STUDY OF MULTIELEMENTAL ADSORPTION ON ACTIVATED CARBON

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In this study, multielemental adsorption on activated carbon (AC) was investigated. The treatment parameters (pH, AC concentration, metal concentration and contact time) in the adsorption process of multiple metals such as Bi, Cd, Co, Ga, Mn, Mo, Ni, In, Pb, Pd, Sn, Rh, Ru and W were experimented. Three types of characteristic behaviors of analyte elements were observed when the pH was varied. The adsorption rate of Bi, Co, Ga, Ni, In, Pb, Sn, Ru and W were over 80% within 30 min.

Keywords: Multielement, adsorption, activated carbon.

1. Introduction

Water pollution is still a major problem in the global context, especially in the developing countries^[1, 2]. The treatment of heavy metals polluted waters is a great concern because of their high toxicity to plants, animals and human beings. Economic developments and technical enhancements mean the consumption and emission of many kinds of metals continue to increase. Recently, more attention has been paid to adsorption of heavy metals from the point of view of recycling. Therefore, studies of the adsorption of as many metals as possible are useful for water purifying and metal recycling^[3]. Until now, there are currently several methods of heavy metals based on separation techniques such as precipitation, filtration and adsorption. Adsorption has been used as a wide and cost-effective technique for removal of metal ions from wastewater. In adsorption techniques, activated carbon (AC) is widely utilized as adsorbent of pollutants and deodorant. AC has good features as adsorbent of heavy metals due to its low-cost, large surface area and lightness. There are some researchs study about adsorption of metal ions from aqueous solution onto AC^[4-6] or functionalized AC^[7]. However, the adsorption behavior of multielement from aqueous solution onto AC has been rarely elucidated.

In this study, adsorption behavior of multielemental from aqueous solution containing Bi, Cd, Co, Ga, Mn, Mo, Ni, In, Pb, Pd, Sn, Rh, Ru and W onto AC was investigated.

2. Experimental section

2.1. Instruments and Chemicals

An inductively coupled plasma mass spectrometer (ICP-MS), model ICPM-8500 (Shimadzu) was utilized for the determination of metal ions. Each solution for ICP-MS measurement contains Re ($m/z = 185$) as internal standard collection. m/z is defined as mass to charge ratio. A pH meter of model HM-25G from TOADKK (Japan) was used for pH adjustment.

HNO_3 , HCl and single-element standard stock solutions (1000 mg dm^{-3}) used were of electronic industrial grade and analyte elements for atomic absorption spectrometry, purchased from Kanto Chemicals Co. (Tokyo, Japan) and Wako Pure Chemicals Co. (Osaka, Japan), respectively. Purified water was prepared by a Milli-Q purification system (Nihon Millipore Kogyo, Tokyo, Japan). Charcoal activated powder (Wako Pure Chemicals Co., Osaka, Japan) was used in this study, without treatment. The properties of AC used for this study has described as following: loss on drying (at 105°C): 10 %, residue after ignition : 2.0%, pH of 5 w/v % slurry at 25°C : 5 – 8, C : 68.11%, H: 0.83 %, N : 0.52 %.

2.2. The adsorption experiment

The adsorption experiments were carried out at room temperature. Typical conditions and procedure of the adsorption experiment were described as follows. At first, 0.50 mg dm^{-3} multielemental solution was prepared by mixing of each element (1000 mg dm^{-3}) in 100 ml of 0.5 M buffer solution. Then, 5 g of AC was added into solution containing heavy metals. The AC contained solution was agitated at 200 rpm during 1 hour. The supernatant solution were filtered by a PTFE membrane filter and then diluted by 0.1 mol dm^{-3} HNO_3 solution. Initial metal concentration in the final solution was determined by ICP-MS.

The adsorption rate [%] was defined as the ratio of final concentration to the initial concentration in the AC treatment, and was calculated by the following equation, where C_i and C_e are the initial and final concentration of metal [mg dm^{-3}] in the solution, respectively.

$$\text{Adsorption rate [\%]} = 100 (C_i - C_e) / C_i \quad (1)$$

3. Results and Discussion

3.1. pH dependence of adsorption efficiency

Aqueous phase pH governs species of metals and also dissociation of active functional sites on the sorbent^[8,9]. To characterize the effect of pH on adsorption of metal ions (14 elements) onto activated carbon, adsorption experiments were conducted in the pH range of 4 - 12. The results are presented in Fig.1. Three types of characteristic behaviors of

analyte elements were observed when the pH was varied. As can be seen in Fig.1-a, the adsorption rate of Bi, Cd, Co, Mn, Ni, In and Pb (group a) increased with increasing pH value. The adsorption rate of Ga, Mo, Pd, Sn and W (group b) was maximized near pH 4 and decreased at higher pH value (Fig.1-b). On the other hand, Fig.1-c shows that the adsorption rate of Rh and Ru (group c) reached maximum around pH 7 and decreased with the lower and higher of pH value.

Fig.1 Effect of initial pH on the adsorption rate of analytes. AC : 0.5 wt%, $[M]_0$: 0.50 mg dm⁻³, contact time : 1 hour.

The elements in the group (a) have a low solubility of their hydroxides. Particularly, the solubility product constant ($\log K_{so}$) of these elements are Bi³⁺ : 4.71, Cd²⁺ : 13.16, Co²⁺ : 13.5, Mn²⁺ : 15.2, Ni²⁺ : 13.3, In²⁺ : 5.1 and Pb²⁺ : 8.0. The K_{so} value is defined as $K_{so} = [M^{n+}] [OH^-]^n$ equation. Therefore, these elements have a large tendency to form hydroxide colloids/aggregates in relative high pH region and their hydroxides are adsorbed onto surface of AC. The elements belonging to the group (b), especially Mo, W and Sn, are generally classified as the oxo-anion forming elements^[11,12]. Pd and Ga have a high solubility of their hydroxides, the solubility product constant ($\log K_{so}$) of these elements is -2.35 and 2.9, respectively^[10]. These elements mainly exist as anionic species in neutral pH and alkaline aqueous solution. The anionic properties of the oxo-anion increase with increasing pH value because of dissociation of proton. It has been also reported that the oxo-anion shows larger affinity to aqueous phase than solid phase like activated carbon^[10, 12]. Therefore, a poor adsorption rate of group (b) at higher pH region was obtained. Group (c) seems to be dependent on a weak acidic functional (-COOH) groups of AC. The minimal adsorption at low pH may be due to the higher concentration and high mobility of H⁺ ions, which are preferentially adsorbed rather than metal ions^[13,14]. At pH 7, there are lower numbers of competing hydrogen ions and more ligands are exposed with negative charges, resulting in greater sorption rate. But for pH greater than 7, decrease in adsorption was observed for these elements, this might be due to the lower polarity of these ions at higher pH values.

3.2. Contact time

Contact time was investigated under following condition: 0.50 mg dm⁻³ of the initial concentration of the elements, pH value at 7 and 0.5 wt % AC.

Table 1 shows the adsorption rate of almost of metal ions increased with the increase of contact time (except W). The adsorption rate of Co, Ni, Ga, Ru, Rh, In, Sn, W, Pb and Bi rapidly reached over 80% at 0.5 h. We observe that contact time had no remarkable affect in the adsorption rate of these 10 metal ions, and the adsorption rate of them maybe dependence on the surface of AC adsorbent.

Table 1 Effect of contact time on the rate of adsorption

Element	m/z	Adsorption rate [%]				
		0.5h	1h	3h	5h	24 h
Mn	55	37.7	45.5	53.1	51.0	64.4
Co	59	83.9	85.0	87.0	85.7	93.7
Ni	62	88.6	89.6	91.9	91.2	95.6
Ga	69	82.8	81.4	81.9	82.8	88.6
Mo	95	16.7	13.6	14.0	14.6	28.3
Ru	101	86.4	87.8	87.1	87.6	92.8
Rh	103	69.4	68.1	63.2	63.8	70.4
Pd	105	54.0	57.3	62.5	68.3	85.4
Cd	111	65.5	70.0	70.7	67.6	78.7
In	115	98.7	99.0	99.6	99.4	99.8
Sn	118	94.3	95.2	96.9	96.9	98.2
W	184	87.3	86.0	81.9	78.8	78.6
Pb	208	99.4	99.3	99.4	99.4	99.4
Bi	209	99.6	99.7	99.8	99.7	99.9

Initial pH 7, [M]₀ = 0.50 mg dm⁻³, AC : 0.5 wt%

Compared with another metal ion, Mn, Mo and Pd ions show a poor adsorption capacity onto AC. The clear reason with regard to decreasing adsorption rate of W with increasing contact time has been unknown yet. It seems to be that W is generally classified as the oxo-anion forming element even at pH 7, so desorption of them being achieved with increasing contact time ^[12].

3.3. AC concentration

AC concentration is also an important factor for the adsorption rate. The effect of AC concentration onto adsorption rate of metals was varied from 0.01 - 10 wt % was depicted in Fig.2.

Fig.2 Effect of AC concentration on the adsorption rate. Initial pH7, [M]₀ : 0.50 mg dm⁻³, contact time : 1 hour.

It is apparent that the adsorption rate of almost all of metals increases with increasing of AC concentration until around 2 wt %, and then reached plateau in the higher. With increasing adsorbent concentration, more surface area is available for adsorption due to increase in active sites on the adsorbent. In higher than 2 wt % of AC concentration, the amount of active sites was sufficient for adsorption of the metal ion.

3.4. Effect of the initial concentration of metal ions

The effect of the initial concentration of metal ions on the adsorption rate was investigated in the concentration range $[0.1-5.0 \text{ mg dm}^{-3}]$ of 5.0 wt % AC. Fig.3 shows that the removal rate decreased with increasing the initial concentration. The lower uptake at higher concentration resulted from an increased ratio of initial number of moles of them to the available surface area, hence fractional adsorption becomes dependent on initial concentration. Similar results were also reported by other researchers^[15].

Fig.3 Effect of initial concentration of analytes on the adsorption rate onto AC. Initial pH 7, AC : 5.0 wt %, contact time : 1 hour.

Table 2 Adsorption rate of analyties onto activated carbon

Element	m/z	Mean [%] ± s.d. [%]	R.S.D. [%]
Mn	55	67.3 ± 0.6	0.9
Co	59	94.3 ± 0.2	0.2
Ni	62	97.6 ± 0.1	0.1
Ga	69	98.7 ± 0.2	0.2
Mo	95	95.4 ± 0.5	0.5
Ru	101	97.1 ± 0.3	0.3
Rh	103	86.3 ± 0.4	0.5
Pd	105	99.3 ± 0.2	0.2
Cd	111	91.7 ± 0.3	0.3
In	115	99.9 ± 0.01	0.01
Sn	118	99.9 ± 0.1	0.1
W	184	99.5 ± 0.4	0.4
Pb	208	99.8 ± 0.05	0.05
Bi	209	99.9 ± 0.01	0.01

Initial pH 7, $[M]_0 = 0.50 \text{ mg dm}^{-3}$, AC : 5.0 wt%, contact time : 1 hour , the mean and standard deviation were obtained by the 6-times replicate measurements.

The adsorption rate of 14 elements under condition (Initial pH 7, $[M]_0 = 0.50 \text{ mg dm}^{-3}$, AC : 5.0 wt %, contact time : 1 hour) are summarized in Table 2. From these results, the adsorption rate of almost all of elements was above 85 %, and most elements showed good repeatability for adsorption rate onto AC. The relative standard deviations (RSDs) for 14 elements were less than 1 % by 6 times replicate measurements.

4. Conclusions

Activated carbon good features as adsorbent of heavy metals from wastewater due to low-cost, large surface area and lightness. From adsorption behavior of multielemental metal ions from aqueous solution containing Bi, Cd, Co, Ga, Mn, Mo, Ni, In, Pb, Pd, Sn, Rh, Ru, W we know that Bi, In, Pb are easily adsorbed onto AC more than the others. Except Mn, the adsorption rate of almost all elements was above 86 % and show good repeatability.

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