

*Original Research*

# Natural Mineral for Remediation of Iron- and Manganese-Contaminated Groundwaters

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## Abstract

Owing to geological structural factors, the groundwater in some areas naturally contains iron and manganese concentrations much higher than the permissible limits. In this study, scoria, a natural silicate mineral, was used to remove iron and manganese from water. For this purpose, filtration and cultivation of microorganisms were performed. The properties of scoria were characterized using BET, XPS, and SEM analyses, and the results showed that scoria is effective for iron and manganese removal. The mesoporous structure of scoria provides basic conditions for iron and manganese removal, and the high surface area provides a large number of adsorbent active sites. The surface of scoria showed significant changes after the experiment.  $Mn^{2+}$  adsorbed on the scoria surface was in the oxidized form, and adsorbed  $Fe^{2+}$  mainly existed as precipitates and colloids. Isolating and cultivating functional bacterial experiments indicated that some microorganisms exist in groundwater that contribute to the removal of iron and manganese; these iron and manganese bacteria, such as gallionella, exiguobacterium and citrobacter, could effectively remove iron and manganese under different initial concentrations of both. Overall, scoria was found to be a promising material for the removal of excessive iron and manganese from groundwater, thus serving as a meaningful reference for drinking water treatment by natural materials.

**Keywords:** iron and manganese, scoria, removal, groundwater, natural materials

## Introduction

Groundwater is one of most common sources of drinking water, and one of the main sources of drinking

water for people in rural areas, especially those in arid and semi-arid regions. The quality of drinking water has important implications for human health. Iron and manganese are micro elements present in the human body and they are common in groundwater because they dissolve in the water when it flows through or over rocks containing these minerals [1-3]. Long-term consumption of water with excessive

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iron and manganese is harmful to human health; for example, excess consumption of manganese can affect the central nervous system, damage brain tissues, and cause neurological disorders such as Parkinson's disease [4-5]. Water with excess iron and manganese also has a bad taste and unpleasant smell; in addition, the excess iron and manganese promote the growth of bacteria in water pipelines [6] and leads to the formation of iron and manganese oxides, causing blockages in pipelines, which increases the cost of water diversion. Overall, it not only affects human health, but also the people's living [7-8]. The occurrence of high iron and manganese concentrations well over the standard limits is common in many countries, especially in northeastern China. Accordingly, there is widespread concern about the methods and technologies used for removing the excess iron and manganese from groundwater.

To date, many methods such as oxidation [9-11], ion exchange [12-13], membrane separation [14-16], biosorption [17] and adsorption [18-19] have been used for removing excess iron or manganese in water treatment processes. The oxidation method involves using efficient oxidants such as chlorine [20], potassium permanganate [21], and sodium hypochlorite [22] to oxidize divalent ions ( $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ ) into iron and manganese oxides for removal. The disadvantage of this method is that by-products are produced during the treatment process. Iron exchange and membrane separation are recognized as an effective means of water purification, but they are often costly because the ion-exchange resins and ultrafiltration membranes need to be constantly changed. Because of the good performance and low cost of adsorptive materials, adsorption is generally considered to be a cost-effective removal technique [23]. Manganese sand, a well-known catalytic adsorbent [24], is widely used in water treatment for iron and manganese removal. Matured manganese sand facilitates the oxidation of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  with oxygen, and the formed iron and manganese oxides can be filtered out. However, it takes several months for manganese sand to mature; in addition, manganese sand hardens easily because of its high density. Hence, the use of manganese sand for iron and manganese removal has limitations, which make it problematic for use in developing regions.

Adsorbent materials play a major role in the water treatment process, and the use of suitable materials is key for water purification via adsorption. Many materials

have been used for removal of iron or manganese so far, modified materials such as functionalized silica gel [25] and glycine modified chitosan resin [26] was used for removal of  $\text{Fe(III)}$  and divalent manganese from solutions, the adsorption capacity was  $20.31 \text{ mg}\cdot\text{g}^{-1}$  for  $\text{Fe(III)}$  and  $1.3 \text{ mmol/g}$  for divalent manganese, respectively. Vermiculites [27] was also utilized for manganese (II) removal and the adsorption capacity was for  $28.32 \text{ mg}\cdot\text{g}^{-1}$ . Indica biomass [28] was studied for  $\text{Fe(II)}$  and  $\text{U(VI)}$  removal, and the results showed that it had a lower affinity for  $\text{Fe(II)}$  ions than for  $\text{U(VI)}$  ions. Although above materials is effective for iron or manganese removal, the modified process will increase the cost of water treatment and limit its practical application, especially in less developed countryside. Scoria, a natural silicate mineral, has been used for the removal of antibiotics [29], fluoride [30], petroleum [31], and heavy metals [32-33] owing to its good absorbability and chemical stability. A new filter material by scoria was synthesized for manganese ion removal [34], but the removal efficiency in iron was not studied in the research. Scoria has several advantages such as widespread availability, porous structure, environmentally friendly nature, and good performance for pollutant removal. However, there are a few reports on the use of scoria as a material for adsorbing iron and manganese simultaneously; its ability to remove iron and manganese from water should be studied further.

In this study, we examined the effectiveness of scoria in removing iron and manganese from solutions of natural and simulated groundwater. The removal mechanism was studied using a Brunauer-Emmett-Teller (BET) model, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) before and after filtration experiments. The iron and manganese bacteria were isolated and cultivated from natural groundwater, and the microbial diversity of the groundwater was analyzed. The removal effects under different initial concentrations were investigated.

## Materials and Methods

### Materials and Chemicals

Scoria was obtained from a volcanic field in the northeast Jilin Province, China. The particle sizes

Table 1. Physical and chemical properties of scoria.

Indexes	Quantity	Indexes	Quantity
Loose bulk density	$550\text{-}700 \text{ kg/m}^3$	Surface area	$8\times 10^3\text{-}1.5\times 10^4 \text{ cm}^2/\text{g}$
Share	2.4-2.6	Intercepted impurities	$10\text{-}13 \text{ kg/m}^3$
Compressive strength	$7.00\text{-}8.45 \text{ kg/cm}^2$	Nonuniformity coefficient	1.4-1.7
Porosity	72-78%	Head loss	<12 cm/m

were 0.8–2 mm. The properties of Scoria are shown in Table 1. The scoria was washed with distilled water and heated in an oven at 45°C for 10 h before the experiment.

### Filtration Experiment

Column filtration experiments were conducted in plexiglas columns with an effective length of 1100 mm and an internal diameter of 45 mm, as shown in Fig. 1. The columns were filled with scoria and filled with deionized water to minimize air entrapment before the experiment. An inlet and outlet were made at the top and bottom of the column to ensure the inflow was well distributed and to prevent the loss of scoria particles. A 30- $\mu\text{m}$ -aperture nylon mesh was placed at the top and bottom of the column. Influent solutions of iron and manganese were prepared by diluting the stock solutions with deionized water. The influent solution was then pumped into the column with a hydraulic retention time of 30 min using a peristaltic pump. The influent and effluent were sampled once a day, and an ultraviolet spectrophotometer (UV-2100, Hengping Inc., China) was used to monitor the iron and manganese concentrations in both. Solutions of natural and simulated groundwater were used as influent solutions for each of the two groups. Based on the concentration of iron and manganese in natural groundwater, the concentrations of iron and manganese in the simulated groundwater group were set as 3.0 mg/L and 1.5 mg/L, respectively.

### Characterization of Scoria

The porous structure of the scoria before and after the filtration experiments was analyzed based

on the surface area using a pore size analyzer (JW-BK132F) by  $\text{N}_2$  adsorption-desorption isotherms at 77 K. Before the analysis, the samples were out-gassed at 50°C under vacuum for 6 h. The pore diameter distribution was determined using the Barrett-Joyner-Halenda (BJH) method [35]. The surface area and pore size distribution were analyzed using the BET mode [36] for the  $\text{N}_2$  desorption data. The micropore volume ( $V_{D-R}$ ) and micropore surface area of the scoria samples were evaluated using Dubinin-Radushkevich equations [37]. XPS analysis was conducted before and after the experiment using a photoelectron spectrometer (ESCALAB™ 250Xi). The surface morphology of the scoria was studied before and after the experiment via SEM.

### Screening of Iron and Manganese Bacteria

The iron/manganese bacteria in groundwater sample were screened by inoculating the natural groundwater in a selective medium for iron/manganese and bacteria (SMIB/SMMB), and then, the SMIB was heated in an oven at a constant temperature (10°C). To study the removal effect of iron/manganese under different iron/manganese concentrations, serial liquid mediums with different iron/manganese concentrations ( $[\text{Fe}^{2+}] = 5, 10, 20, 50, \text{ and } 100 \text{ mg/L}$ ;  $[\text{Mn}^{2+}] = 2, 5, 10, 20, \text{ and } 50 \text{ mg/L}$ ) were used. The screened iron/manganese bacteria were inoculated in serial liquid medium for iron/manganese bacteria (BLMB), and then the BLMB was placed in an incubator at a constant temperature (10°C), and the iron and manganese concentrations in the BLMB were sampled and tested once a day. The composition of the medium for the iron and manganese bacteria is as follows:

Selective medium composition for iron bacteria (SMIB): 10 g  $\text{C}_6\text{H}_8\text{FeNO}_7$ , 0.5 g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.1 g  $\text{K}_2\text{HPO}_4$ , 0.2 g  $\text{CaCl}_2$ , 0.5 g  $\text{NaNO}_3$ , 0.5 g  $\text{NH}_4\text{NO}_3$ , 16 g agar, and 1000 mL deionized water. The pH of SMIB was adjusted to 6.8–7.2 using HCl and NaOH.

Selective medium composition for manganese bacteria (SMMB): 0.8 g peptone, 0.2 g yeast extract powder, 0.2 g  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ , 0.1 g  $\text{K}_2\text{HPO}_4$ , 0.2 g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.2 g  $\text{NaNO}_3$ , 0.1 g  $\text{CaCl}_2$ , 0.1 g  $(\text{NH}_4)_2\text{CO}_3$ , 16 g agar, and 1000 mL deionized water. The pH of SMIB was adjusted to 6.8–7.2 using HCl and NaOH.

Basic liquid medium for iron and manganese bacteria (BLMB): 0.5 g peptone, 0.3 g  $\text{C}_6\text{H}_{12}\text{O}_6$ , 0.2 g yeast extract powder, 0.1 g  $\text{K}_2\text{HPO}_4$ , 0.2 g  $\text{NaNO}_3$ , 0.1 g  $\text{CaCl}_2$ , 0.1 g  $(\text{NH}_4)_2\text{CO}_3$ , ferric ammonium citrate,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (the quantities were modified according to serial iron/manganese concentrations required;  $[\text{Fe}^{2+}] = 5, 10, 20, 50, \text{ and } 100 \text{ mg/L}$ ;  $[\text{Mn}^{2+}] = 2, 5, 10, 20, \text{ and } 50 \text{ mg/L}$ ), and 1000 mL deionized water with a pH of 6.8–7.2.

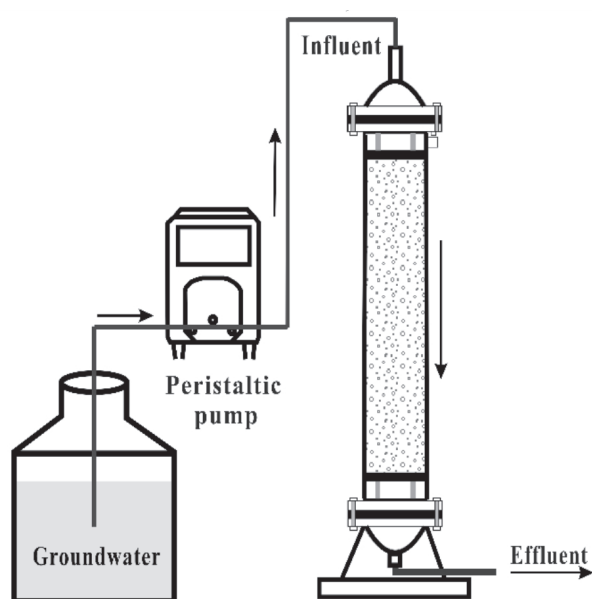


Fig. 1. Schematic of scoria filtration set-up.

## Results and Discussion

### Material Characterization

Based on the  $N_2$  adsorption-desorption isotherms, the average pore size of the scoria was calculated to be 6.86 nm, and the pore volume and the BET surface area were 0.018  $cm^3/g$  and 3.069  $m^2/g$ , respectively. The specific surface area ( $S_{BET}$ ), micropore surface area ( $S_{DR}$ ), micropore volume ( $V_{DR}$ ), and mesopore volume ( $V_{BJH}$ ) of the scoria samples are listed in Table 2. The values in Table 2 indicate that the micropore volume was much smaller than the mesopore volume for each sample. Both the micropore volume and mesopore volume of the scoria after the experiment were much larger compared to that of raw scoria, which may due to the impregnation and swelling caused by the solution to some extent. The porous nature of scoria was determined with  $N_2$  adsorption-desorption isotherms, as shown in Fig. 2a). The isotherm can be classified as a type-IV isotherm, which is characteristic of mesoporous material [38]. Desorption data were used to analyze the pore size distribution using the BJH model, and the average value was 4.423 nm, as shown in Fig. 2b). The high surface area of the scoria provided a large number of adsorbent active sites. When these sites were exposed to iron and manganese ions, colloidal particles such as  $Fe^{3+}$  and manganese compounds formed. The mesoporous structure of scoria provides the basic conditions for the adsorption of ions and colloidal

particles in a solution, which results in effective iron and manganese removal.

The surface elemental composition of the scoria was determined using the XPS technique. The XPS spectrum and high-resolution spectrum are shown in Fig. 3. Fig. 3a) shows that C, O, Si, Al, Fe, and Ca are the main elements in scoria. The high-resolution XPS spectra of O1s are shown in Fig. 3(b-c). Three peaks could be fitted to O1s, indicating that three types of O were present. The peaks at 531.1 eV, 531.6 eV, and 532.6 eV can be assigned to  $-OH$  [39], manganese oxide ( $Mn-OH$ ), and adsorbed oxygen  $OH^-$ , respectively [40]. The peak of  $Mn-OH$  and  $OH^-$  increased in the O1s score level spectra. This shows that the proportion of  $Mn-OH$  and  $OH^-$  in the scoria after the experiment was greater than that before the experiment, and the binding energy of scoria before and after the filtration experiments corresponded to the same oxidation state, indicating that the  $Mn^{2+}$  adsorbed on the scoria surface was in oxidized form [41]. A similar conclusion was proposed in a study on Mn removal [42]. The high-resolution XPS spectrum of Fe 2p is shown in Fig. 3e). It has two main peaks at 724.95 and 711.25 eV, corresponding to  $Fe\ 2p_{1/2}$  and  $Fe\ 2p_{3/2}$ , respectively [32]. The high-resolution XPS spectra for  $Fe\ 2p_{3/2}$  are shown in Fig. 3d), where there are two peaks that can be fitted, which are attributed to the  $Fe-O$  bond. There was no significant change in the Fe 2p peak before and after the experiment, which might be due to the fact that precipitates and colloids were formed by  $Fe^{3+}$  in solution and they were trapped during the experiment by the scoria.

Table 2. Physical properties of scoria samples.

Sample	$S_{BET}$	$D_{DR}$	$S_{DR}$	$V_{DR}$	$D_{BJH}$	$S_{BJH}$	$V_{BJH}$
	( $m^2/g$ )	(nm)	( $m^2/g$ )	( $cm^3/g$ )	(nm)	( $m^2/g$ )	( $cm^3/g$ )
Raw scoria	3.069	15.350	7.106	0.00134	6.862	10.360	0.018
Scoria (after experiment)	5.34	12.671	14.653	0.00158	5.400	20.588	0.028

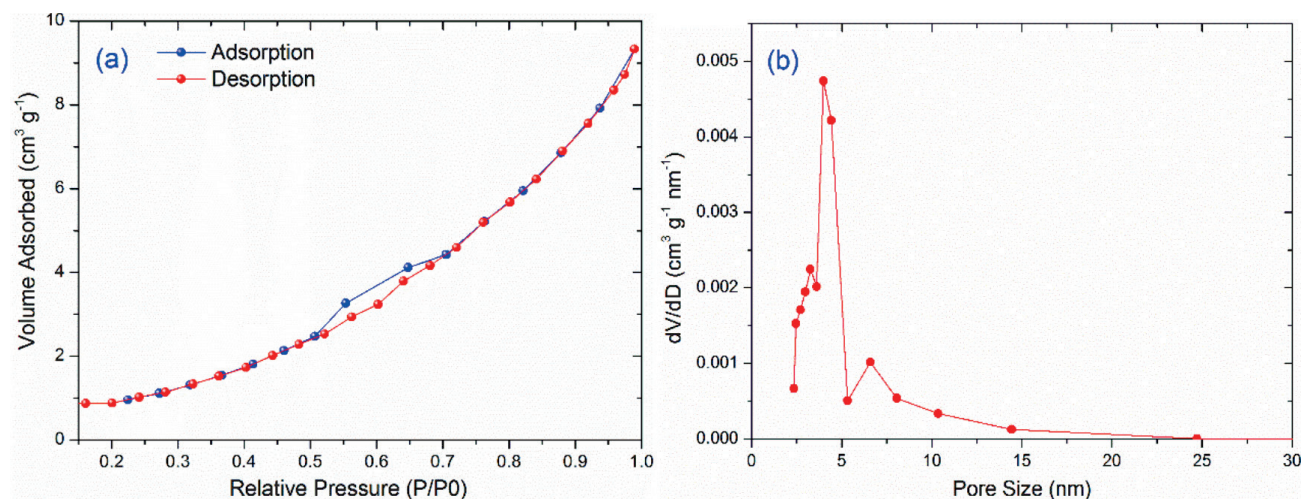


Fig. 2. a)  $N_2$  adsorption-desorption isotherms of scoria and b) distribution curve of scoria pore size.



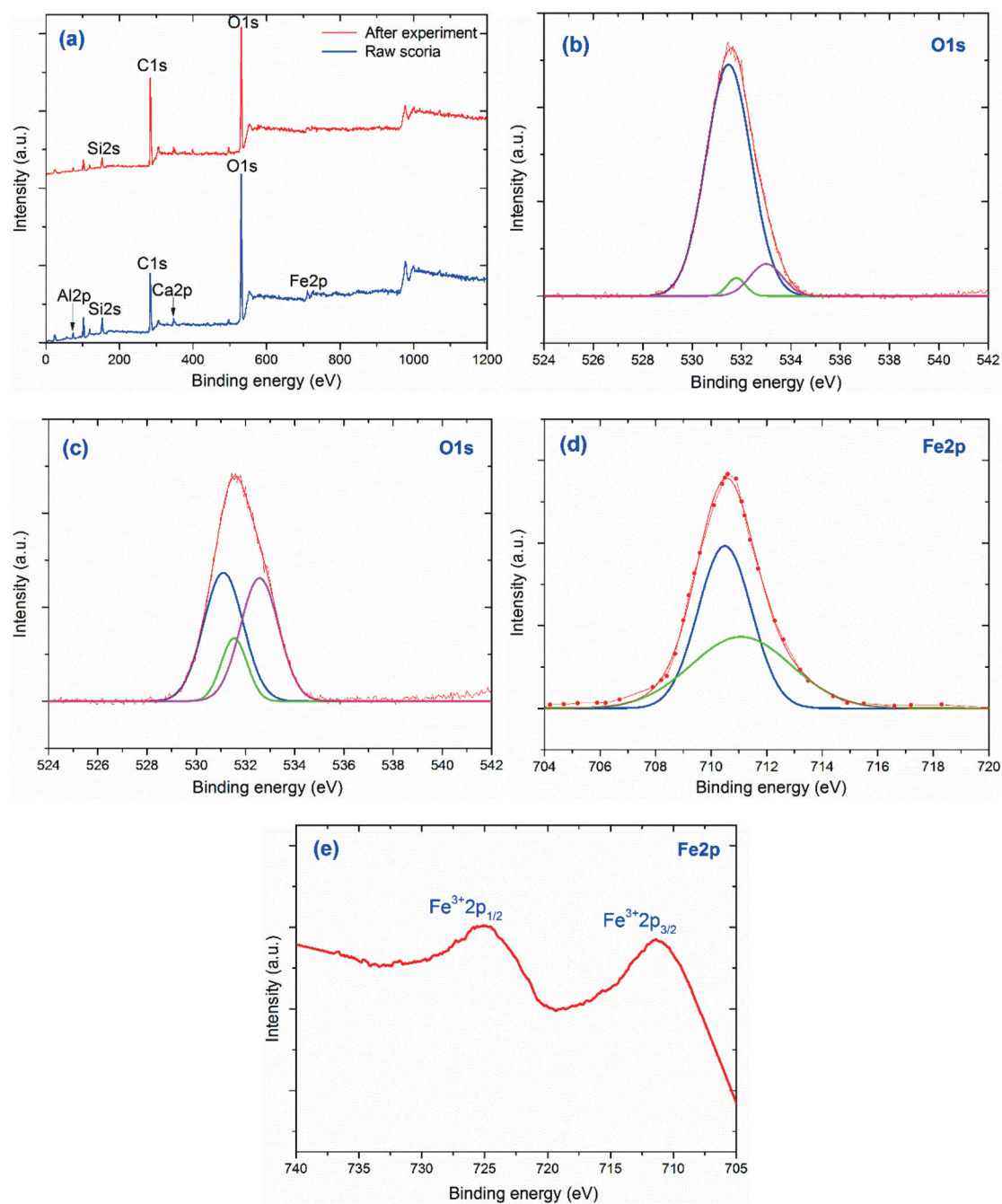


Fig. 3. a) XPS wide scan; b) high-resolution XPS spectra for O1s of raw scoria; c) O1s of scoria after experiment; d) high-resolution XPS spectra for Fe2p of raw scoria; and e) Fe2p of scoria after experiment

Changes in the surface morphology of the scoria are shown in the SEM images in Fig. 4. There are several small pores on the surface of raw scoria; however, after the filtration experiment, the surface was relatively smoother and more irregular than that before the experiment (Fig. 4b), as more granular substances were present on the surface after filtration. In addition, the surface after filtration became smoother and some floccules and membranes collected on the surface. These floccules and membranes formed as a result of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  being hydrolyzed in solution. The adsorption of colloid particles, floccules, and membranes onto

the surface of the scoria resulted in the changes in the scoria surface. The surface area of scoria was increased by the floccules and membranes, which facilitated the adsorption and oxidation of iron and manganese in the solution.

#### Scoria Filter for Iron and Manganese Removal

The filtration experiment results are shown in Fig. 5 and Fig. 6. Scoria was very effective for iron and manganese removal in both groups. During the 39 days of the filtration experiment, the concentrations

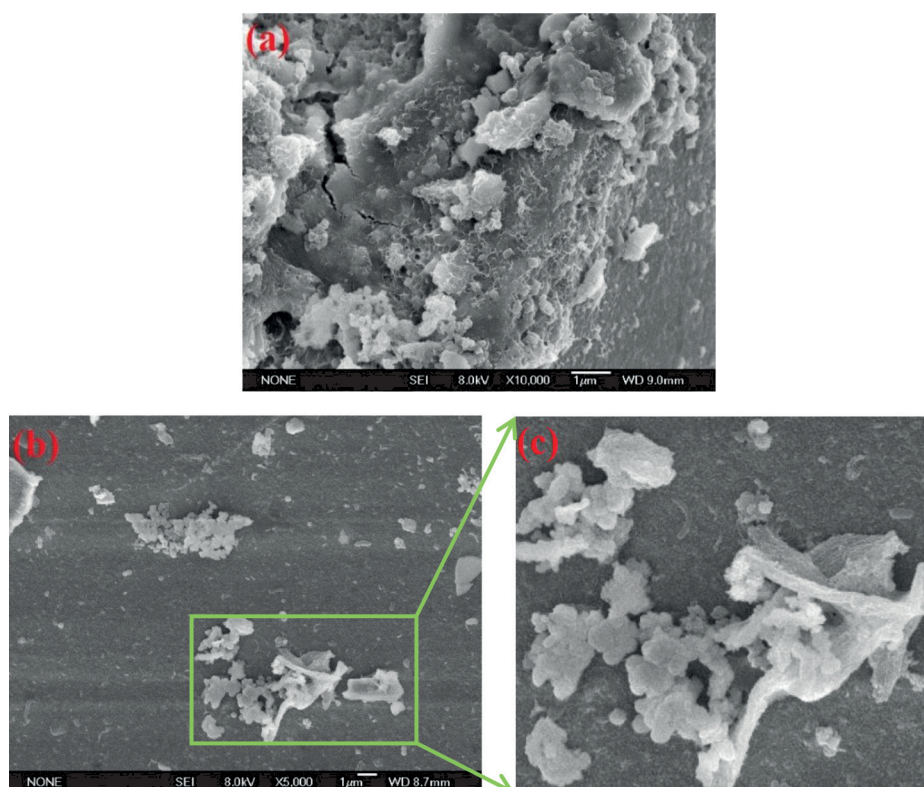


Fig. 4. SEM micrograph images a) before and b) and c) after the experiment.

of iron and manganese were lower than 0.3 mg/L and 0.1 mg/L (Guidelines for Drinking-water Quality, WHO), respectively. The concentration of iron was greater than 0.3 mg/L (GB5749-2006, China) from the 48<sup>th</sup> day and that of manganese was greater than 0.1 mg/L from the 46<sup>th</sup> day. However, in the simulated groundwater group, the concentration of iron was greater than 0.3 mg/L from the 40<sup>th</sup> day and that of manganese was greater than 0.1 mg/L from the 39<sup>th</sup> day. The main reason for the differences is quite likely the microorganisms in the influent using the iron and manganese as the nutrients for growth in the

natural groundwater group, i.e., some of the iron and manganese was consumed by the microorganisms; hence, the filtration system could be operated for longer to meet the national standards.

During the 60-day filtration experiment, brown flocculent precipitate, which consisted of multivalent oxides of iron and manganese, attached itself to the surface of the scoria. These oxides transformed Mn (II) into Mn (IV) and promoted the adsorption of Mn (II) and Fe. Moreover, they facilitated the formation of manganese oxides. The main removal mechanisms of iron and manganese were adsorption and catalytic

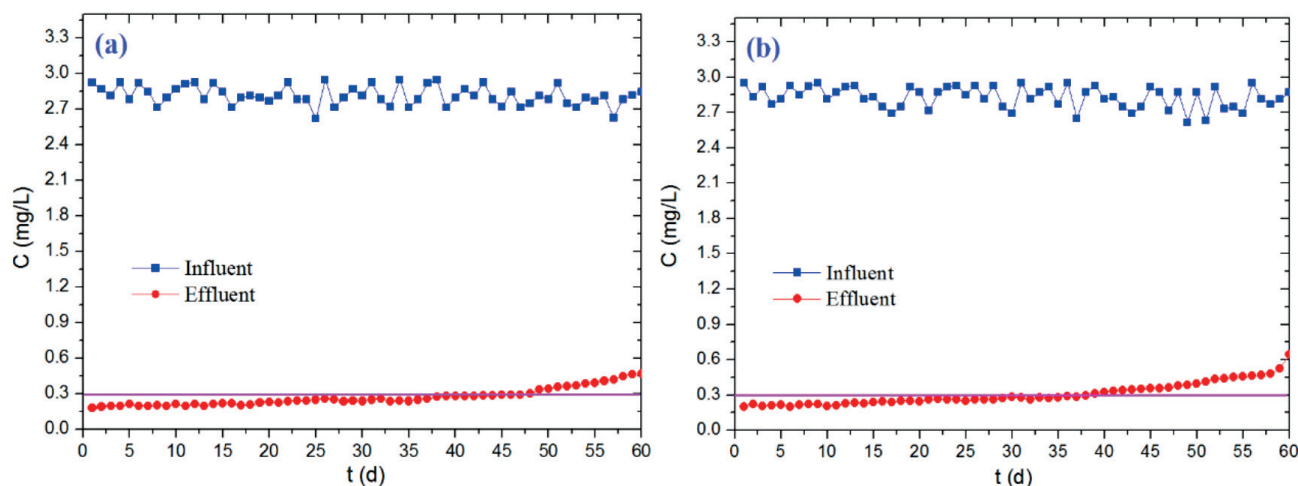


Fig. 5. Iron removal efficiency in a) natural groundwater and b) simulated ground water.



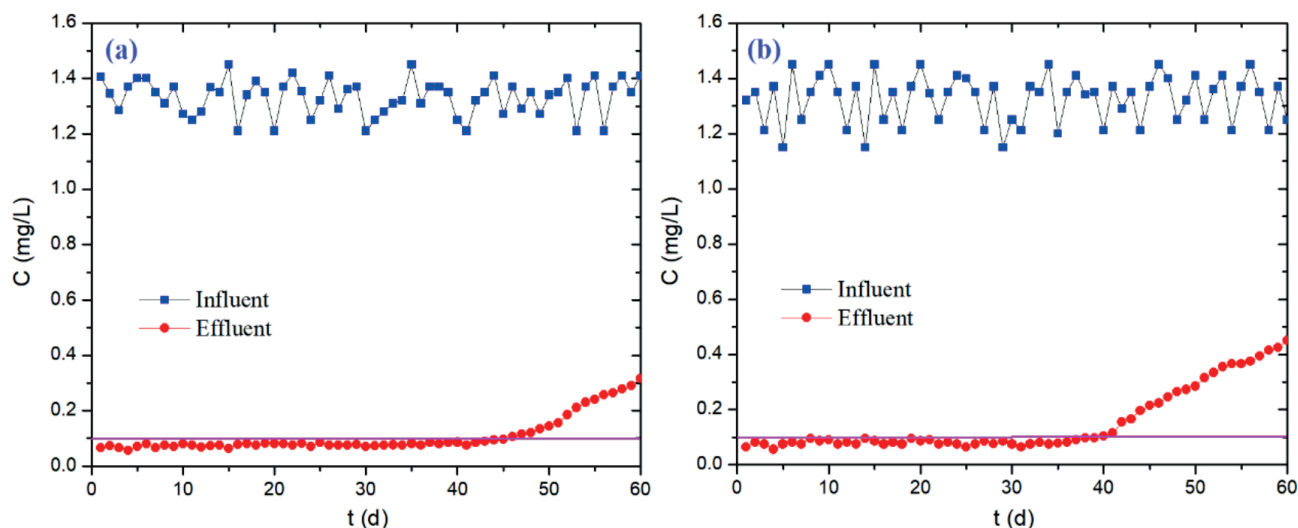


Fig. 6. Manganese removal efficiency in a) natural groundwater and b) simulated ground water.

oxidation. The BET analysis showed that the scoria has large surface area and high pore volume. The large surface area provides active sites for adsorbing  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  in solution. Some of the  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions were oxidized to iron and manganese oxides with higher valence states such as  $\text{Fe}_2\text{O}_3$  and  $\text{MnO}_2$  owing to the dissolved oxygen. The changes in valency were observed via XPS analysis.

In the conventional means of biological drinking water treatment for iron and manganese removal, it takes ~100 days or more for the manganese oxidizing biofilm to ripen. Hence, using this method for iron and manganese removal can not only save time and but also provide the desired results.

#### Specialized Bacteria for Iron and Manganese Removal

As observed in the filtration experiment results, some functional bacteria might exist, which can consume the iron and manganese in groundwater. To test this hypothesis, an experiment involving functional microorganisms for iron and manganese removal was conducted. Selective media were used to isolate the

specialized bacteria, and the microorganisms were inoculated in selective media with different cultures via a repeated plate-streaking method. Then, the selective medium was placed in a constant-temperature oven at  $10^\circ\text{C}$ , nourished, and then observed. Gram's staining experiment was conducted for polarity identification to determine the microbial characteristics of the isolated microorganisms, and the morphological structure was observed using a microscope. The experimental results are shown in Fig. 7 and Fig. 8.

As shown in Fig. 7, the iron bacterial colonies are orange, surface drying, round or ovular, rough-edged, single scattered, and have raised centers and dried surface, while the manganese ones are round, single scattered, white and opaque, damp on the surface, and have edge regularization. In addition, the manganese bacterial colony is much smaller than the iron one. As shown in Fig. 8, a gram stain revealed that gram negative and positive bacteria coexisted in both selective media, and the main kinds of microbes in the selective media were bacterium and brevibacterium species.

The removal of iron and manganese by selected bacteria were studied at different initial concentrations in a liquid medium (BLMB) and the results are shown in Fig. 9. The iron and manganese bacteria were found

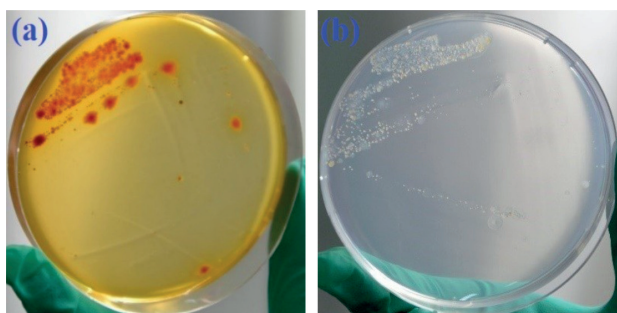


Fig. 7. a) Isolated iron and b) manganese bacteria colonies in a selective medium.

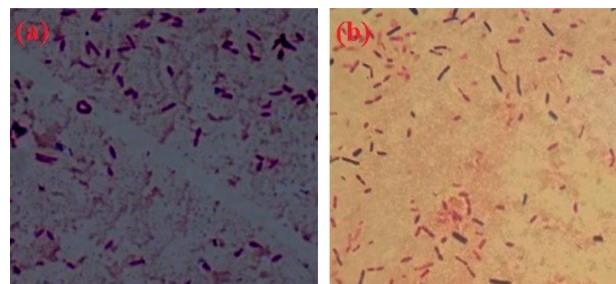


Fig. 8. Light microscopy images of bacteria for a) iron and b) manganese removal.

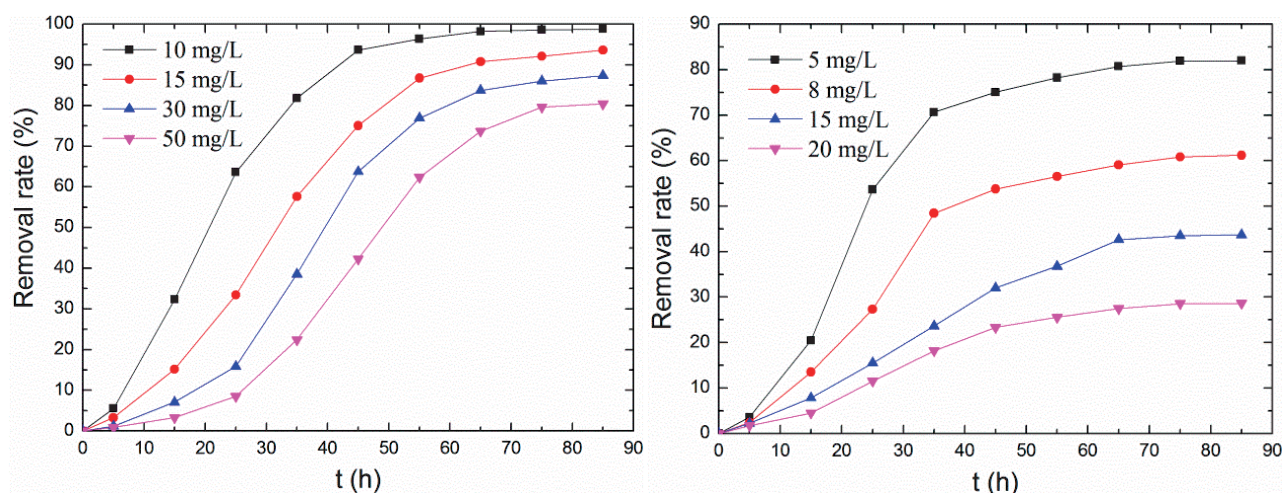


Fig. 9. Removal rates of iron (left) and manganese (right) with selected bacteria

to have good iron and manganese removal abilities. As shown in Fig. 9a), the removal rate of iron increased quickly from the 5th hour and it reached up to 94% in the 45th hour, where the concentration of iron in the liquid medium was 10 mg/L. In general, the changes in the removal rates were generally consistent under different initial concentrations of iron. The removal rate grew rapidly in the first 55 hours and kept stable for the next few hours. The removal rate of iron reached more than 80% in the late stage after 75 hours, which indicated that the iron bacteria were capable of removing iron regardless of the initial iron concentration.

As shown in Fig. 9b), the removal rate of manganese remained low in first 4 days because there was little manganese bacteria in the early growth stage to consume the manganese. The manganese removal rate began to increase rapidly between the 4th and 8th days; the removal rate increased to 70% in first 6 days while

the initial concentration was 2 mg/L. The bacteria proliferated between the 2nd and 6th days, leading to the consumption of a large amount of nutrients including manganese during this period. The removal effects of manganese varied according to the initial concentrations, with the removal rate changing from 16% to 88%. However, the changes in the removal rate curves for different initial manganese concentrations were mostly consistent.

### Analysis of Microbial Diversity in Groundwater

As presented in Section 3.3, it is certain that iron and manganese can be consumed by bacteria that naturally exist in groundwater. The species of microbes in groundwater samples were studied via high-throughput sequencing technology to determine the types of iron and manganese bacteria naturally present

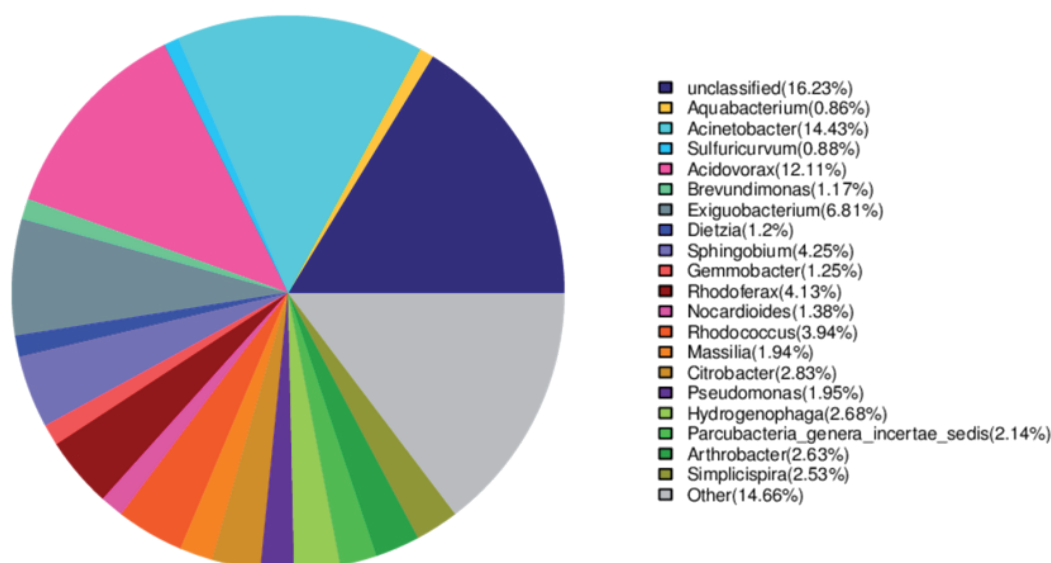


Fig. 10. Genus-level groundwater sample community structure distribution map.



in the groundwater. As shown in Fig. 10, the main microbes were gallionella (38.39%), exiguobacterium (10.47%), citrobacter (9.87%), sulfuricurvum (7.44%), pseudomonas (7.09%), flavobacterium (4.63%), acinetobacter (4.58%), ralstonia (0.19%), bacillus (0.19%), polaromonas (1.97%), rhodoferax (1.77%), massilia (1.43%), methyloferax (1.06%), parclubacteria genera incertae sedis (0.44%), sideroxydans (0.37%), and so on. Among the bacteria detected, gallionella, exiguobacterium, and citrobacter were the dominant microflora in the groundwater sample. Functional bacteria such as gallionella and exiguobacterium contribute to iron and manganese removal. Gallionella spp. and the gallionella family are known as iron-oxidizing bacteria [43-44]; hence, they were responsible for iron removal. Exiguobacterium, citrobacter, pseudomonas, and bacillus were responsible for manganese removal [45-47].

The influent iron and manganese were partly consumed by the functional bacteria, which led to better iron and manganese removal in the natural groundwater group. The iron bacteria constituted 38.39% of the total microbial biomass in the groundwater sample, while the manganese bacteria accounted for 27.62%. The greater content of iron bacteria compared to manganese bacteria in the groundwater was the major reason why the removal of iron was better than that of manganese over 60 days.

## Conclusions

A natural silicate mineral (scoria) was studied for the removal of iron and manganese from groundwater. Scoria was found to be effective for the purification of water containing excessive amounts of iron and manganese. The structure and surface morphology of the scoria were studied via characterization techniques, and the results revealed that the mesoporous structure of scoria is suitable for the adsorption of ions and colloidal particles. Floccules, membranes, and oxides were formed on the surface of the scoria after the filtration experiment. The  $Mn^{2+}$  adsorbed onto the scoria surface was in the oxidized form, and the precipitate and colloids formed as a result of  $Fe^{3+}$  were trapped in the surface of scoria during the experiment. Some naturally existing microorganisms in groundwater such as gallionella, exiguobacterium, citrobacter, pseudomonas, and bacillus were found to have significantly positive effects on iron and manganese removal, confirming the self-purification ability of groundwater.

Based on these results, considering its cost and high removal efficiency, it can be concluded that scoria is a promising material for the removal of excessive iron and manganese from groundwater. However, to expand its practical use in the decontamination of contaminated water, further studies are needed to probe its application in water purification in the future.

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## Conflicts of Interest

There are no conflicts to declare.

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