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A Novel Method of Removing Mn(II)Ions from Water by a Combination of New Symbiotic Microbes

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Abstract

Typically, manganese (II) ions are incompletely removed from water as MnO_2 on increasing the pH of the water to 10. The water then has to be neutralized before it can be used. We propose a new and effective method for removing Mn(II) from water using a new combination of symbiotic microbes consisting of manganese-oxidizing bacteria and filamentous algae. The microbes rapidly oxidize Mn(II) to Mn (IV) at a neutral pH with no organic matter required as a nutrient and MnO_2 is precipitated immediately. This differs from the use of heterotrophic manganese-oxidizing bacteria where organic nutrients are required.Our results suggest that this method will be useful in developing new systems for removal of manganese(II) ions from industrial and mining wastewater and drinking water. In addition, there are other possibilities such as recycling of dry batteries which are presently discarded without treatmen

Introduction

Manganese (Mn) compounds are toxic substances that cause harm to the central nervous system, namely, a mental disability or resemblance to Parkinson's disease. Consequently, it is necessary to remove Mn(II) ion from industrial and mining wastewater and drinking water. Staining skin and inhalation by solid compounds of Mn are also avoided [1].

In Japan, standard value of Environmental Regulation (ER) for soluble Mn, i.e. Mn(II) ion, is <0.05mg/l based on the Basic Environment Law. This is set as administrative object to prevent water pollution, for protection of human health and the preservation of the living environment. On the other hand, business offices and factories, to which the Water Pollution Control Law applies, must observe rule relating to the Regulation of Discharge of Effluent (RDF). The standard value of RDF for Mn(II) is <10mg/l, and is lax against the standard value of ER (<0.05) in Japan.

Up to the present, Mn(II) ion in water is incompletely removed as MnO_2 on increasing the pH of the water to 10, and the oxidation by aeration based on the Oxidation-Reduction reactions shown in Fig. 1. However, such a treatment has a problem that the costs of equipment and the running costs are very expensive. It is also bad for human health to add a lot of alkaline, acid, and artificial organic coagulants in such treatment. Accordingly, the developing an other removing method of Mn(II) is strongly desired. Microbial oxidation of Mn is expected as the useful method for this purpose. However, adequate method has not been developed.

On the other hand, it is a worldwide environmental problem that an enormous quantity of dry batteries is presently discarded without treatment. Annual quantity of waste dry battery in Japan is about 100,000 tons.

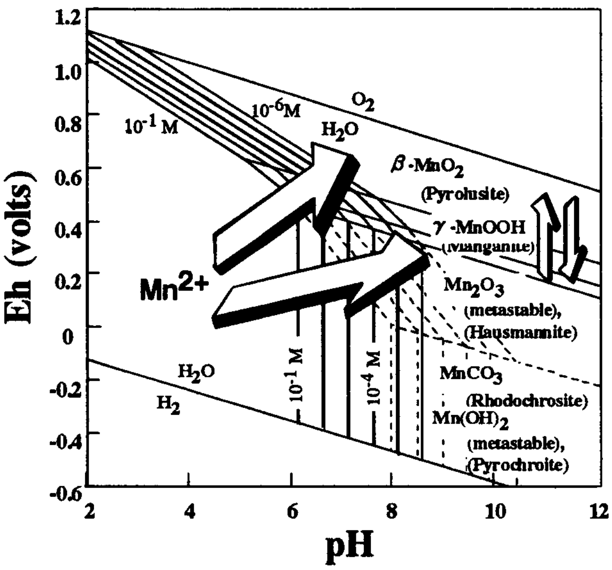

Fig. 1 Stability diagrams for the phases and minerals of manganese as a function of Eh and pH

About ten percent of these is used for TV tube parts and etc. During discharging of electricity, MnO_2 in the battery changes to MnOOH (see Figure 1). Although reproduction of MnO_2 from MnOOH is necessary to use Mn again for the battery, such an adequate technology has not been developed.

We here newly report a novel method for removing Mn (II) ions from water using a combination of symbiotic microbes consist of Mn-oxidizing bacteria and microbial algae. The microbes were discovered at a unique living ore deposit of MnO_2 in Hokkaido, Japan. The microbes rapidly oxidize Mn(II) to Mn(IV) at an acidic to a neutral pH with no organic matter required as a nutrient, and MnO_2 is precipitated immediately. This differs from the use of heterotrophic Mn-oxidizing bacteria where

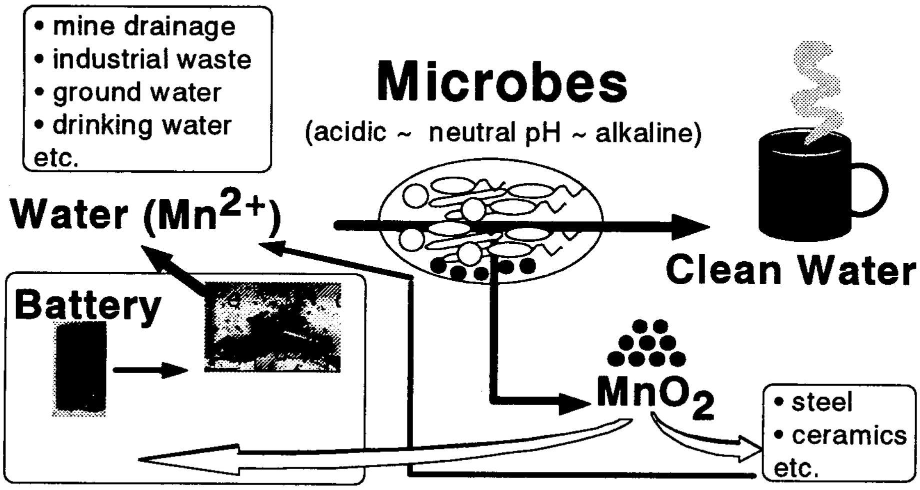

Fig. 2 General concept of a new microbial method for clean or recycling of manganese

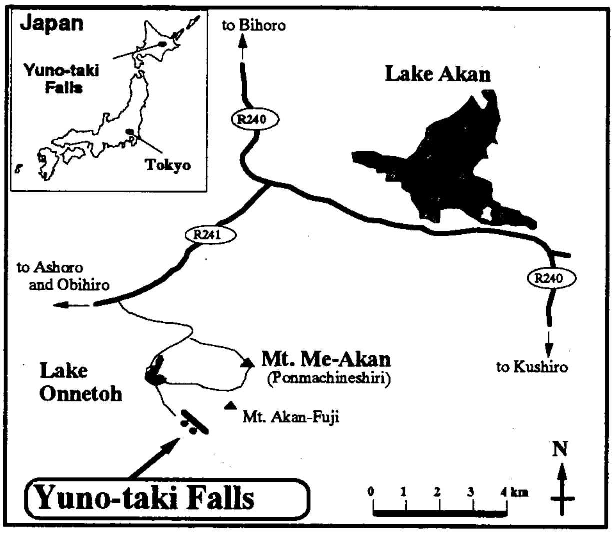

Fig. 3 A location map of the research area

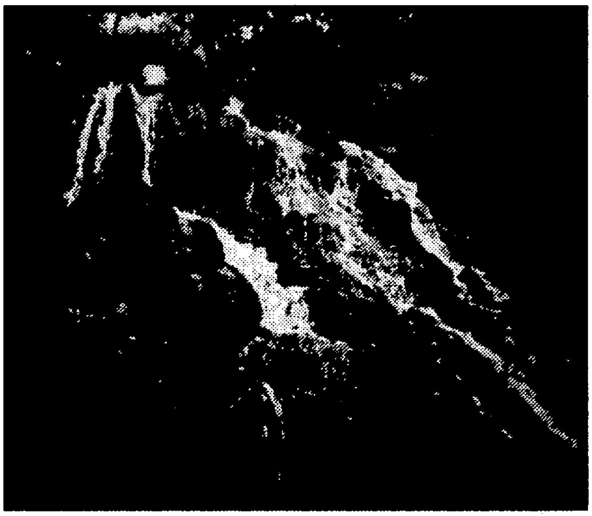

Fig. 4 The Yuno-taki Falls. Hot spring water is Emanating from the crack at the top of lava precipice.

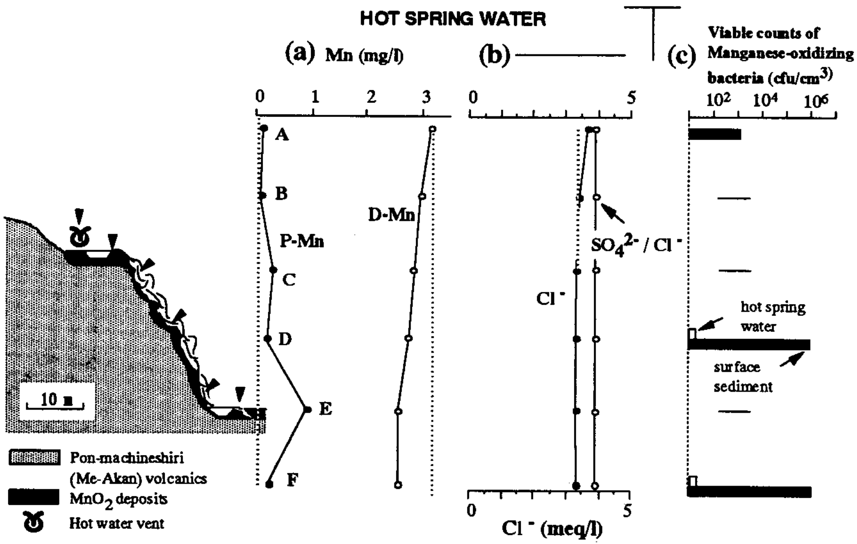

Fig. 5 Distribution of : (a) D-Mn and P-Mn, (b) Cl- and DO42-/Cl- ratio in falling hot spring water, and (c) viable count of manganese-oxidizing bacteria in surface and hot spring water.

organic nutrients are required. In addition, there are other possibilities such as recycling of dry batteries mentioned above. Fig.2 shows the concept of the method[2].

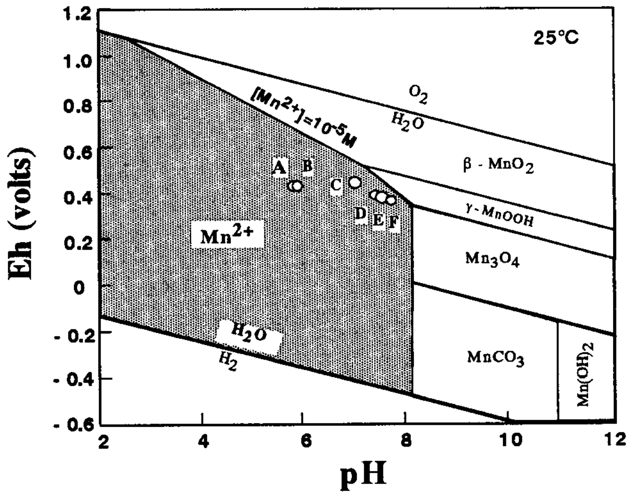

Fig. 6 pH-Eh stability diagrams for the phases and minerals of manganese, showing the data of falling hot spring water (position A to F in Fig. 5)

Current methods for removing Mn(II) ion from water

In case of utilizing underground water or well water for drinking, the concentration of Mn(II) ion in those water are often higher than ER of 0.05mg/l. As the pH of the natural water is weak acidic to neutral, Mn(II) ion is incompletely removed as MnO_2 on increasing the pH of the water to 10 with oxidation by aeration. Besides, porous zeolite that combined with catalytic manganese

←10μm→

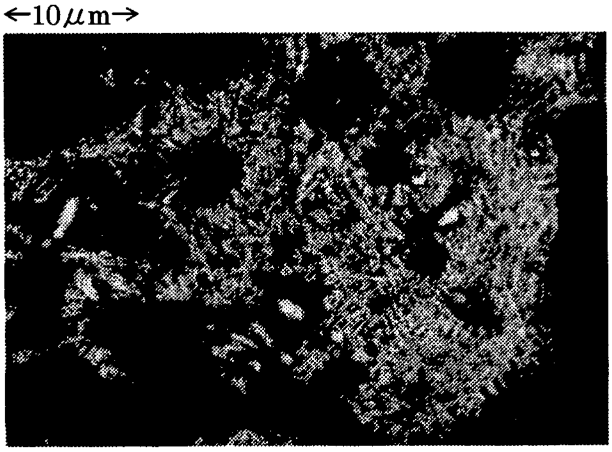

Fig 7 A phase-contrast micrograph of symbiotic microbial mat that consisting of manganese-oxidizing bacteria, filamentous algae, and Mn oxide particles

oxide is applied for such waters whose pH should be risen to 7.5 or over beforehand[3]. These treatments have been putting to practical use for many types of water that contain low or high concentration of Mn(II).

However, developing a new method without such additives is desired especially for low concentration of Mn(II).

In Japan, Metal Mining Agency of Japan (MMAJ) and

←10μm→

Fig.8 A micrograph of pure manganese-oxidizing bacterial strain that isolated from symbiotic microb; l mat

mining companies have been applying an above mentioned technology, i.e. regulating to pH 10, to control the mining pollution at many locations. Removing heavy metal ion, especially Mn(II), from drainage is necessary to prevent mining pollution. Generally, concentration of Mn(II) in mine drainage is extremely high. As it is often about 100mg/l or over, neutralization technology above mentioned is also applied for strong acidic (e.g. pH 1.8 or 3.5) drainage at sulfur or Kuroko mine, and for weak acidic to neutral (e.g. pH 6.2) drainage at manganese mine. Depending of high cost of these technology, developing a new easy and low cost method is strongly expected[4].

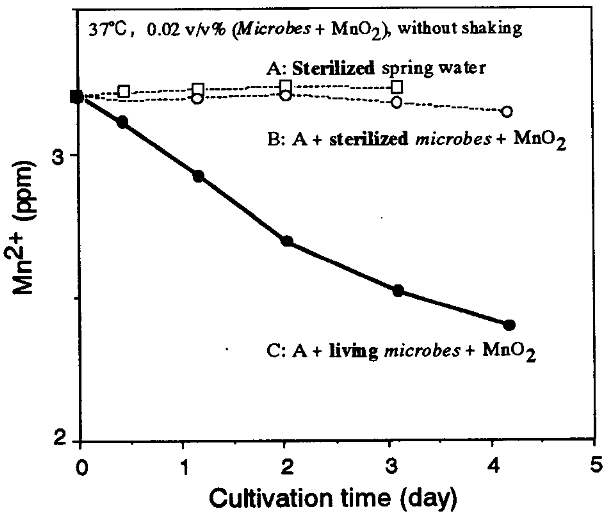

Fig 9 Liquid culture experiment using hot spring water and 0.02

These treatments require the addition of alkaline to pH 10, and the water then has to be neutralized by adding acid before it can be used. Furthermore, the certain

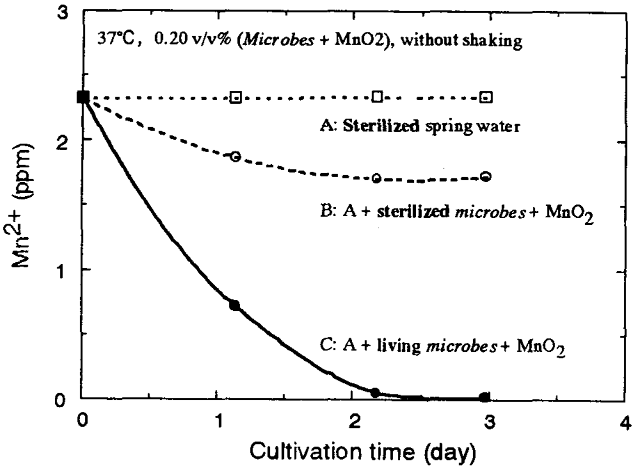

Fig. 10 Liquid culture experiment using hot spring water and 0.20 v/v % of sediment(microbes and MnO2)

organic polymer coagulant in above process potentially induces cancer. Up to the present, however, practical clean technology for Mn(II) in water by using Mn-oxidizing microbe has not been established.

Discovery of a unique living ore deposit of MnO_2

During researching the microbial mineralization of manganese in modern and ancient ore deposits for many years[5,6], we suspected that the Mn-depositing or Mn-oxidizing microbes will contribute to develop a new effective method for removing Mn(II) in wate[7,8].

Manganese oxide minerals have been precipitating from the hot spring water to form thick piles at the wall of the Yuno-taki Falls in east Hokkaido, Japan (Fig. 3 and 4). d D-values of water indicate that water of this spring and surrounding lakes are thought to be of meteoric origin. Concentration of dissolved manganese (D-Mn, i.e. Mn^{2+}) in hot running water decreases toward the bottom of the wall, but that of particulate manganese (P-Mn, i.e. MnO_2) increases (Fig. 5). Chemical compositions (Table I), pH and Eh (Fig. 6) of the spring water suggest that this decreasing trend of D-Mn is not mainly caused by dilution effect of shallow groundwater of high dissolved oxygen or by an autoxidation of Mn^{2+}. From a quantity of flow and the difference in concentration of D-Mn, it is estimated that ca. 1.1 ton/year of manganese (calculated as MnO_2) precipitate and parts of them form a wall-sediment those analytical value is shown in Table 1.

Many manganese-oxidizing bacteria (ca. 106 cfu/cm3) were detected in the surface sediments of the waterfall, while they are extremely few in the falling water. Under the epifluorescence microscopic observations, bright red fibrous algae were also abundant in dense mat of the surface sediments. These facts suggest that the symbiotic microbes (Fig.7,8) consisting of manganese-oxidizing bacteria (Fig.8) and filamentous algae may contribute to manganese oxidation.

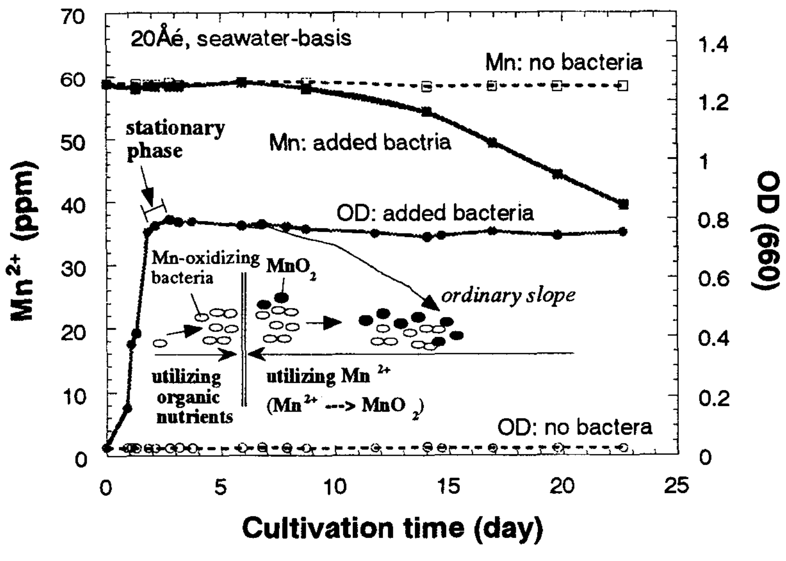

Fig. 11 Liquid culture experiment using pure manganese -oxidizing bacterial strain isolated from symbiotic microbial mat of the Yuno-taki Fall. The seawater-basis culture medium contains organic nutrients and Mn(II) at 7.5.

Evidence of Microbial formation of MnO deposit at the Yuno-taki Falls, and its application to a new technology of clean and recycling for manganese

Since the possibilities of microbial formation process of manganese oxide is suggested, liquid culture experiments were done to evaluate the ossibilities by using the native samples. Native samples of the hot spring water and the deposit (within 3 mm depth from the surface) contain living microbes, organic compounds, and manganese oxide particles. This hot spring water (≈ 37 °C) also contains saturated DO and approximate null of dissolved organic carbon (DOC).

the sterilized medium, i.e. no bacteria , have never changed for 23 days cultivation. Before starting the experiment, it was generally expected that OD will drop soon after stationary phase as shown in Fig. 11 (ordinary slope). In other words, biomass will drop as a result of nutrient consumption. However, it actually happened that OD did not drop after stationary phase, despite organic nutrients must be consumed. As the Mn^{2+} dropped soon as same timing as a tendency of expected ordinary slope for OD, it has a great potential that this manganese-oxidizing bacteria may be a chemoheterotrophs. These results strongly suggest that the bacteria utilize Mn^{2+} as an energy source after using organic nutrient, and might be intaking the organic

Table 1 Chemical composition of hot spring water and surface sediment from the Yuno-taki Falls. Analytical values of the sediment are presented on 110°C-dried basis.

Hot Spring Water (Position A)						Surface Sediment (Position D)		
HCO_3^-	(mg/l)	237	Mn^{2+}	(mg/l)	3.05	Mn	(%)	51.73
F^-	(mg/l)	0.32	Fe^{2+}	(mg/l)	<0.01	Fe	(%)	0.03
Cl^-	(mg/l)	132	Ca^{2+}	(mg/l)	102	Ca	(%)	3.12
NO_3^-	(mg/l)	9.14	Mg^{2+}	(mg/l)	125	Mg	(%)	3.02
SO_4^{2-}	(mg/l)	690	Na^+	(mg/l)	127	Na	(%)	0.10
DOC	(mg/l)	<1	K^+	(mg/l)	32	K	(%)	0.56
			Co^{2+}	(mg/l)	<0.01	Co	(mg/kg)	25
			Ni^{2+}	(mg/l)	0.02	Ni	(mg/kg)	276
			Cu^{2+}	(mg/l)	0.11	Cu	(mg/kg)	573
			Zn^{2+}	(mg/l)	0.01	Zn	(mg/kg)	475
			Pb^{2+}	(mg/l)	0.07	Pb	(mg/kg)	42
			Sr^{2+}	(mg/l)	0.12	Sr	(mg/kg)	303
			Li^{2+}	(mg/l)	0.13	Li	(mg/kg)	57
						S total	(%)	0.08
						C inorg.	(%)	0.10
Σ anion	(meq/l)	22.14	Σ cation	(meq/l)	21.81	C org.	(%)	0.75

As shown in Fig. 9, after 4 days of the incubation, the concentrations of D-Mn (Mn^{2+}) in the native and sterilized hot spring waters (A) and in the sterilized sediment solution (B: 0.02 v/v%) were essentially unchanged. The native sediment solution (C), however, showed a 25% decrease in the Mn^{2+} concentration by the same incubation. These results strongly suggest that microbial contribution is a dominant factor to the decrease in Mn^{2+} [5]. As shown in Fig. 10, adding more volume of sediment (0.20 v/v%) gave a more effective result that decreasing of Mn^{2+} is rather faster than the result of Fig. 9 [2,7]. The formed black deposit is manganese oxide.

To confirm that bacterially mediated precipitation of manganese oxide, isolated manganese-oxidizing bacterial strain (Fig. 8) was used for liquid culture experiment by 1/2 TZ-Mn culture medium that contains organic nutrients and Mn(II) at pH 7.5. Fig. 11 shows a result of experiment. Optical density (OD, i.e. absorption) at 660nm is proportional to the bacterial biomass. The OD value and the Mn^{2+} concentration in

nutrients from the microbial algae as a result of symbiosis. Accordingly, the microbes must be useful to solve many water pollution and discarded materials for manganese.

Conclusion

During studying coevolution of microbes and the ore deposit formations in modern and ancient earth, it has been also hoped for a new application to clean and recycling of manganese. A unique concept of this proposal, shown in Fig. 2, is the fruit of many years of multidisciplinary research in the Yuno-taki Falls. This method using above mentioned symbiotic microbes has the great advantage as follows [2]. (a) Although the water to be treated is weak acidic to neutral pH, the microbes can easy to oxidize high and low concentarion of Mn(II) to Mn(IV). (b) Such alkalify and antialkaline process like former methods are not necessary. (c) The microbes are effective to Mn oxidation in such a highly saline solutions like seawater or mine drainage and etc. (d) As MnO_2 particle adhere to the microbes, it is not necessary to use artificial organic coagulants which potentially induce cancer. (e)

Although the Mn-oxidizing bacteria require organic nutrient, the bacteria need not such feeding because the algae might be provide nutrient. (f) The bacteria potentilly utilize Mn^{2+} as an energy source after using organic nutrients. (g) After the discarded dry

batteries or steels etc. are dissolved, reproduction of MnO_2 will be done by the new system. (e) It is not only economical but also good for human health and conservation of Earth's Environments.

Acknowledgments

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