ADSORPTION BEHAVIOR OF CHROMIUM(III,VI) ON ACTIVATED CARBON AND
OXINE-IMPREGNATED ACTIVATED CARBON

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The adsorption behavior of chromium(III,VI) onto activated carbon (AC, Merck Co. Ltd.) and oxine-impregnated activated carbon (AC(HOx)) was investigated by use of a column method. The adsorption of chromium(III,VI) onto activated carbon, and of chromium(VI) onto AC(HOx) showed remarkable pH-dependency. The optimum pH for the adsorption of chromium(VI) from 1.00×10^{-3} mol dm⁻³ chromium(VI) solution were about 2.5 for activated carbon and about 3.0 for AC(HOx). The amount of chromium(VI) adsorbed onto adsorbents at the optimum pH was 13.5 mg for 5.0 g of activated carbon and 22.0 mg for 5.0 g of activated carbon impregnated with 0.5 g of oxine. Chromium(VI) adsorbed onto activated carbon at pH 4.9 was completely desorbed with 0.10 mol dm⁻³ NaOH solution in the form of chromium(III) (33%) and chromium(VI) (67%). While less than 6% of the total chromium(VI) adsorbed onto AC(HOx) at pH 4.9 was desorbed with 0.10 mol dm⁻³ NaOH solution. It seems probable that the chromium(VI) which was adsorbed onto activated carbon in the forms of $\text{Cr}(\text{OH})(\text{H}_2\text{O})_5^{2+}$ appeared from the reduction of some portion of chromium(VI) with activated carbon, HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$. On the other hand, chromium(VI) may be adsorbed onto AC(HOx) mainly in the form of Cr(III)-oxine complex.

Recently, the use of activated carbon and activated carbon impregnated with chelating reagents has become of interest in the preconcentration of trace metal ions in an aqueous solution¹⁾²⁾. Mercury(II) in a river was preconcentrated and determined by atomic absorption spectrophotometry³⁾. In a preceding paper, the specific adsorption of molybdenum(VI) onto activated carbon and oxine-impregnated activated carbon was described⁴⁾. As much as 1.15 g and 0.56 g of molybdenum(VI) was found to be adsorbed onto 5.0 g of activated carbon and onto 5.0 g of activated carbon impregnated with 0.5 g of oxine, respectively. The unusual adsorption behavior of molybdenum(VI) was explained by the specific adsorption of polymerised species.

Yoshida et al.⁵⁾ studied the adsorption behavior of chromium(III,VI) onto activated carbon by a batchwise method. Chromium(VI) was assumed to be adsorbed onto activated carbon in the forms of HCrO_4^- and CrO_4^{2-} in the pH range from 4.5 to 6.0. In an acid solution, chromium(VI) was reduced to chromium(III) by activated carbon.

The reaction of chromium(III) with oxine in an aqueous solution is very slow.

The formation of chromium(III)-oxine complex is achieved by warming the solution. The chromium(III)-EDTA complex was easily formed by the reduction of chromium(VI) with reducing reagents in the presence of EDTA⁶⁾. The presence of the reactive and transient Cr^{IV} -EDTA or Cr^{V} -EDTA complexes was proposed⁷⁾.

It is interesting to study the adsorption behavior of chromium(VI) onto AC(HOx). The formation of Cr^{IV} - or Cr^{V} -oxine complex may be assumed when chromium(VI) solution was passed through the column packed with AC(HOx). The adsorption behavior of chromium(III,VI) onto activated carbon and AC(HOx) was studied by use of a column method.

EXPERIMENTAL

Apparatus. A Hitachi 170-30 type atomic absorption spectrophotometer was utilized for the determination of chromium(III,VI). A Hitachi 101 type spectrophotometer was used to determine the oxine concentration. The pH measurements were carried out using a Hitachi-Horiba M 7 type pH meter. The flow rate was controlled by means of a pump (Atto Co. Ltd.).

Activated Carbon and Reagents. Activated carbon: Activated carbon powders (Merck, GR grade No. 2186) were used without further purification.

Standard chromium(III) solution: A 0.10 mol dm^{-3} chromium(III) solution was prepared by dissolving 4.002 g of chromium(III) nitrate-water (1/9) (Kanto Co. Ltd.) in 100 ml of 0.10 mol dm^{-3} nitric acid. A 0.10 mol dm^{-3} chromium(VI) solution was prepared by dissolution of 1.942 g of dipotassium chromate (Kanto Co. Ltd.) in 100 ml of redistilled water. The working solutions of these metal ions were prepared by diluting the stock solutions with redistilled water, and then these solutions were adjusted to the desired pH using sodium hydroxide solution and nitric acid.

8-hydroxyquinoline (oxine) (Kanto Co. Ltd.) was recrystallized from hot ethyl alcohol. Diphenylcarbazide (Kanto Co. Ltd.) was used for the determination of chromium(VI).

All the reagents were of analytical grade.

Preparation of Oxine-Impregnated Activated Carbon. 5.0 g of oxine in 120 ml of ethyl alcohol and 50.0 g of activated carbon was vigorously stirred for 60 min. Ethyl alcohol was evaporated up at room temperature, and then AC(HOx) was dried in an oven at 50°C for 3 hrs.

The Procedure for the Adsorption. 5.0 g of activated carbon or 5.0 g of AC(HOx) were packed into a pyrex column (17 mm i.d. and 200 mm in height). The chromium(III) or chromium(VI) solution was passed through a column packed with an adsorbent at the flow rate of 1.0 ml/min. The pH of the eluate was slightly higher than that of the feed solution when the feed solution was passed through the column packed with activated carbon or AC(HOx). The pH of the feed solution was described. The eluate was collected in 25 or 50 ml fractions. The break-through curves for the adsorption of chromium(III,VI) were obtained by determining chromium(III,VI) in an eluate.

As mentioned in a preceding paper⁴⁾, oxine impregnated on activated carbon is stable enough not to be desorbed with 1.0 mol dm^{-3} nitric acid.

RESULTS AND DISCUSSION

Effect of pH on the Adsorption of Chromium(III,VI) onto Activated Carbon. Fig. 1 shows the effect of pH on the adsorption of chromium(III,VI) from 1.00×10^{-3} mol dm^{-3} solution onto activated carbon. The amount of chromium(III) adsorbed increases with increasing the value of pH. Chromium(III) adsorbed was estimated from the volume passed until the 10% break-through point. The increase in the amount of chromium(III) adsorbed with increasing pH value may be explained by the adsorption of hydrolysed species of chromium(III). The pH-adsorption curve is very similar to the pH-distribution curve of $\text{Cr}(\text{OH})(\text{H}_2\text{O})_5^{2+}$ as described by Baba et al.⁸⁾. This suggests that chromium(III) may be adsorbed mainly in the form of $\text{Cr}(\text{OH})(\text{H}_2\text{O})_5^{2+}$. The proton-dissociation constants (pK_a) of chromium(III) are 3.81 for $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and 6.22 for $\text{Cr}(\text{OH})(\text{H}_2\text{O})_5^{2+}$.⁹⁾

Yoshida et al.⁵⁾ also showed that chromium(III) was not adsorbed onto 100 mg of activated carbon at all below pH 4. However, as shown in Fig. 1, 0.18 mg of chromium(III) per 100 mg of activated carbon was estimated to be adsorbed at pH 4.0. The discrepancy between these results obtained at pH 4.0 may be ascribed to the kind of activated carbon used.

The optimum pH for the adsorption of chromium(VI) onto activated carbon was about 2.5. Thus, the amount of chromium(VI) adsorbed below pH 4.3 was larger than that of chromium(III) (Fig. 1). Fig. 2 shows the distribution curve of chromium(VI) species with 1.00×10^{-3} mol dm^{-3} chromium(VI) solution at various pH values. Between pH 0 and 4.0, chromium(VI) exists as HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, H_2CrO_4 and HCrO_4^- . HCrO_4^- is the main species. The adsorption behavior shown in Fig. 1 can not be simply explained by considering only the chromium(VI) species, because chromium(VI) is reduced to chromium(III) by activated carbon in an acidic solution⁵⁾.

Fig. 1 Effect of pH on the adsorption of Cr(III) and Cr(VI) onto activated carbon. Activated carbon: 5.0 g; Flow rate: 1.0 ml/min; Feed solution: (A) 1.00×10^{-3} mol dm^{-3} Cr(III); (B) 1.00×10^{-3} mol dm^{-3} Cr(VI).

Fig. 2 Effect of pH on the distribution of 1.00×10^{-3} mol dm^{-3} Cr(VI).

As mentioned above, chromium(VI) was concluded to be adsorbed onto activated carbon in the forms of HCrO_4^- and CrO_4^{2-} over the pH range of 4.5 to 6.0 based on the fact that chromium adsorbed was desorbed with 0.10 mol dm^{-3} NaOH solution to provide chromium(VI)⁵⁾. We examined the desorption of chromium adsorbed at various pH

values onto activated carbon with 0.10 mol dm^{-3} NaOH solution to get more detailed information on the species of chromium adsorbed. The ratio of chromium(III) desorbed to total chromium desorbed decreases with increasing the pH value of the chromium(VI) solution passed, as shown in Table 1. This illustrates that chromium(VI) is reduced to chromium(III) in an acidic solution as mentioned by Yoshida et al.⁵⁾ Below pH 1.5, the amount of chromium(VI) adsorbed is equal to that of chromium(III) adsorbed (Fig. 1). Chromium(VI) may be adsorbed onto activated carbon in the form of HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ and Cr(III) appeared from the reduction of chromium(VI) by activated carbon. The decrease in the adsorption of chromium(VI) with increasing the pH value above pH 2.5 may be attributed to the decrease in the contribution of chromium(III) to the chromium adsorption because of the small rate¹⁰⁾ of the reduction of chromium(VI) with activated carbon to chromium(III) at high pH.

The Adsorption of Chromium(III,VI) onto AC(HOx). The adsorption of chromium(III, VI) onto AC(HOx) from $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ chromium(III,VI) solution was examined. The pH effect on the adsorption of chromium(III) onto AC(HOx) is different from that onto activated carbon (Fig. 3). Chromium(III) adsorbed increases slightly with increasing the pH value, and approaches to saturation above pH 3.5. Chromium(III) adsorbed onto AC(HOx) was found to be 3.5 mg per 5.0 g of AC(HOx) at pH 4.5. Chromium(III) adsorbed onto AC(HOx) is smaller than that adsorbed onto activated carbon at pH 4.5. Chromium(III) may be adsorbed onto AC(HOx) in the form of Cr(III) rather than Cr(III)-oxine complex because of the inertness of aquachromium(III) for ligand exchange reaction, and the small amount of adsorption of Cr(III) may be ascribed to the partial occupation of the adsorption site of activated carbon with oxine. The

Fig. 3 Effect of pH on the adsorption of Cr(III) and Cr(VI) onto AC(HOx).
AC(HOx): 5.0 g; Flow rate: 1.0 ml/min.
Feed solution: (A) $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ Cr(III);
(B) $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ Cr(VI).

amount of chromium(VI) adsorbed onto AC(HOx) decreases with a variation in the pH on both sides of the optimum pH, about 3. Chromium(VI) adsorbed onto AC(HOx) is larger than that onto activated carbon in spite of the fact that the adsorption site of activated carbon is occupied by oxine. This suggests that oxine adsorbed onto activated carbon may participate in the adsorption of chromium(VI).

The desorption of chromium adsorbed onto AC(HOx) was also examined as for activated carbon using a 0.10 mol dm^{-3} NaOH solution as an eluent. The result is shown in Table 1. Thus, 6% of all the chromium adsorbed by passing 100 ml of 1.00×10^{-3}

10^{-3} mol dm^{-3} chromium(VI) solution at pH 4.9 through the column packed with 5.0 g of AC(HOx) was desorbed by 50 ml of 0.10 mol dm^{-3} NaOH solution. However, chromium adsorbed was completely desorbed by 50 ml of 0.10 mol dm^{-3} NaOH solution, when chromium(VI) was adsorbed by treating activated carbon with 100 ml of 1.00×10^{-3} mol dm^{-3} chromium(VI) solution at pH 4.9 by the general procedure for the adsorption of chromium(III,VI). It seems likely that a large portion of chromium(VI) is adsorbed onto AC(HOx) in the form of Cr(III)-oxine complex.

Chromium(VI) does not react with oxine, and the rate of the complex formation reaction of chromium(III) with oxine in aqueous solution is very small. We have described the reaction of chromium(VI) with reducing reagents in the presence of EDTA⁶⁾ and also the mechanism for the H_2O_2 catalysed reaction of Cr(III) with EDTA⁷⁾.

Table 1 Desorption of chromium from activated carbon and AC(HOx) with 50 ml, 0.10 mol dm^{-3} NaOH solution

Feed solution *1	Adsorbent	pH *2	Desorption recovery	
			Total Cr(VI)	Cr(III) (%) *3
Cr(VI)	AC	2.4	78	60
Cr(VI)	AC	4.9	100	33
Cr(VI)	AC(HOx)	2.4	14	82
Cr(VI)	AC(HOx)	4.9	6	56

Adsorbents: 5.0 g; Flow rate: 1.0 ml/min.

*1 Feed solution: 100 ml of 1.00×10^{-3} mol dm^{-3} (Adsorbed chromium weight: 5.2 mg).

*2 pH of the feed solution.

*3 Ratio of desorbed chromium(III) to total chromium desorbed.

The presence of a reactive $\text{Cr}^{\text{IV(V)}}$ -EDTA complex was proposed as mentioned above. Based on these facts and the results obtained in this work, the mechanism of the adsorption of chromium(VI) onto AC(HOx) may be proposed as follows. Oxine reacts with $\text{Cr}^{\text{IV(V)}}$, which is formed in the course of the reduction of Cr(VI) by activated carbon, to provide $\text{Cr}^{\text{IV(V)}}$ -oxine complex. This complex may be subsequently reduced to Cr(III)-oxine complex by activated carbon.

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