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Dissimilatory Iron Reduction Processes of Soil from Three Gorges Reservoir Area and Effect on Chemical Form of Fe

DE-WEI MU[1], NING ZUO[1,*], JI-LUN MIAO[1] and TU-JIN WANG[2]

[1]Scientific Institute of Chongqing Southwest Port & Waterway Engineering, Chongqing Jiaotong University, Chongqing, P.R. China
[2]Key Laboratory of Eco-environments of Three Gorges Reservoir Region, Ministry of Education, Chongqing University, Chongqing, P.R. China

*Corresponding author: Tel: +86 13657647278; E-mail: 401839655@qq.com

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Purple soil and yellow soil from three gorges reservoir area are submerged and incubated under a nitrogen atmosphere at constant temperature (25°) to study the dissimilatory iron reduction processes and its effect on chemical form of iron. The results show that the pH and oxidation reduction potential decrease with the transition of soil redox condition and it is especially obvious for the yellow soil. The content of Fe(II) increases to 3495.21 mg/kg for yellow soil and 536.44 mg/kg for purple soil. There are no obvious changes of redox condition and Fe(II) for sterile soil. It suggests that dissimilatory iron reduction should be driven by metabolic activity of microbe. With the transition of soil redox condition, the content of oxide-Fe increases significantly and the content of Fe(II) and oxide-Fe are significantly and positively correlated, which indicate that the transformation of Fe speciation is the result of dissimilatory iron reduction.

Keywords: Three gorges reservoir area, Soil, Dissimilatory iron reduction, Iron oxide, Chemical form.

INTRODUCTION

Oxide-Fe is an important part of the soil, it has high activity and large amplitude of changes. Reduction of oxide-Fe in soils has been the subject of extensive attention, especially the environmental effect of iron reduction, has already become a hot problem in the research of soil environmental chemistry[1]. Because of submerged Fe(III) easy to accept electronic, it can affect the pH value and the generation of Fe_2S_3 and it plays an important role in soil redox[2]. The state changes of soil redox can affect adsorption and desorption characteristics of soil and has an important impact on release and migration of heavy metals, phosphorus and other pollutants. It is found that the effect of phosphorus in soil is restricted by form transformation of Fe at a large extent, waterflooding process can make oxide-Fe reduction and result in the obvious increase of phosphorus efficiency in the soil and morphologic change of inorganic phosphorus. Reduction activation of oxide-Fe has direct contact with the form redistribution of heavy metals in soil and the bioavailability[3]. There are more researches about the dissimilatory iron reduction process of soil at present, which are mainly in the aspects of the impact of heavy metals, humic acid and sulfide on dissimilatory iron reduction and the environmental effect of dissimilatory iron reduction[4]. It is usually thought that Fe(III) reduction is the principal forms of iron oxide biotransformation in the anaerobic environment, is a kind of microbial metabolism process using Fe(III) as the terminal electron acceptor, the reduction product of dissimilatory Fe(III) is Fe(II), but there is no direct evidence that the dissimilatory reduction of iron is the result of microbial activity in soil. Its microbiology mechanism research gaps still exist. At the same time, there is no relevant description about dissimilatory iron reduction for morphological redistribution of iron impact and having or not direct link between dissimilatory iron reduction and morphological redistribution of iron.

After the completion of the Three Gorges Reservoir, large soil is inundated. After it completely operates, the reservoir area is up to 1084 km^2, lost land is 632 km^2. Under the submerged anaerobic reductive environment, soil is provided with pollutant the dual role of sources and sinks, iron component activation and morphological redistribution of soil plays an important role to contaminant sorption. Therefore, it is of great significance for prevention and control of pollutants to investigate under the submerged condition dissimilatory reduction process and form redistribution of Fe in the soil. The study uses the typical purple soil and yellow soil as the experimental material, conducts submerged anaerobic culture, at the same time uses sterile soil as control. The analysis of microbiology mechanism of dissimilatory iron reduction process and makes a analysis to the relationship between dissimilatory reduction process of iron and changes of iron form, in order to provide a theoretical basis for the prevention and control of heavy metals and phosphorus pollutants in the reservoir.

EXPERIMENTAL

Soil testing: The purple soil for experiment is collected from Chongqing District of Fuling, pH (quality ratio of soil and water is 5:1) is 8.59, the content of organic matter is 11.9 g/kg, the total Fe content is 43.7 g/kg. Yellow soil is from Chongqing Fengjie County, pH is 8.74, the content of organic matter is 33.7 g/kg, the total Fe content is 23.4 g/kg. After the soil is collected back, it needs to go through the natural air dry and pass 200 mesh sieves.

Preparation of microbial inoculation fluid: Collect fresh bottom mud in the democracy lake of Chongqing University. Prepare mud with the soil and wate\\ ratio of 1:1, shake for 30 min with 150 rpm in the oscillator, filtrate quickly with Buchner funnel, collect the filtrate as microbial inoculation fluid.

Soil culture: Fetch 300 g soil into 3 L reagent bottle, add 1.5 L distilled water and the water and soil ratio of 5:1, stirring evenly, add 0.5 mL microbial inoculation fluid, pass the N_2 to cover water, cover the cap and conduct anaerobic cultivation in the thermostat with 25 °C. Then fill the N_2 once a day during cultivation, every 10 min, with three replicates. Sampling test according to the submerged time distance with 1, 3, 6, 11, 18, 27, 37, 48, 60 days.

On the side conduct the experiment of sterile soil culture as the control. Take 6 g soil tested into 50 mL beaer, conduct heat sterilization for 20 min at 121 °C. On the clean bench, under sterile conditions according to the water and soil ratio of 5:1 add 30 mL sterile distilled water, plug the cotton plug, put test tube into anaerobic workstation for homoiothermal anaerobic culture at 25 °C, with three replicates. Sampling test according to the submerged time distance with 1, 3, 6, 11, 18, 27, 37, 48, 60 days.

Determine pH and oxidation reduction potential at each stage , take proper amount of anaerobic soil and centrifuge for 10 min with 5000 r/min, remove the saturated water, take wet soil samples after centrifugation, determine moisture and Fe(II) content and analyze morphological classification of Fe.

Determination method: Analyze the morphological classification of Fe according to the Tessier sequential extraction procedure[5]. Exchangeable state, carbonate bound state, oxides state, bound to organic matter state and residual state express respectively by Exc-, Carb-, Oxide-, Org- and Res-. Fe levels are measured by A Analyst 800 type atomic absorption spectrometer. The determination method for Fe(II) content is as follows: take 1 g centrifugal wet soil into a 50 mL volumetric flask, fetch 0.5 mol/L hydrochloric acid leaching solution to volume, extract for 24 h at 30 °C, make the extraction through 0.22 μm aperture membrane, fetch quantitative filtrate, determine the concentration of Fe(II) by *o*-phenanthroline spectrophotometric.

RESULTS AND DISCUSSION

Change features of pH and oxidation reduction potential during the soil submerged anaerobic process: Varying of pH and oxidation reduction potential for purple soil, yellow soil and sterile soil with submerged anaerobic culture are as shown in Figs. 1 and 2.

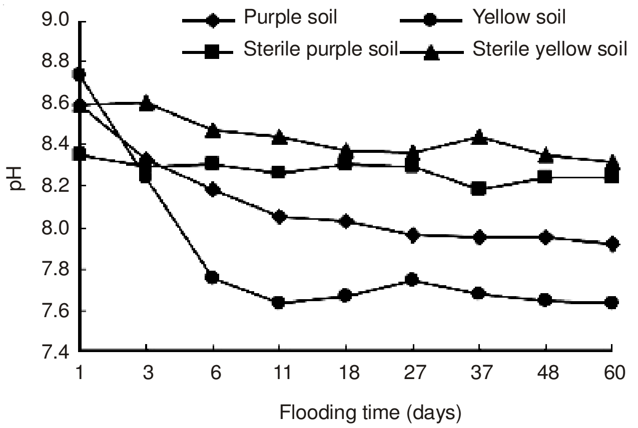

Fig.1. Variation characteristics of pH after flooding

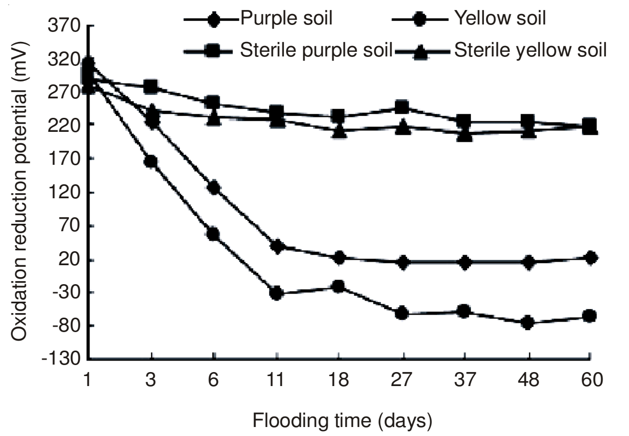

Fig. 2. Variation characteristics of oxidation reduction potential after flooding

It can be found from Fig. 1 that the pH of submerged soil is decreased and close to neutral, the pH changes of yellow soil are more significant. From the beginning of submerged experiment to the end, the pH of purple soil decreases gradually from 8.59 to 7.92, the pH tends to smoothly at the late stage of cultivation. In the whole culture stage, the pH of yellow soil decreases quickly from 8.74 to 7.63, in the late stage of culture the pH is in a stable condition. Fig. 2 showed that the soil oxidation reduction potential decreases rapidly after flooding, from beginning to end submerged cultivation, the oxidation reduction potential of purple soil is reduced from 313 to 23 mV, the oxidation reduction potential of yellow soil is reduced from 298 to 66 mV, the late stage of cultivation the oxidation reduction potential tends to smoothly. While the pH and oxidation reduction potential of the control of sterile soil suggested that there are no significant changes in the whole culture stage, it is visible that the anaerobic reduction process of submerged soil is mainly controlled by the microbial activity. The soil characteristics such as organic matter content will have an effect on microbial activity and then affects the reduction degree of the soil, high organic matter content in the soil will provide adequate nutrition for the growth of microorganisms and has a significant role in promoting anaerobic reduction of the soil.

Dissimilatory iron reduction process of submerged soil: Under anaerobic conditions the change of Fe(II) content in different soils is shown in Fig. 3.

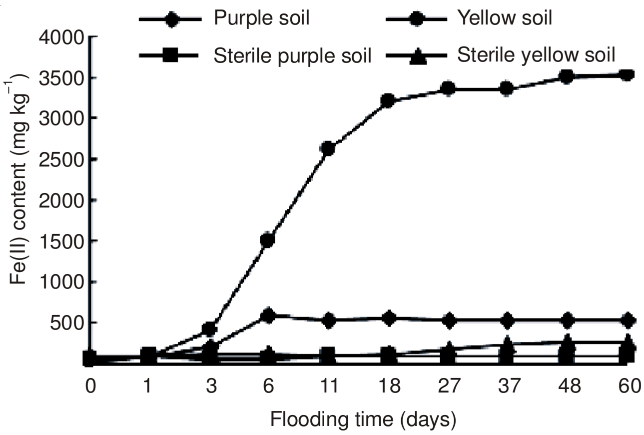

Fig. 3. Variation characteristics of Fe(II) content after soil flooding

From Fig. 3 it is find that two kinds of soil Fe(II) increase at first and then stabilizes gradually, in addition, in the early stage the two kinds of soil Fe(II) grow slowly. In the 60 days of submerged anaerobic culture, yellow soil Fe(II) increases most, from the initial 42.96 to 3495.21 mg/kg, a net increase of 3452.25 mg/kg. While purple soil Fe(II) increases less, from the initial 71.19 to 536.44 mg/kg, only net increase of 465.25 mg/kg. It is visible that dissimilatory iron reduction process of soil is connected with the nature of soil, high organic matter content provides adequate nutrition for the growth of microorganisms and has a significant role in promoting dissimilatory iron reduction. From the organic matter contents of the two soils, it can be found that the content of yellow soil is significantly higher than that of purple soil, which is helpful for dissimilatory iron reduction. At the same time, the dissimilatory iron reduction degree of soil is connected with the components of iron in soil, in total iron only part lepidocrocite of the amorphous iron oxide and crystalline iron oxide can be reduced by microorganisms, while hematite and goethite can not be reduced. It can be found from Fig. 3 that Fe(II) concentration of the two kinds of soil treated by sterilization will not increase even in submerged anaerobic culture. This provides direct evidence for the soil dissimilatory iron reduction process being driven by bacteria.

Characteristics changes of iron form in the submerged soil anaerobic reduction process: Under anaerobic incubation the features of soil iron morphology are as shown in Figs. 4 and 5.

From Figs. 4 and 5 we can find that amorphous iron from the two kinds of soil exists primarily in Oxide-Fe, the contents of Exc-Fe, Carb-Fe and Org-Fe are very low, Oxide-Fe content of purple soil is 1404.71 mg/kg, that of yellow soil is 1104.14 mg/kg. With the sustainable waterlogging time, Oxide-Fe component ratio of the two kinds of soil increases, in the early culture stage it grows slowly and on the 6th day it begins to grow, Oxide-Fe content of the two kinds of soil tends to be stable in the late culture period, yellow soil is most obvious, to the end of incubation, Oxide-Fe content of the purple soil increases to 1641.51 mg/kg, an increase of 16.85 %, yellow soil increases to 2286.16 mg/kg, an increase of 107.05 %. The waterflooding results in Fe components of the two kinds of soil being activated from Res-Fe to Oxide-Fe with different degree. While the changes of Exc-Fe, Carb-Fe, Org-Fe are subtle throughout the culture period.

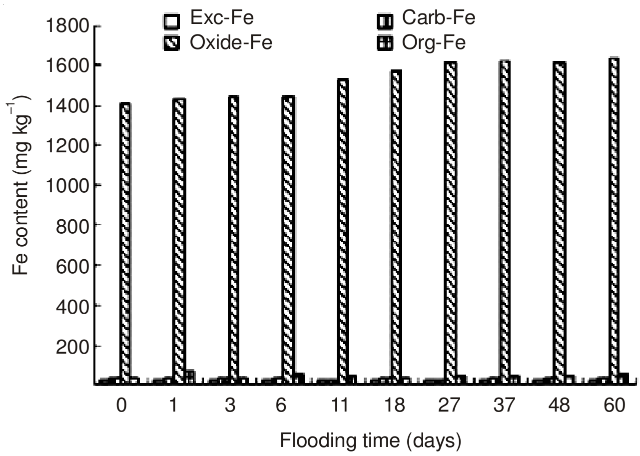

Fig. 4. Variation characteristics of Fe form after purple soil flooding

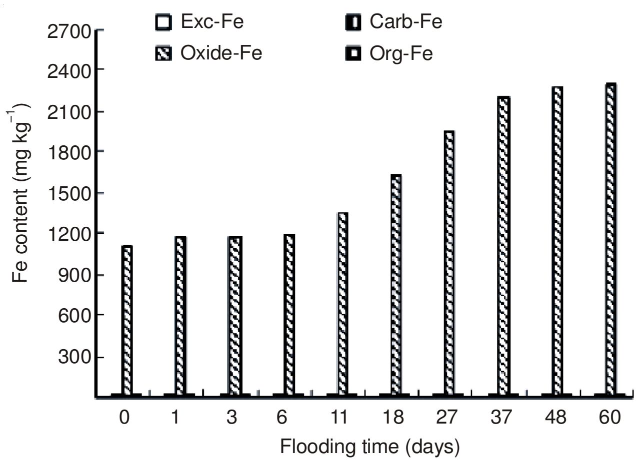

Fig. 5. Variation characteristics of Fe form after yellow soil flooding

The results in Figs. 6 and 7 indicate that the two kinds of soil through aseptic processing, in flooded anaerobic culture conditions, soil iron does not change significantly, always in a steady state during the whole culture period.Thus it can be seen, the iron speciation in soil in flooded anaerobic culture under the same change is mainly driven by bacteria.

Analysis of correlation between soil waterlogging dissimilatory iron reducing and transformation of iron form: The correlation between soil waterlogging dissimilatory iron reducing and transformation of iron form is shown in Table-1.

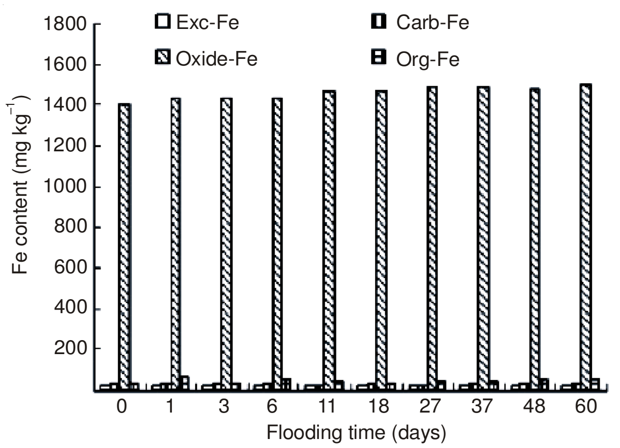

Fig. 6. Variation characteristics of Fe form after sterile purple soil flooding

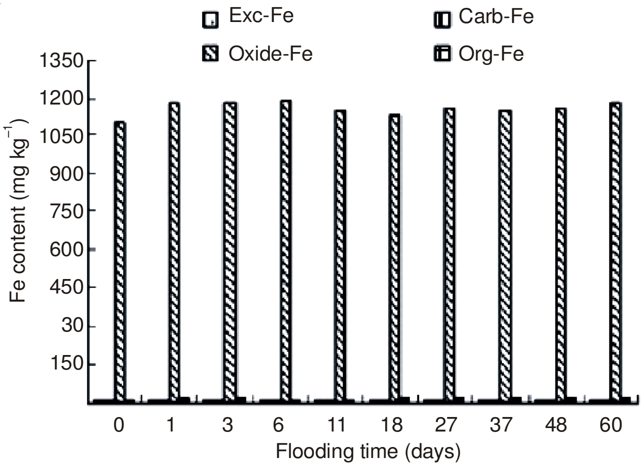

Fig. 7. Variation characteristics of Fe form after sterile yellow soil flooding

TABLE-1
PEARSON CORRELATION COEFFICIENT BETWEEN Fe(II) CONTENT AND Fe COMPONENT OF SOIL WATERLOGGING

Component	r	
	Purple soil	Yellow soil
Fe(II) and Exc-Fe	-0.211	0.242
Fe(II) and Carb-Fe	-0.089	0.154
Fe(II) and Oxide-Fe	0.685^{*}	0.871^{**}
Fe(II) and Org-Fe	-0.013	0.140

Note: *p < 0.05; **p < 0.01

From Table-1, it can be found that Fe(II) content in soil has significant positive correlation with Oxide-Fe content, but not correlated with Exc-Fe content, Carb-Fe content and Org-Fe content. It is visible that iron dissimilatory reduction is directly related to the form of iron to Oxide-Fe activation.

According to reports in the literature[6], dissimilatory iron reduction process is mainly the reduction of part lepidocrocite from amorphous iron oxide and crystal state iron oxide, its reduction product is mainly siderite ($FeCO_3$), magnetite (Fe_3O_4) or blue iron ($Fe_3(PO_4)_2·8H_2O$) *etc*.

Thus it can be seen, in the dissimilatory iron reduction process part of the reduction product from crystalline iron oxide the product is transformed into Oxide-Fe in the Tessier sequential extraction procedure and part of the crystalline iron oxide reduction products such as blue iron still exists in crystalline iron oxide (Res-Fe), can not be transformed into Oxide-Fe in the Tessier continuous extraction process. Therefore, iron oxide composition of the soil changes in flooded anaerobic condition, the activation is mainly caused by dissimilatory iron reduction.

Soil iron activation in flooded anaerobic reduction conditions has an important environmental significance. Usually Oxide-Fe has a strong adsorption capacity of pollutants, which is relatively stable in the environment and isn't easy to migrate and transform. It is of positive significance for the purification of water environment. In the Three Gorges Reservoir area, with the reservoir water level rising greatly, large areas of soil are flooded, in submerged condition it has been controversial that the soil is the pollutant source or sink. But under the condition of flooded soil the activation of iron will help increase the absorption capacity of soil on nitrogen and phosphorus nutrients and heavy metal, from this point of view, soil has the trend to transform into pollutants sink in waterlogged conditions.

Conclusion

pH and oxidation reduction potential decrease with the transition of soil redox condition and it is especially obvious for yellow soil. The content of Fe(II) increases to 3495.21 mg/kg for yellow soil and 536.44 mg/kg for purple soil. There are no obvious changes of redox condition and Fe(II)for sterile soil. It suggests that dissimilatory iron reduction should be driven by metabolic activity of microbe. With the transition of soil redox condition, the content of Oxide-Fe increases significantly and the content of Fe(II)and Oxide-Fe are significantly and positively correlated.

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