

Reductive Adsorption of Chromium(VI) with Activated Carbon

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Abstract Reductive adsorption of chromium (Cr) has been investigated, employing coal-based activated carbon with batchwise study. The adsorption was carried out by varying parameters such as pH of the aqueous solution and contact time. Cr(III) was hardly adsorbed on activated carbon, and it was precipitated at high pH region. High adsorption amounts of Cr(VI) was obtained at pH range 4.5 – 5.5. In the adsorption process, reduction of Cr(VI) to Cr(III) was occurred at especially acidic pH region, and thus most of Cr remained in the aqueous solution in this pH region was Cr(III).

1 Introduction

Increasing attention is being given to human health hazards caused by the contamination of toxic heavy metals in the water environment and their accumulation in human body has been a serious health problem. Chromium (Cr) is one of the contaminants which exists in hexavalent form (Cr(VI)) and trivalent form (Cr(III)), and Cr(VI) possesses significantly higher level of toxic than Cr(III). Cr(VI) poisoning in human being is harmful to the nervous system, bleed, live and bone (Chen *et al.*, 2018). Cr and its compounds are widely used in various industries field such as electroplating, metal polishing and leather tanning (Beheshti *et al.*, 2016). The maximum level concentration in wastewater is reported at 0.05 mg/L for Cr(VI) and 5 mg/L for Cr(III) (Ali *et al.*, 2015; Chen *et al.*, 2018). Hence, removal of Cr(VI) has received more and more attention.

Presently, several methods and technologies have been adopted to remove Cr(VI) from water, such as ion exchange (Ali *et al.*, 2015), adsorption (Kobyas *et al.*, 2004), membrane technology (Çengelöglu *et al.*, 2003), and reduction (Chen *et al.*, 2018). Among available methods, adsorption is one of preferable method for removal of Cr(VI) in aquatic environment. In addition, reduction of Cr(VI) to Cr(III) is effective for detoxication, since the toxic of Cr(III) is much lower than that of Cr(VI) 100 times (Chen *et al.*, 2018). Various of materials, such as iron compounds (Ali *et al.*, 2015), ion exchange resin (Pehlivan and Cetin, 2009), activated carbon (Chen *et al.*, 2018; Kobyas *et al.*, 2004), magnetic chitosan (Zheng *et al.*, 2018) and nickel oxide (Behnajady and Bimeghdar, 2014), were also reported. Among these materials, activated carbon offers an attractive and low-cost option for the removal of contaminants from water environment. Several researches on adsorption of Cr(VI) with activated carbon have been reported in literature (Kobyas *et al.*,

2004; Nethaji *et al.*, 2013). However, reduction of Cr(VI) to Cr(III) with activated carbon during the adsorption processing was scarcely investigated.

In the present work, the reductive adsorption of Cr(VI) with coal-based activated carbon was investigated.

2 Experiment

2.1 Material

Coal-based activated carbon, M010, was supplied by Mitsubishi Chemical Co. (Tokyo, Japan). Cr(NO₃)₃·9H₂O was supplied from Alfa Aesar (Ward Hill, USA). CrO₃ and all other reagents were supplied by Wako Pure Chemical Industries (Osaka, Japan) as analytical grade reagents. The activated carbon was characterized by a zeta potential analyzer (ELSZ-1000, Otsuka Electronics Co., Ltd.).

2.2 Experiment

Aqueous feed solutions were prepared by dissolving CrO₃ or Cr(NO₃)₃·9H₂O in deionized water. Batchwise experiment was carried out by shaking mixture of M010 (50 mg, activated carbon particle size, 0.5 – 1.0 mm) and aqueous feed solution (10 mL) at 298 K. Cr concentration was fixed at 1.0 mmol/L, and pH values were adjusted by adding amount of NaOH or H₂SO₄. After filtration, total Cr concentration ([Cr]_{total}) was determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu ICPE-9000), while Cr(VI) concentration was analyzed by UV/vis spectrophotometer (UV-660, JASCO) at 540 nm after reacting with 1,5-diphenylcarbazide (DPC) indicator (Çengelöglu *et al.*, 2003; Wiryawan *et al.*, 2018). Cr(III) concentration was determined by [Cr(III)] = [Cr]_{total} – [Cr(VI)]. The adsorption

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amount of Cr on M010, q (mmol/g), was determined by equation:

$$q = \frac{([\text{Cr}]_{\text{feed}} - [\text{Cr}]_{\text{total}}) \cdot V}{m} \quad (1)$$

where $[\text{Cr}]_{\text{feed}}$ and $[\text{Cr}]_{\text{total}}$ are initial and equilibrium concentrations of Cr in aqueous solution [mmol/L], V is the volume of solution [L], and m is weight of adsorbent [g].

3 Results and Discussion

3.1 Characterization of activated carbon M010

Characterization of M010 was carried out in a previous work (Yamaguchi *et al.*, 2010). Pore volume and specific surface area were determined by N₂ adsorption as 0.531 cm³/g and 1390 m²/g. Amount of surface functional group of M010 was analyzed by Boehm titration as 0.190 mmol/g phenolic and 0.040 mmol/g basic. Figure 1 shows the zeta potentials of M010 in aqueous solution at various of pH. The isoelectric point (IP) was determined as 5.95.

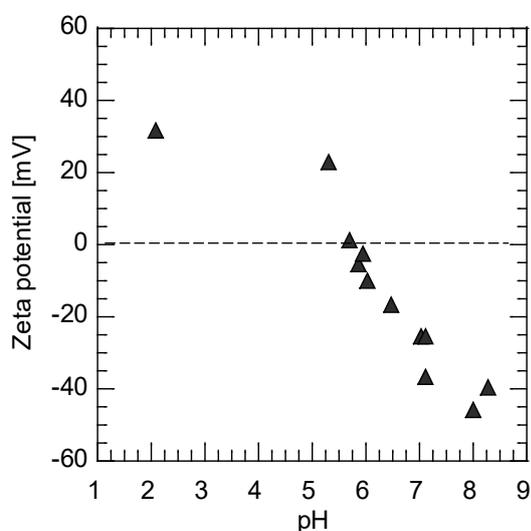


Figure 1. The zeta potential of M010 in aqueous solution with various pH.

3.2 Effect of pH on reductive adsorption of Cr(VI)

The pH of the aqueous solution plays an important role to determine the adsorption performance, since species distribution of Cr in an aqueous solution is strongly affected by pH of aqueous solution. Figure 2 shows the effect of pH on adsorption amount of Cr(VI) on M010. The adsorption amount is increased in acidic pH region, and then is decreased in pH > 6.0. The adsorption amounts were sharply depended by pH, and high adsorption amount of 0.22 mmol/g was obtained in $\text{pH}_{\text{eq}}=4.5-5.5$. The different adsorption amount could be explained that the electrostatic attraction between adsorbate ($\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-}) and surface of adsorbent were occurred below pH 5.95 (IP=5.95).

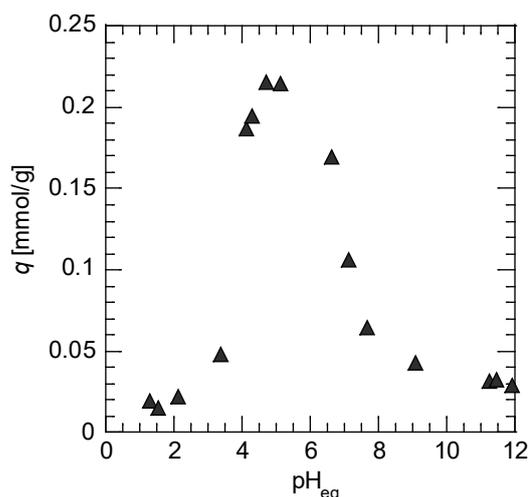
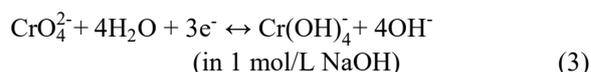
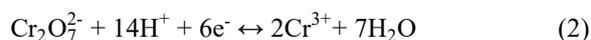


Figure 2. Effect of pH on adsorption of Cr(VI) with M010.

Figure 3 shows the percentage of Cr species remained in aqueous solution, after adsorption. Most of Cr remained in solution at pH < 4.0 was Cr(III), while that at pH > 4.0 was Cr(VI). Reduction of Cr(VI) in aqueous solution was proceeded as follows Eqs. (2) and (3) (Bard *et al.*, 1985; Milazzo *et al.*, 1978):



In acidic pH region, Cr(III) reduced by M010 could be released into aqueous solution, and then adsorption – reduction was cycled. In addition, Cr(III) reduced and remained in solution could be precipitated (Bernardo *et al.*, 2009) and adsorbed by M010. Figure 4 shows the effect of pH on the precipitation percentage of Cr(III). Cr(III) was started precipitation from pH=4.5, and the most of Cr(III) was precipitated in pH range 5.0 – 10.0.

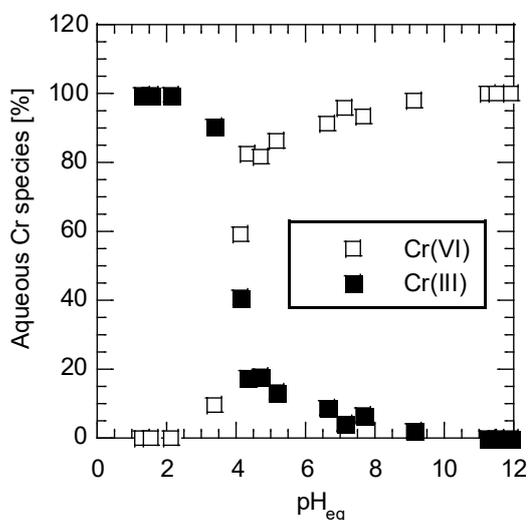


Figure 3. Cr species remained in aqueous solution.

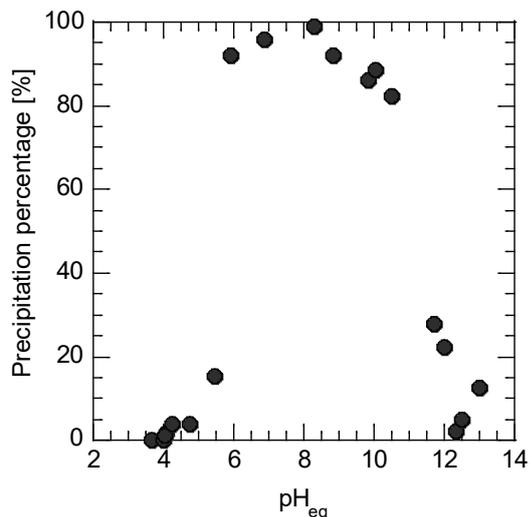


Figure 4. Effect of pH on precipitation percentage of Cr(III).

Figure 5 shows the effect of pH on adsorption of Cr(III) at pH < 4.5. Cr(III) was hardly adsorbed on M010 in acidic pH region. This is because the surface of M010 has positive charge in pH < 5.95, while Cr(III) exists as

cationic Cr³⁺ in acidic pH region. Therefore, the reductive adsorption of Cr(VI) could be described as the adsorption of Cr(VI) – reduction of Cr(VI) to Cr(III) – release of Cr(III) in aqueous solution.

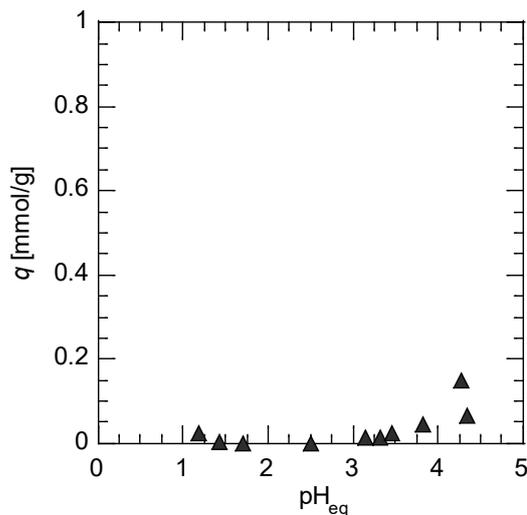


Figure 5. Effect of pH on adsorption of Cr(III).

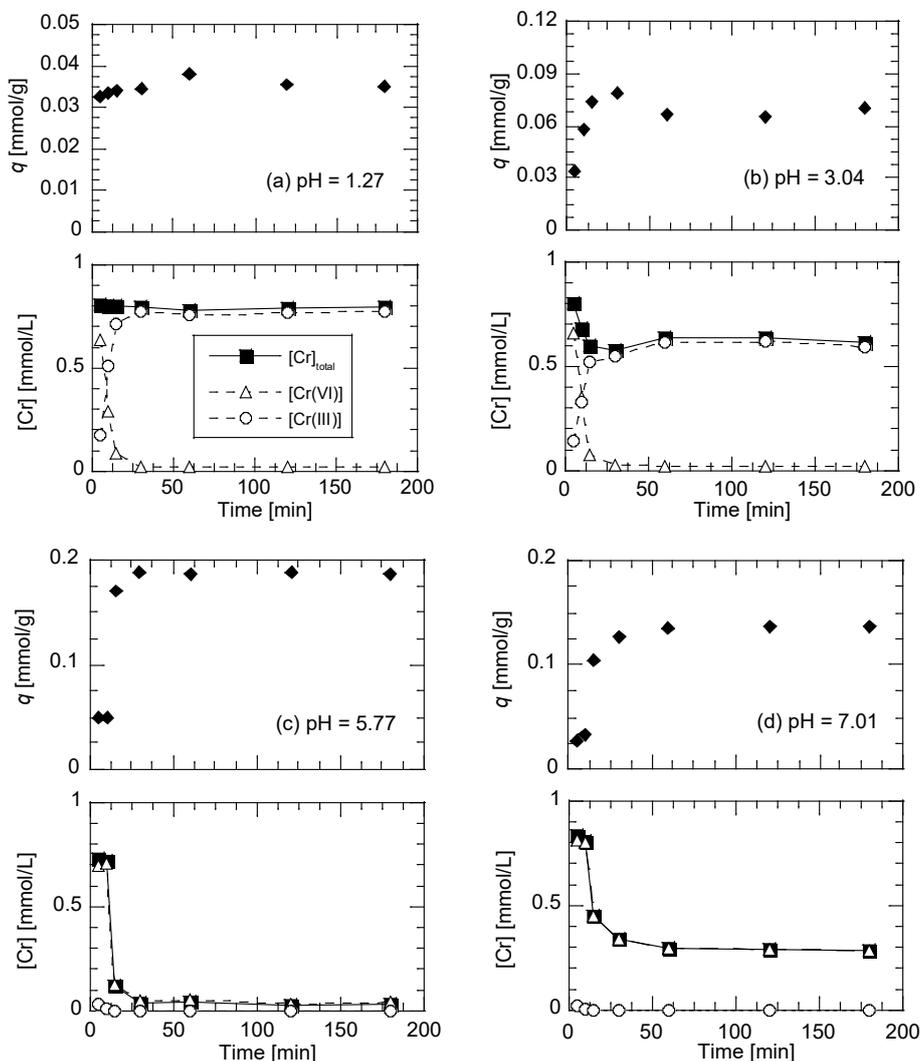


Figure 6. Time-course and variation of pH on reductive adsorption of Cr(VI) on M010.

3.3 Time-course with variation of pH in reductive adsorption of Cr(VI)

Time-course variation of the reductive adsorption of Cr(VI) with variation of pH values was investigated. Figure 6 shows time-course variation of adsorption amount of Cr on the M010, together with the concentration of Cr(VI) and Cr(III) in the aqueous solution. The reductive adsorption was achieved to be equilibrium within 30 min in all pH regions investigated. In the cases at acidic pH region (pH=1.27 and 3.04), the concentration of Cr(III) in the aqueous solution was therefore increased with operation time, while the concentration of Cr(VI) was decreased. On the other hand, the reduction hardly occurs at higher pH region (pH = 5.77 and 7.01) and thus the concentration of Cr(III) in the aqueous solution was almost zero.

The detail information on the kinetics of the reductive adsorption of Cr(VI) on M010 should be investigated in the future, to reveal the mechanism of the reductive adsorption system.

4. Conclusion

Reductive adsorption of Cr(VI) with activated carbon M010 was investigated using batchwise study. The reductive adsorption of Cr(VI) was equilibrium at 30 min. Reductive adsorption of Cr(VI) was sharply affected by the pH of aqueous solution. High adsorption amount obtained within pH 4.0 – 5.5, while reduction of Cr(VI) was occurred in aqueous solution in acidic region.

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