ADSORPTION OF FERROUS IRON IN WATER ON FILTER PAPER INCLUDING CEDAR BARK

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ABSTRACT

Biosorbents can be used in the processes for the treatment or pre-treatment 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 Among biomass wastes, bark accounts for a significant proportion of wood by-products of the timber industry. It has been shown that these barks have large adsorption capacities for removing metal cations from aqueous solutions Recently, we showed that cedar bark is able to adsorb oxometallic anions, such as MoO_4^{2-}, WO_4^{2-}, and VO_4^{2-} In this way, the barks can adsorb a wide range of metals from the 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 requires secondary treatment of the contaminated aqueous solutions. So we prepared functional filter paper containing cedar bark as a new method for preventing contamination of soluble organic compounds and it was found that filter paper with cedar bark selectively adsorbs ferric ion, oxometallic and tetrachloroauric anions. We considered the appliction of metal adsortive filter paper to the removal of iron in ground water. In ground water such as wells and springs, iron and manganese are the most common dissolved chemical species. These presence in water caused the bad odours, rusty taste and colour and staining clothing.

In this study, we examined the fundamental study on removal of metals (Fe(II), Fe(III), Cu(II), Ni(II), Zn(II), Mn(II), and V(V)) involved in ground water with filter paper including cedar barks. Ferric ion showed the highest adsorption capacity and was partly reduced to ferrous ion by the cedar barks. Ferrous ion has relatively high capacity among the divalent cations. Adsorption behaviors of these ions obeyed the Langmuir-type adsorption isotherm. Filter paper including cedar barks is found to be promising for recovery of iron from ground water.

Keywords: adsorption, ferrous ion, filter paper, cedar bark, rare metal, oxometallic ion, gold

1. Introduction

Biosorption is to adsorb metals from dilute aqueous solutions on the biomass. Biosorbents can be used in the processes for the treatment or pre-treatment 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 (Gadd, 2009). Not only is biosorption a cost-effective tool for these processes, it may also provide a new utilization of 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 large adsorption capacities for removing metal cations from aqueous solutions (Matsumoto, 2014). This adsorption ability might be attributed to the barks' pectin and tannin contents, whose carboxylic and phenolic groups can bind metal ions (Martin-Dupont, 2002). Recently, we showed that cedar bark is able to adsorb oxometallic anions, such as MoO_4^{2-}, WO_4^{2-}, and VO_4^{2-} (Matsumoto, 2009). In this way, the barks can adsorb a wide range of metals from the 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 requires secondary treatment of the contaminated aqueous solutions. So we prepared functional filter paper containing cedar bark as a new method for preventing contamination of soluble organic compounds (Matsumoto, 2014) and it was found that filter paper with cedar bark adsorbs ferric ion, oxometallic and tetrachloroauric anions. We considered the appliction of metal adsortive filter paper to the removal of iron in ground water. In ground water such as wells and springs, iron and manganese are the most common dissolved chemical species. These presence in water caused the bad odours, rusty taste and colour and staining clothing (Ityel, 2011).

In this study, we examined the fundamental study on removal of metals (Fe(II), Fe(III), Cu(II), Ni(II), Zn(II), Mn(II), and V(V)) involved in ground water with filter paper including cedar baeks.

2. Experimental

The adsorption tests of various metal ions, Fe(II), Fe(III), Cu(II), Ni(II), Zn(II), Mn(II), and V(V). on the filter papers with cedar bark were measured to evaluate the adsorption ability, by shaking 50 mg of adsorbents (filter paper with cedar bark or powder of cedar bark) in 10 mL of the test solution containing 10 mmol/dm^3 of individual metal ions at 100 rpm for 24 hours. It was confirmed that adsorption equilibrium is attained within 6 hours. The pHs were adjusted by using 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 measured to evaluate the maximum adsorption capacity of both adsorbents by shaking 50 mg of adsorbents with 10 mL of test solutions containing individual metals ranging from 0.5 to 20 mmol/dm^3. The initial and residual concentrations of metal ions in the filtrate were measured by 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. Total iron concentration was detremined by ICP and ferrous ion was absorptiometrically determined by using 1,10-phenanthroline[Okura, 1978]. The amount of adsorbed metal ions was calculated from the difference in metal concentration between the initial solution and the filtrate, and the dry weight of the adsorbent. The amount of metal adsorbed on the adsorbent (q_e (mmol/g-sorbent)) was calculated using the following equation:

$$q_e = \frac{C_\mathrm{i} - C_\mathrm{f}}{M} \times V \qquad (1)$$

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 batch experiment of adsorption of iron, we checked the oxidation state of ferrous and ferric ions in the aqueous solution in the presence of filter paper including cedar bark because ferrous ions were easily oxidized to ferric ions by dissolved oxygen (Alicilar *et al*, 2008). Surprisingly, under this experimental condition, total iron concentration determined by ICP was almost similar to ferrous ion concentration determined by spectrophotometry. This is suggested that ferrous ions keep their oxidation state throughout the experiment. Figure 1 shows the adsorption, q_e, of ferric ions and total iron and ferrous ion concentrations. Contrary to adsorption of ferrous ion, immediately after the beginning ferrous ions were emerged, suggesting that ferric ions were reduced to ferrous ions by the adsorbent. As found in previous paper (Matsumoto *et al.*, 2014), the adsorption of Au ions on the filter paper containing cedar bark was accompanied by their reduction to zero-state Au what resulted in formation of gold metal microparticles on the adsorbent surface. Therefore, it is found that cedar barks have reducing ability of metallic ions in the aqueous solution.

3.2. Adsorption of metal ions in single system

Figure 2 shows the pH effect on the adsorption of each metal. In this figure, adsorption experiments were carried out by using the aqueous solution containing single metal ion. For metal ions that existed the cationic state such as Fe(II), Fe(III), Cu(II), Ni(II), Zn(II) and Mn(II) under this experimental condition, adsorption increased with increasing pH. This means that the adsorption progressed via cation exchange reaction. On the other hand, adsorption of V(V) had the maximum value at pH 3. Mono-anionic forms, $H_2VO_4^-$, may be relevant in the adsorption reaction.

Figure 3 lists the amount of metal adsorbed under the optimum pH and acidity for each metal in this study. For Fe(III) adsorption, as reported previously, the abnormally highest adsorption suggests that the chelating mechanism of ferric ions by the bark is complex, involving several intermediate steps (Gaballah and Kilbertus, 1998). Among the divalent metal cations, adsorption ability of Fe(II) was relatively high. The adsorption isotherms of metals on the filter papers containing cedar bark were examined. The results show that the amount of metal adsorbed increases with increasing metal concentration and tends to approach constant values for each metal species at high concentrations, suggesting a typical Langmuir-type adsorption. The maximum adsorption capacities, q_m, and adsorption equilibrium constants, K, were estimated from these experimental data using a non-linear least square method and are tabulated in Table 1.

3.3. Adsorption of metal ions in mixed system

Figure 4 shows the adsorption of metals in the mixed system. In this figure, each metal concentration was same and total metal concentration was adjusted to metal concentration in the single metal system. Adsorption behaviours of metals except V(V) were similar to those in Fig. 2. Adsorption of V(V) increased with increasing pH unlike that in Fig. 2. As presumed the results described above, diluted vanadium (V) may reduced to V(III), which adsorbed via the cation exchange mechanism.

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

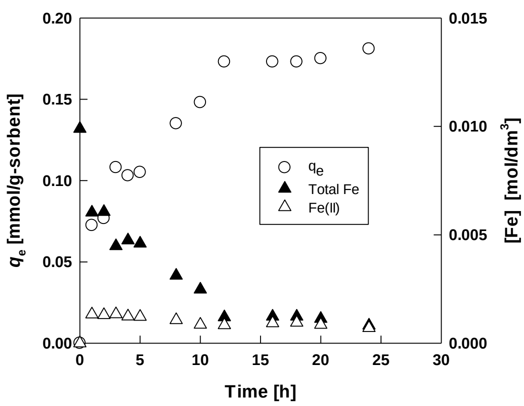

Figure 1: Time course of ferric ion adsorption

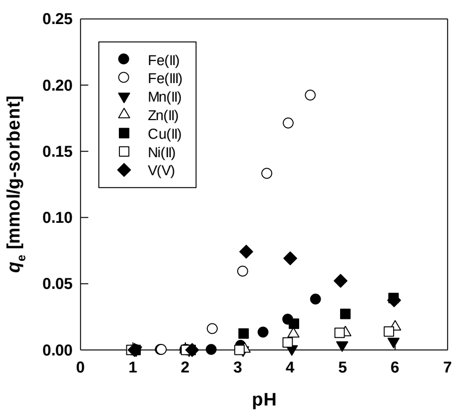

Figure 2: pH effect on adsorption of metals on filter paper including cedar bark in single system

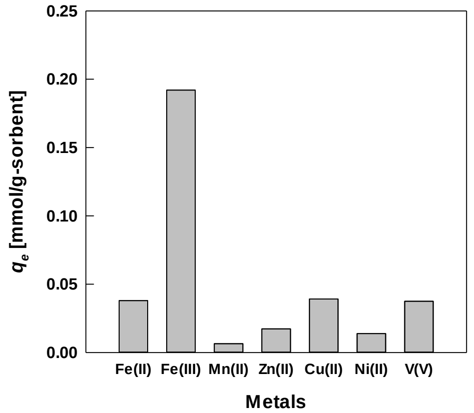

Figure 3: Adsorption of metals on filter paper including cedar bark

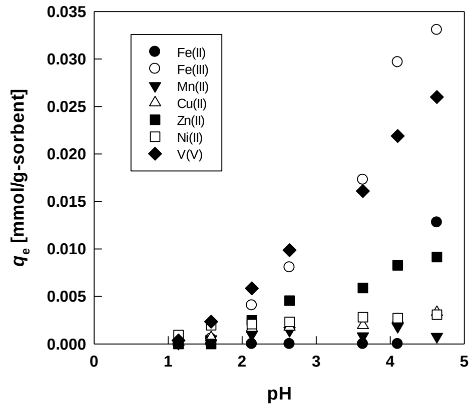

Figure 4: pH effect on adsorption of metals on filter paper including cedar bark in mixed system

4. Conclusions

We carried out the adsorption of metals involving Fe(II), Fe(III), Cu(II), Ni(II), Zn(II), Mn(II), and V(V), which coexisted in the groundwater, from aqueous solution using filter paper including cedar barks. Ferric ion showed the highest adsorption capacity and was partly reduced to ferrous ion by the cedar barks. Ferrous ion has relatively high capacity among the divalent cations. Next we will test the continuous treatment of actual ground water by using filter paper including cedar barks.

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