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Recovery of Chromium (VI) from Wastewater with Iron (III) Hydroxide

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Cr(VI) in wastewaters was adsorbed on iron(III) hydroxide at pH4.5 and, after the separation of the precipitate, Cr(VI) was desorbed in alkaline solution of pH10.5. By this procedure, Cr(VI) was selectively recovered from wastewaters containing Cd(II), Pb(II), Zn(II), Cu(II), and Cr(III). Phosphate and sulfate ions interfered with Cr(VI) adsorption. The phosphate interference was suppressed by increasing the amount of iron(III) hydroxide, and the sulfate interference was appreciably suppressed by the use of calcium hydroxide instead of sodium hydroxide as a neutralizing agent.

1. Introduction

Chromium(VI) is employed in the manufacture of inks, dyes, and paint pigments, and in chrome tanning and electroplating operations. However, chromium(VI) has been demonstrated to be a public health hazard. Its discharge into waters is restricted by legislated water quality criteria.

In the treatment of chromium(VI) in wastewaters, chromium(VI) is generally reduced to chromium(III) with sulfur dioxide, sodium bisulfite, or iron(II) sulfate, and the chromium(III) formed is then precipitated as chromium(III) hydroxide with sodium hydroxide or calcium hydroxide¹⁻³). These reduction methods, however, can not be used if the recovery of chromium(VI) is requested. For recovery, the ion exchange⁴) and evaporation⁵) methods have been suggested, but the former method is expensive and the latter needs considerable energy.

In a previous paper⁶), we proposed a mechanism of the adsorption and desorption of chromium(VI) onto iron(III) hydroxide. This paper reports a method of recovering chromium(VI) from wastewaters by the adsorption and desorption processes.

2.2 Procedure

Appropriate volumes of 1.00 mol dm⁻³ iron(III) and 0.20 mol dm⁻³ chromium(VI) solutions were pipetted into a volumetric flask, and the solution was diluted to 200 ml with distilled water. The initial pH of this solution was about 2. By adding a 1.0 mol dm⁻³ NaOH solution, the pH of the solution was brought to 4.5, where a precipitate is formed. The suspension thus obtained was stirred at a rate of 200 rpm for 30 min at 25°C. The precipitate was separated from the supernatant, washed several times with water whose pH was adjusted to 4.5, and dispersed in an appropriate volume of water of pH10.5. This suspension was again stirred for 30 min at 25°C, and the precipitate was filtered off with a glass filter (3G5). The use of filter paper was avoided because it would reduce a part of chromium(VI) to chromium(III).

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Chromium(VI) in an alkaline solution absorbs the ultraviolet light at 370 nm, but chromium(III) does not. Hence, chromium(VI) in solution can be selectively determined by UV absorption at 370 nm in the presence of chromium(III). Total chromium was determined by an atomic absorption method using ammonium perchlorate as a releasing agent which prevented interference from other metal ions and anions⁷⁾. The amount of the adsorbed chromium(VI) was determined by the difference between the initial and the final concentration of chromium(VI) in the supernatant.

The experiments on the recovery of chromium(VI) were performed in the presence of various heavy metal ions and anions. The heavy metal ions were determined by the atomic absorption method. Sulfate and phosphate ions were determined by the barium chloranilate⁸⁾ and molybdenum blue⁹⁾ methods, respectively. These colorimetric methods are subject to interference from chromium(VI). The value obtained by the barium chloranilate method is due to sulfate and chromium(VI) ions, but can be corrected by subtracting chromium(VI) value determined from the absorbance at 370 nm. The value obtained by the molybdenum method can be freed from interference by the addition of a large amount of stannous chloride as a reducing agent of chromium(VI).

3. Results and Discussion

3.1 Recovery of chromium(VI) in the presence of heavy metals

Adsorption or coprecipitation of chromium(VI), cadmium(II), zinc(II), copper(II), and chromium(III) on iron(III) hydroxide was examined as a function of pH. As shown in Fig. 1, chromium(VI) was not adsorbed at pH's greater than 8.5 and in the range 8.5 – 4.5 the adsorption of chromium(VI) increased as the pH decreased. Below pH4, the iron(III) hydroxide was colloidal and it took considerable time to separate the iron(III) hydroxide from the solution by sedimentation. On the other hand, all of the heavy metal ions were completely coprecipitated with iron(III) hydroxide at pH's above 10 where chromium(VI) was not adsorbed. On the basis of these results, chromium(VI) can be recovered from solutions containing cadmium(II), zinc(II), copper(II), and chromium(III) by following the procedure described earlier. The results will be shown later.

3.2 Effect of the amount of iron(III) hydroxide on adsorption of chromium (VI)

The adsorption of chromium(VI) increased with increasing amount of iron(III) hydroxide, as shown in Fig. 2. With an initial concentration of 1.0 mmol dm⁻³ chromium(VI) and 10 mmol dm⁻³ iron(III) hydroxide, adsorption of chromium(VI) was 99% at pH4.5. In the case of 10 mmol dm⁻³ chromium(VI), the concentration of iron(III) hydroxide needed to adsorb the chromium(VI) to this extent was also ten times the concentration of chromium(VI).

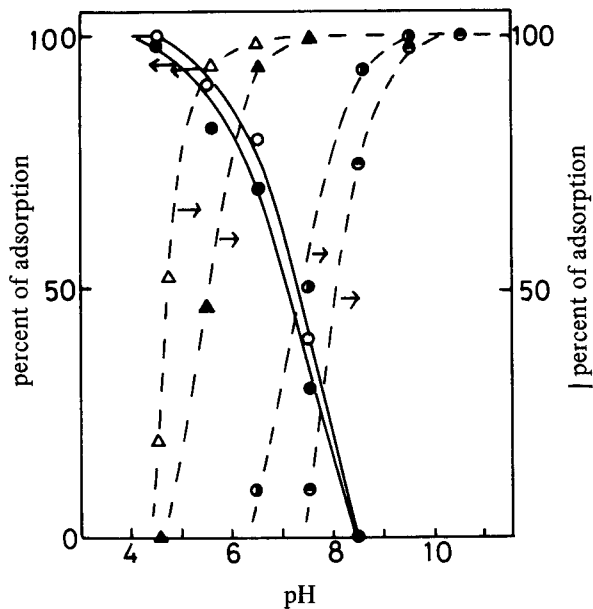


Fig. 1 Adsorption of Cr(VI) in the presence (○) and absence (●) of various metal ions, and coprecipitation of various metal ions with iron(III) hydroxide as a function of pH. Initial concn. of Cr(VI) : 1.0 mmol dm^{-3} , Fe(III) : 10 mmol dm^{-3} , heavy metal ions : 0.2 mmol dm^{-3} Cr(III) Δ , Cu(II) \blacktriangle , Zn(II) \circ , Cd(II) \bullet .

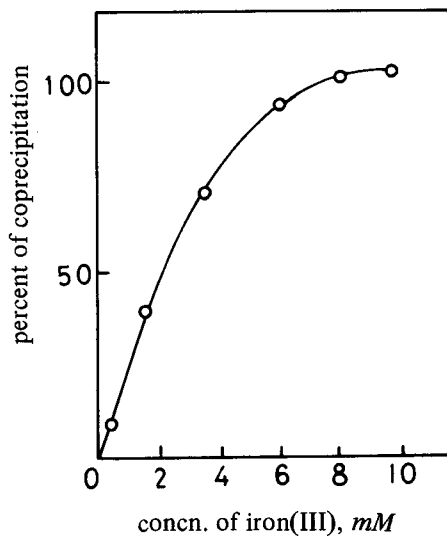


Fig. 2 Adsorption of Cr(VI) as a function of iron(III) hydroxide concentration (pH4.5). Initial concn. of Cr(VI) : 1.0 mmol dm^{-3} .

3.3 Recovery of chromium(VI) in the presence of anions

Chloride, phosphate, and sulfate ions compete with HCrO_4^- for surface binding sites of iron(III) hydroxide and, therefore, recovery of chromium(VI) in the presence of these anions was studied in detail.

In a system of 1.0 mmol dm^{-3} chromium(VI), 10 mmol dm^{-3} iron(III) hydroxide, and 30 mmol dm^{-3} chloride ion (1065 ppm), the recovery of chromium(VI) was 95%, being slightly less than in the absence of chloride ion.

Table 1 shows the effect of phosphate ion on the adsorption of chromium(VI) on iron(III) hydroxide at pH4.5. The adsorption of chromium(VI) decreased with the addition of phosphate ion. This is presumably due to the decrease of iron(III) hydroxide available for the adsorption of chromium(VI), because iron(III) hydroxide is changed stoichiometrically to FePO_4 upon the addition of phosphate ion. However, chromium(VI) was again adsorbed when iron(III) hydroxide was added in an amount corresponding to that of iron(III) reacted with phosphate ion, and it was recovered at an efficiency of 96% in an alkaline solution of pH10.5.

Sulfate ion frequently coexists with chromium(VI) in wastewaters. In the system of 1.0 mmol dm^{-3} chromium(VI), 10 mmol dm^{-3} iron(III) hydroxide, and 15 mmol dm^{-3} sulfate at pH4.5, chromium(VI) was not adsorbed. The elimination of the interference was tried by using alkaline earth metal ions such as calcium and magnesium ions which form insoluble salts with sulfate ion. By addition of more than 20 mmol dm^{-3} calcium hydroxide, about 90% of the chromium(VI) was again adsorbed on iron(III) hydroxide at pH4.5 (Fig. 3). Further, calcium hydroxide facilitated the separation of the supernatant from the iron(III) hydroxide, since the sedimentation was rapid. When calcium hydroxide was used, however, the adsorption of chromium(VI) was not complete even at pH4.5 (Fig. 3) and, moreover, only 65% of the adsorbed chromium(VI) was desorbed even at pH 10.5. This is explained by considering that some of the Ca(OH)_2 particulates in suspension covered the chromium(VI) on iron(III) hydroxide, and prevented the complete desorption even at pH10.5.

Table 1 Effect of phosphate on adsorption of Cr(VI) at pH 4.5^{a)}

PO_4^{3-} added mmol dm ⁻³	$[\text{PO}_4^{3-}] / [\text{Fe(III)}]$ %	adsorption of Cr(VI) %
0.53	5.3	97
1.1	11	91
2.1	21	81
3.2	32	67
5.3	53	38

a) Concn. of Cr(VI) : 1.0 mmol dm^{-3} , Fe(III) : 10 mmol dm^{-3} .

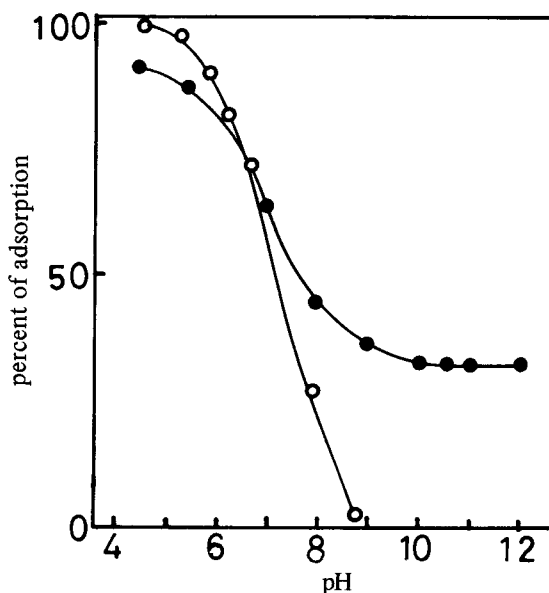


Fig. 3 Adsorption of Cr(VI) as a function of pH. NaOH (○) or Ca(OH)₂ (●) as neutralizing agent. Initial concn. of Cr(VI) : 1 mmol dm⁻³, Fe(III) : 10 mmol dm⁻³.

3.4 Recovery of chromium(VI) from artificial and real wastewaters

Various anions and cations coexist with chromium(VI) in real wastewaters. The applicability of this procedure was tested on artificial and real wastewaters, using calcium hydroxide as the neutralizing agent.

Table 2 shows the recovery of chromium(VI) from an artificial wastewater containing various kinds of heavy metals and anions. This experiment was performed twice. The mean value of the recovery was 80%. Heavy metals were not detected in the recovered solutions. It is to be noted that chromium(VI) was recovered completely even in the presence of lead which forms an insoluble salt, PbCrO₄, with chromium(VI). The selective recovery of chromium(VI) in the presence of chromium(III) is of practical importance. As shown in Table 3, the concentration of total chromium measured by the atomic absorption method was in accordance with that of chromium(VI) measured by the UV absorption method within experimental error. This result indicates that chromium(VI) was completely separated from chromium(III) and recovered by the present method.

Subsequently, this procedure was applied to the real wastewaters from the factories utilizing chromium(VI). The results are shown in Table 4. A and D factories employ chromium(VI) for metal cleaning, and B and C for electroplating. A 30 – 77 % of chromium(VI) was recovered from these wastewaters. No heavy metals except for chromium(VI) were detected in any of the recovered solutions. It should be noted that chromium(VI) was completely separated from chromium(III) in all the real wastewaters examined.

Table 2 Recovery of Cr(VI) from solution containing various ions

Initial	Concentration of ions/ppm	
		After treatment ^{a)}
Cr(VI)	50	39.6
Cd(II)	50	ND ^{b)}
Cu(II)	50	ND
Pb(II)	50	ND
Zn(II)	50	ND
PO ₄ ³⁻	200	ND
SO ₄ ²⁻	400	trace

a) Mean of 2 trials. b) ND : not detected.

Table 3 Recovery of Cr(VI) from solutions containing Cr(III) and Cr(VI)^{a)}

Cr(III) added / ppm	Recovery of Cr	
	Total Cr found ^{b)} /ppm	Cr(VI) found ^{c)} /ppm
1	9.9	9.9
5	9.9	10.1
10	9.8	9.9
15	9.8	10.0
20	9.7	9.8

a) Initial concentration of Cr(VI) : 10.0 ppm.

b) Atomic absorption method.

c) UV absorption method (370 nm).

Table 4 Recovery of Cr(VI) from industrial wastewaters

Factories	Concn. of heavy metals / ppm								
	Fe	Ni	Zn	Pb	Cu	Cd	Cr(III)	Cr(VI)	
A	W ^{a)}	0.9	<0.1	0.4	0.3	4.0	0.02	7.5	14.5
	R ^{b)}	<0.1	<0.1	<0.05	<0.1	<0.05	<0.01	<0.1	11.2
B	W	175	<0.1	18	<0.1	46	<0.01	38	437
	R	<0.1	<0.1	<0.05	<0.1	<0.05	<0.01	<0.1	180
C	W	8.2	11.5	160	<0.1	<0.05	<0.01	15	505
	R	<0.1	<0.1	<0.05	<0.1	<0.05	<0.01	<0.1	146
D	W	812	<0.1	14	<0.1	117	0.3	247	392
	R	<0.1	<0.1	<0.05	<0.1	<0.05	<0.01	<0.1	136

a) W : wastewater. b) R : recovered solution.

4. Conclusion

Removal of chromium(VI) could be performed by adsorption on iron(III) hydroxide at pH4.5. After this, iron(III) hydroxide was separated from the wastewaters, and chromium(VI) was desorbed from the iron(III) hydroxide by dispersing it into an alkaline solution with a pH above 8.5.

In the presence of cadmium(II), lead(II), chromium(III), copper(II), and chromium(VI), the desorption must be made at pH10.5. When a large amount of phosphate ion is present, the iron(III) hydroxide must be added in excess. When sulfate ion is present, calcium hydroxide is to be used as a neutralizing agent. However, the recovery in this case is less than that in the case of sodium hydroxide as a neutralizing agent.

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