4. The results of removing NO_3^- from different initial pH of test water sample

Figure 4 shows that the influences of pH value on DNB removing NO_3^- is remarkable. under the other conditions in same, when pH value is below 5 or above 8, the removing rate of NO_3^- is less than 60%. When the pH value is between 5 and 8, the rate can be over 90%. So the optimum pH is from 5 to 8 with DNB dealing with NO_3^- in wastewater.

E. Comparison of removal the NO_3^- in the test water sample 2with iron powder and DNB

2.0g·L^{-1} iron powder, 10%DNB, 2.0g·L^{-1} iron powder and 10%DNB are added into the test water sample 2 respectively. Other conditions are same to D. Then the removing rate of NO_3^- are compared. The results are shown in Figure 5.

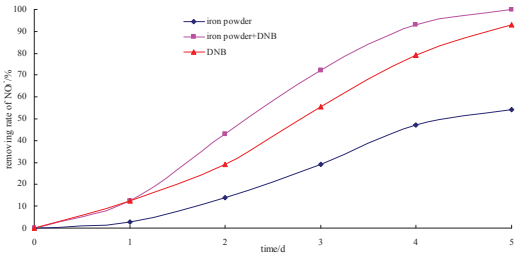

Figure 5. Comparison of removing NO_3^- with iron powder, DNB, DNB +iron powder

Figure 5 shows that in these conditions, compared with 2 g·L^{-1} iron powder, the removing rate of NO_3^- with DNB is higher over 30%. The rate with DNB and 2.0g·L^{-1} iron powder is also higher than that with DNB only.

IV. CONCLUSIONS

1) Over 93% of NO_3^- in unneutralized polluted groundwater (pH value about 1.46) can be removed with 16.5 g·L^{-1} iron powder in 4 days.

2) NO_3^- in neutralized polluted groundwater (pH value about 7.62) can also be removed with 2 g·L^{-1} iron powder. The removing rate of NO_3^- is enhanced with time and the highest removing rate reaches 54% in 5 days.

3) When the DNB inoculation is 10%, carbinol was used as carbon source, ρ(COD)/ρ(NO_3^-) is 1.5, the temperature is 35℃, the pH value is 5 to 8, the removing rate of NO_3^- is over 90% in 5 days. The removing rate of NO_3^- from wastewater with DNB is affected under either too high or too low pH value.

4) Under the same conditions, the removing rate of NO_3^- in wastewater with DNB is obviously higher 30% than with 2.0 g·L^{-1}iron powder. The rate with DNB and 2.0g·L^{-1} iron powder is also higher than that with DNB only. Comparing to DNB, the iron powder can be used in larger range of pH of the polluted groundwater.

In summary, both iron powder (Fe^0) and DNB can be used to remove the NO_3^- in polluted groundwater of mining areas out of commission of in-situ leaching uranium mines. And the pH subject range of iron powder(Fe^0) is larger than that of DNB. When the pH of solution is around neutral, DNB is more efficient than iron powder. It may be a good idea to use both together.

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