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# Adsorption of ferrous ion in water on filter paper including cedar bark

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ABSTRACT

In ground water such as wells and springs, iron (Fe(II)) and manganese (Mn(II)) are the most commonly found dissolved chemical species. The presence of these metal ions can cause water to exhibit bad odors, taste poorly and to color or stain clothing. In this study, using filter paper made with cedar bark, we have examined the fundamental study on the removal of iron (Fe(II), Fe(III)) and manganese (Mn(II)), along with other metals (Cu(II), Ni (II), Zn(II), and V(V)) found in groundwater. Recently, we have prepared functional filter paper made with cedar bark, as a new method for preventing the contamination of soluble organic compounds. It was found that filter paper with cedar bark adsorbs metal ions. Thus, we considered the application of metal adsorptive filter paper in the removal of iron and manganese in groundwater. Ferric ion demonstrated the highest adsorption capacity and was partly reduced to ferrous ion by the cedar bark. Ferrous ion maintained its oxidation state throughout the experiment, and showed relatively high adsorption capacity amongst the divalent cations. Adsorption behaviors of these ions were seen to obey the Langmuir-type adsorption isotherm, and it was concluded that the ability of filter paper made with cedar bark to reduce and absorb metals, would be promising in the treatment of groundwater.

*Keywords:* Adsorption; Ferrous ion; Filter paper; Cedar bark

## 1. Introduction

Biosorption is the adsorption of metals from dilute aqueous solutions on the biomass. Biosorbents can be used in processes pertaining to the treatment or pretreatment of industrial waste streams and natural waters, and is an alternative to conventional sorbents using synthetic resins for the removal and recovery of metals from aqueous solutions [1]. Not only is biosorption a cost-effective tool for these processes, it may also provide a new utilization for biomass wastes. Among these wastes, bark accounts for a significant proportion of wood by-products of the timber industry. It has been shown that these barks have significant adsorption capacities in the removal of metal cations from aqueous solutions [2,3]. This adsorption ability may be attributed to the barks' pectin and tannin contents, whose carboxylic and

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phenolic groups can bind metal ions [4]. Recently, we have demonstrated that cedar bark is able to adsorb oxometallic anions, such as $MoO_4^{2-}$, $WO_4^{2-}$, and $VO_4^{2-}$ [2]. In this way, the bark can adsorb a wide range of metals from aqueous solutions. However, a problem with the use of barks for metal recovery from aqueous solutions is that they release soluble organic compounds into the treated water. This results in the need for a secondary treatment of the contaminated aqueous solutions. Hence, we prepared functional filter paper made with cedar bark, to use in a new method to prevent the contamination of soluble organic compounds [3]. It was found that filter paper with cedar bark adsorbs ferric ion, oxometallic, and tetrachloroauric anions. Thus, we considered the application of metal adsorptive filter paper for the removal of metal, especially iron, in ground water.

In anaerobic ground water such as that found in wells and springs, iron and manganese are the most commonly observed dissolved metal species. These metal species were found to cause unpleasant odors and a rusty taste in the water, as well as the coloring and staining of clothing [5]. Iron in anaerobic groundwater is present in a dissolved state, and exists in its reduced Fe(II) form. This form is easily oxidized to Fe(III) through contact with oxygen in the air, or with dissolved oxygen in the water. From that, oxidized Fe(III) precipitates as the insoluble hydroxide in water. The concentration level of Fe(II) in groundwater ranges from 0.5 to 50 mg/L, while the WHO-recommended level for drinking water is less than 0.3 mg/L [6]. Therefore, the simultaneous removal of ferric and ferrous ions from groundwater is desirable. Mn(II) oxidation to Mn(III/IV) using oxygen and bacteria is also a thermodynamically favorable process to form manganese oxide. The average concentration of manganese is 10 μg/L, while the recommended level of manganese is less than 0.1 mg/L [6]. Conventional treatment for iron and manganese removal from groundwater consists of oxidation and depth filtration. This conventional process works well in the absence of dissolved organic matter and when the filterability of manganese oxides is poor [6].

In this study, using filter paper made with cedar bark, we have examined the fundamental study on the removal of iron (Fe(II), Fe(III)) and manganese (Mn(II)), along with other metals (Cu(II), Ni(II), Zn(II), and V(V)) found in groundwater.

## 2. Materials and methods

The preparation method for the adsorbent (filter paper made with cedar bark) has been detailed in one of our previous papers [3]. Tests were conducted on various metal ions (Fe(II), Fe(III), Cu(II), Ni(II), Zn(II), Mn(II), and V(V)), in order to evaluate the adsorption ability of each on the adsorbent. The process was done by shaking and mixing 50 mg of adsorbents in 10 mL of the test solution containing 10 mmol/dm$^3$ of individual metal ions at 100 rpm over 24 h. It was confirmed that adsorption equilibrium could be attained within 6 h. The pH values were adjusted using a 0.1 mol/dm$^3$ $HCl/CH_3COONa$ buffer solution. After attaining equilibrium, the mixtures were filtered to separate the solid adsorbent.

The adsorption isotherms were then measured to evaluate the maximum adsorption capacity of the adsorbent. This was done by shaking and mixing 50 mg of adsorbents with 10 mL of test solution containing individual metals ranging from 0.5 to 20 mmol/dm$^3$. The initial and residual concentrations of the metal ions in the filtrate were measured using inductively coupled plasma atomic emission spectrometry (ICPS-8100, Shimadzu, Japan). The pH values of the solution were measured with a pH meter (F-52, Horiba, Japan) before and after the adsorption experiment. The total iron concentration was then determined by ICP, and the ferrous ion was absorptiometrically obtained using 1,10-phenanthroline [7]. The amount of adsorbed metal ions was calculated from the difference in the metal concentration between the initial solution and the filtrate, and the dry weight of the adsorbent. The amount of metal adsorbed in the adsorbent ($q_e$ (mmol/g sorbent)) was calculated using the following equation:

$$q_e = \frac{C_i - C_f}{M} \times V \tag{1}$$

where $C_i$ and $C_f$ are the metal concentrations (mM) before and after, adsorption respectively, $V$ is the volume of the test solution (L) and $M$ is the dry mass of the adsorbent (g).

## 3. Results and discussion

### 3.1. Adsorption of ferrous and ferric ions

Prior to the batch experiment regarding the adsorption of iron, we investigated the oxidation state of ferrous ions in the aqueous solution with the inclusion of filter paper made with cedar bark. This experiment was undertaken because ferrous ions are easily oxidized to ferric ions by dissolved oxygen [8]. Surprisingly, under this experimental condition (the inclusion of filter paper made with cedar bark), the total iron concentration determined by an ICP was almost similar to the ferrous ion concentration determined by spectrophotometry.

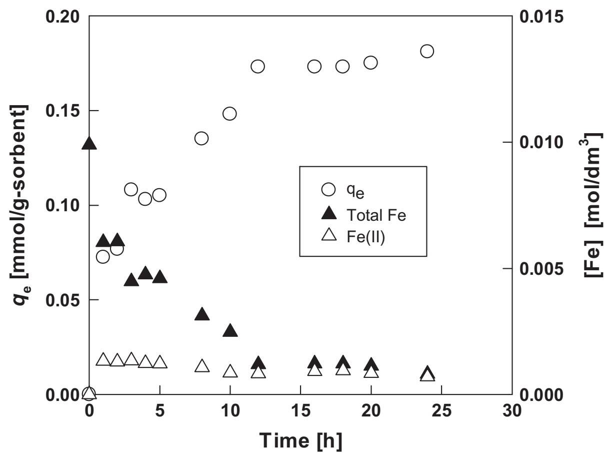


Fig. 1. Time-course of ferric ion adsorption.

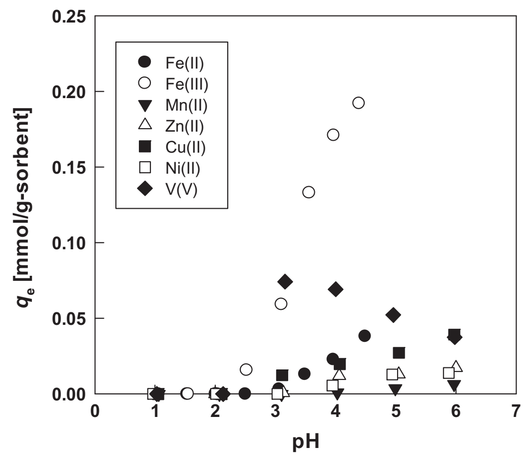


Fig. 2. pH effect on the adsorption of metals on filter paper with cedar bark in single system.

This suggests that ferrous ion maintains its oxidation state throughout the experiment.

Fig. 1 shows both the adsorption of ferric ions ($q_e$), and total iron and ferrous ion concentrations (Fe), plotted against time. Immediately after the commencement of the experiment, an emergence of ferrous ions was observed; suggesting that the ferric ions were reduced partly to ferrous ions by the adsorbent. As found in a previous paper [3], the adsorption of Au ions on filter paper containing cedar bark was accompanied by their reduction to zero-state Au, resulting in the formation of gold metal microparticles on the adsorbent surface. Therefore, it was concluded that due to the presence of cellulose, cedar bark has a general ability to reduce metallic ions in an aqueous solution. It is highly preferable for the treatment of groundwater that this reduction ability prevents the oxidation of Fe(II) and Mn(II), which in turn results in an easier removal of the aqueous solution with the metal adsorptive filter paper.

### 3.2. Adsorption of metal ions in single system

Fig. 2 shows the pH effect on the adsorption of each metal. In this figure, adsorption experiments were carried out using an aqueous solution containing a single metal ion. For metal ions such as Fe(II), Fe (III), Cu(II), Ni(II), Zn(II), and Mn(II) (which exist in the cationic state when using filter paper made with cedar bark), adsorption increased with increasing pH. This meant that the adsorption progressed via cation exchange reaction. However, the adsorption of V(V) displayed a maximum value at pH 3. Mono-anionic forms, $H_2VO_4^-$, may be relevant in the anion exchange reaction as described in the previous paper [2,3].

Fig. 3 lists the amount of metal adsorbed at pH 6 for each metal. For Fe(III) adsorption, as reported previously [3], the abnormally highest level of adsorption suggests that the chelating mechanism of ferric ions by the bark is complex, involving several intermediate steps [9]. Among the divalent metal cations, the adsorption ability of Fe(II) was relatively high; on the other hand, that of Mn(II) was low amongst the investigated metals. However, while the average concentration of manganese in groundwater is lower than that of the regulation standard [6], the cedar bark prevention of the oxidation of manganese is still important to avoid problems such as those listed above. The adsorption isotherms of metals on the filter papers containing cedar bark were also examined under their optimum pH conditions. The results of Fe(II) and Fe (III) adsorption are shown in Fig. 4, indicating that the amount of metal adsorbed increases with an increas-

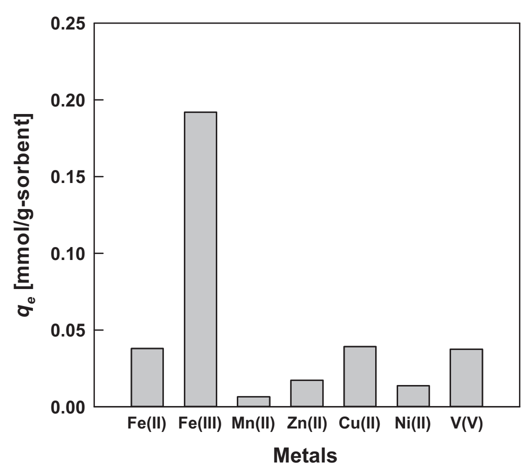


Fig. 3. Adsorption of metals on filter paper with cedar bark.

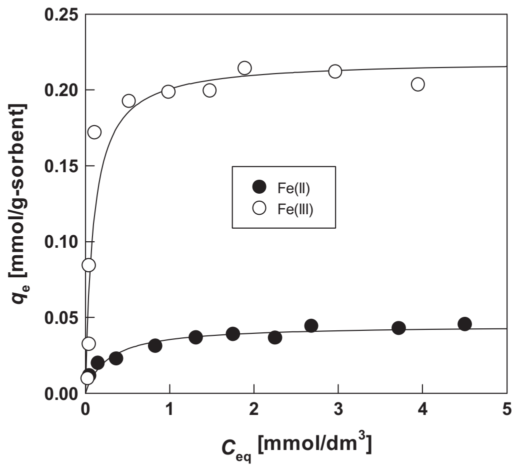


Fig. 4. Adsorption isotherm of Fe(II) and Fe(III) on filter paper with cedar bark.

Table 1
Langmuir parameters of metal adsorption

| Metals | $q_m$ (mmol/g) | $K$ ($dm^3$/mmol) |
|---|---|---|
| Fe(II) | 0.0450 | 3.73 |
| Fe(III) | 0.213 | 11.3 |
| Mn(II) | 0.0233 | 0.759 |
| Zn(II) | 0.0359 | 1.49 |
| Cu(II) | 0.0963 | 1.91 |
| Ni(II) | 0.0201 | 2.66 |
| V(V) | 0.101 | 2.55 |

ing metal concentration and tends to approach constant values for each metal species at high concentrations. The other metal ions showed a similar tendency. This suggests a typical Langmuir-type adsorption. The maximum adsorption capacities, $q_m$, and adsorption equilibrium constants, $K$, were estimated from this experimental data using a non-linear least square method and are displayed in Table 1. Solid lines in Fig. 4 were calculated by Langmuir adsorption isotherm with these parameters. The experimental data expressed well the Langmuir adsorption model. Ferric ion (Fe(III)) has the highest values of $q_m$ and $K$. Ferrous ion (Fe(II)) has the highest $K$ value among the divalent cations investigated, suggesting that adsorption from its low concentration is favorable. Solid lines in Fig. 5 were calculated using these parameters.

### 3.3. Adsorption of metal ions in mixed system

Fig. 5 shows the adsorption of metals in the mixed system. In this figure, each metal concentration was the same, and total metal concentration was adjusted to the metal concentration in the single metal system. The adsorption behaviors of the metals, with the exception of V(V), were similar to those shown in Fig. 2. The adsorption of V(V) increased with increasing pH, like adsorptions of other metals, but unlike the adsorption in the single system. The vanadium species in the aqueous solution is known to be complex and dependent on the pH level, vanadium concentration, and redox potential. In the dilute solution compared with the single metal system, vanadium (V) may be reduced to V(III), which is adsorbed via the cation exchange mechanism.

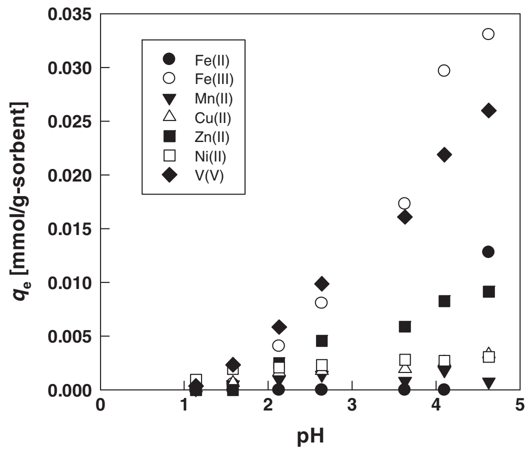


Fig. 5. pH effect on adsorption of metals on filter paper with cedar bark in mixed system.

## 4. Conclusion

Using filter paper made with cedar bark, we carried out the adsorption of metals which normally coexist in groundwater (Fe(II), Fe(III), Mn(II), Cu(II), Ni(II), Zn(II), and V(V)), in an aqueous solution. Ferric ion demonstrated the highest adsorption capacity, and was partly reduced to ferrous ion by the cedar bark. Ferrous ion also showed a relatively high capacity among the divalent cations and maintained its oxidation state. The adsorption ability of Mn(II) was low in contrast to the investigated metals. However, while the average concentration of manganese in the groundwater is lower than that of regulation standard, the cedar barks prevention of the oxidation of manganese is still important to avoid cumbersome problems.

Filter paper with cedar bark demonstrated the capacity to reduce and adsorb metallic ions, and maintain the oxidation states of Fe(II) and Mn(II), which were dominant oxidation states of iron and manganese in groundwater. Even though Fe(II) was oxidized to Fe(III), the filter paper was able to trap the

Fe(III) effectively and prevent the precipitation of hydroxides of ferric ion due to its higher adsorption capacity. Thus, filter paper made with cedar bark is promising in its application pertaining to the treatment of groundwater. Moving forward, we intend to test the continuous treatment of actual groundwater by using filter paper including cedar bark.

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## References

[1] G.M. Gadd, Biosorption: Critical review of scientific rationale, environmental importance and significance for pollution treatment, J. Chem. Technol. Biotechnol. 84 (2009) 13–28.

[2] M. Matsumoto, S. Tachibana, H. Nakanishi, K. Kondo, Adsorption of oxometallic ions on raw wood particles, Kagaku Kogaku Ronbunshu 35 (2009) 55–59.

[3] M. Matsumoto, D. Kawabata, T. Takatani., Y. Yoshida and K. Kondo, Selective adsorption of oxometallic and gold ions on filter paper containing cedar bark. Solvent Extr. Ion Exch. 32 (2014) 111–118

[4] F. Martin-Dupont, V. Gloaguen, R. Granet, M. Guilloton, H. Morvan, P. Krausz, Heavy metal adsorption by crude coniferous barks: A modelling Study, J. Environ. Sci. Health, Part A 37 (2002) 1063–1073.

[5] T.J. Casey, Iron and Manganese in Water, Aquavarra Research R&D Publications, Paper 3, Dublin, 2009.

[6] D. Ellis, C. Bouchard, G. Lantagne, Removal of iron and manganese from groundwater by oxidation and microfiltration, Desalination 130 (2000) 255–264.

[7] Y. Okura, Absorptiometric determination of ferrous iron coexisting with ferric iron with 1,10-phenanthroline, Bunsekikagaku 27 (1978) 477–480.

[8] A. Alicilar, G. Meriç, F. Akkurt, O. Sendil, Air oxidation of ferrous ion in water, J. Int. Environ. Appl. Sci. 3 (2008) 409–414.

[9] I. Gaballah, G. Kilbertus, Recovery of heavy metal ions through decontamination of synthetic solutions and industrial effluents using modified barks, J. Geochem. Explor. 62 (1998) 241–286.