Reducing Hexavalent Chromium to Trivalent Chromium with Zero Chemical Footprint: Borohydride Exchange Resin and a Polymer-Supported Base

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ABSTRACT: Aqueous hexavalent chromium, Cr(VI), is rapidly reduced to trivalent chromium, Cr(III), by exposure to (polystyrylmethyl)trimethylammonium borohydride and with Amberlite-supported mild bases in a heterogeneous reaction (Scheme 2) for the reduction of Cr(VI) to Cr(III) by metal oxides or chlorination. Physical methods of Cr(VI) removal used in water treatment sites and some point of use applications depend on adsorption, filtration, or ion exchange technologies. Alternatively, Cr(VI) elimination strategies rely on the chemical transformation of Cr(VI) to Cr(III). This redox reaction has been accomplished on the interfacial surface of commercial activated carbon adsorbents, Fe(0) and biochar. Soluble reducing reagents, such as L-ascorbic acid, Fe(II), H2S, and sodium borohydride (NaBH4) buffered with sodium borate, among others, are also effective. However, a serious consequence of removing Cr(VI) under reduction conditions is the introduction of new pollutants to the water source. As an example, the reduction of chromate to Cr(III) with a sodium borate buffered solution of NaBH4 is shown in Scheme 1. Inherent in this protocol is the cross-contamination of the water source with sodium borohydride (4 molar excess), boronic acid byproducts, and sodium borate buffer (1000 μM) which necessitates an additional remediation step.

We report on an environmentally benign approach for Cr(VI) reduction which relies on the use of borohydride exchange resin, A (Scheme 2). Specifically, borohydride is attached to a water insoluble ion exchange resin (Amberlite). This reagent has found uses in organic synthesis for the reduction of a variety of functional groups through hydride delivery mechanisms. In other instances, borohydride serves as a single electron donor reducing agent in the reduction of acridinium cation and selenium. Furthermore, to avoid contamination of the source water with high concentrations of buffer, we employ insoluble bases to act as mild buffering agents, such as attached to Amberlite (B). A distinct advantage of this heterogeneous reaction (Scheme 2) for the reduction of Cr(VI) to Cr(III) is the simplified post reaction work-ups requiring only filtration of the resin-bound borate reagents (A and C) and bases (B). Afterward, only Cr(III) species would remain in the water.

EXPERIMENTAL PROCEDURE

Reagents were purchased from Fisher Scientific or Sigma-Aldrich and used without purification. Polymer-supported reagents were obtained from Biotage USA: macroporous borohydride (A) (MP-BH4; 2.95 mmol/g; 655 μm mean bead size), ISOLUTE Si-Tris-amine (B1; #9495-0010; 1.6 mmol/g), and ISOLUTE Si-carboxylate (B2; #800267; 2.9 mmol/g). Amberlite IRA-400 chloride form was purchased from Fisher Scientific. Deionized water is used throughout. Spectroscopic measurements of the chromate solution concentration were monitored on a Metash Model V-5000 Visible Spectrophotometer at 372 nm. The average of duplicate or triplicate experiments and the range of chromate reductions are reported.

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Scheme 1. Reaction of NaBH₄, Sodium Borate, and Potassium Dichromate at pH 8–10 to Furnish Cr(III) and Boric Acid Species

\[
\text{K}_2\text{Cr}_2\text{O}_7 + \text{NaBH}_4 + \text{sodium borate} \xrightarrow{\text{H}_2\text{O}} \text{Cr(OH)}_3 + \text{NaB(OH)}_4 = \text{KOH} + \text{I}_2 + \text{sodium borate}
\]

Scheme 2. Reaction of Polymer-Supported BH₄ (A), Polymer-Supported Base (B), and Potassium Dichromate at pH 8–9 Furnishes Reduced Borohydride (C), along with (B), and after Filtration, Only Solutions of Cr(III)

■ TYPICAL PROCEDURE (SCHEME 3) FOR THE PREPARATION OF AMBERLITE-SUPPORTED BASE B₃

To a solution (20 mL) of aqueous K₂Cr₂O₇ (200 μM) were added MP-BH₄ (A) (20 mg) and a polymer-supported base (B) (20 mg). The mixture was stirred for 120 min, or earlier times for kinetic analysis, (1” × 1” stir bar at 300 rpm), and an aliquot was removed for spectroscopic analysis. The percent removal of Cr(VI) was calculated in eq 1.

\[
\text{% Removal of Cr(VI)} = \left( \frac{\lambda_{\text{max}}[\text{stock}] - \lambda_{\text{max}}[\text{sample}]}{\lambda_{\text{max}}[\text{stock}]} \right) \times 100\% \quad (1)
\]

where \(\lambda_{\text{max}}[\text{stock}]\) is the UV absorption at 372 nm of the stock solution of Cr(VI). The \(\lambda_{\text{max}}[\text{sample}]\) is the UV absorption at 372 nm of the sample treated with (A).

■ RESULTS AND DISCUSSION

Sodium borohydride can be utilized as a one-electron-reducing agent for the removal of Cr(VI) from water sources. However, its use, along with high concentrations sodium borate buffer (1000 μM), presents a challenge for complete water remediation by introducing new chemical pollutants. To exploit the reducing ability of borohydride, we adopted water-insoluble borohydride variant in the form of polymer-bound A which is removed upon completion of water remediation, as in C. To understand the molar requirements needed for a resin-bound one-electron-reducing agent to reduce Cr(VI) to Cr(III), we varied the molar ratio of A and Cr(VI). Table 1 shows the results of reducing a 200 μM solution of K₂Cr₂O₇. The results indicate that 10 molar equivalents of A is necessary to completely reduce Cr(VI) levels within 120 min. Fewer molar equivalents of A require longer reaction times (data not shown). The need for excess reagent may reflect chromat’s slow accessibility to some borohydride reagent within the porous resin.

To determine the minimum amount of buffer needed to slow the decomposition of borohydride to boric acid, the concentration of sodium borate was varied. The results in Table 2 indicate that sodium borate is effective at low concentrations—94% reduction of Cr(VI) at 25 μM. However, in the absence of buffer (pH 6.3), the competitive reaction of hydrolysis of borohydride to boric acid occurs faster than chromate reduction.

With these results in hand, we sought to further reduce the remediation footprint by using commercial insoluble mild organic bases (B₁–B₂) or attaching mild bases to Amberlite to form insoluble reagents B₃–B₅. Scheme 3 shows the reaction of Amberlite (IRA-400 chloride form) with N-cyclohexyl-2-aminoethanesulfonic acid (CHES) in the aqueous base to form B₄.

The physical properties of the bases B₁–B₅ are shown in Table 3.

The results from Table 4 using insoluble bases B₁–B₅ to aid in pH maintenance indicate that B₂–B₅ furnish suitable environments for the removal Cr(VI) to occur, with reduction values of 82–99%. Reports on the complexation of chromate with tertiary alkyl amines have been reported, which in the case of B₁ may be responsible for the decrease in Cr(VI) reactivity with the borohydride reagent. With these bases, a range of pH values (7.55–8.96) were effective in controlling the reduction of Cr(VI).

Table 1. Reduction of a 200 μM Solution of K₂Cr₂O₇ in 1000 μM Sodium Borate with Varying Molar Amounts of MP-BH₄ (A) after 120 min in a Stirring Environment

| Cr(VI) volume (mL) | Cr(VI) μmol | MP-BH₄ (A) quantity (mg) | MP-BH₄ (A) μmol | molar ratio A:Cr(VI) | reduction of Cr(VI) (%) |
|------------------|------------|--------------------------|----------------|---------------------|------------------------|
| 10               | 2.0        | 20                       | 60.0           | 30:1                | 100                    |
| 20               | 4.0        | 20                       | 60.0           | 15:1                | 100                    |
| 30               | 6.0        | 20                       | 60.0           | 10:1                | 97 ± 3                 |
| 40               | 8.0        | 20                       | 60.0           | 7.5:1               | 79 ± 6                 |
| 50               | 10.0       | 20                       | 60.0           | 6:1                 | 75 ± 6                 |

Table 2. Reduction of a 200 μM Solution of K₂Cr₂O₇ (20 mL) in Varying Concentrations of Sodium Borate with 15 Molar Equivalents of A

| sodium borate conc. (μM) | reduction of Cr(VI) (%) |
|--------------------------|------------------------|
| 1000                     | 100                    |
| 100                      | 100                    |
| 50                       | 97 ± 2                 |
| 25                       | 94 ± 3                 |
| 0                        | 25 ± 11                |
After removal of all insoluble material, the source water, containing Cr(III), has a pH value of 8.7 – 8.9 compared to a pH of 6.3 for the initial 200 μM Cr(VI) solution.

To establish the potential reusability of the bases attached to the insoluble beads, a series of Cr(VI) reduction reactions were undertaken, wherein B4 was confined to a tea bag. After each reaction was complete (30 min), the bag was removed and immersed into a new Cr(VI) solution with MP-BH4. The results (data not shown) show that over the course of three reactions, the percent reduction of Cr(VI) varied by only 9%. Thus, the base-containing beads can be reused in additional remediation reactions.

To understand the contribution of the physical environment to the success of the heterogeneous reaction of chromate with MP-BH4 (A) and B4, the reaction was evaluated under different mixing conditions. Figure 1 shows the rate of Cr(VI) reduction in a stirring versus a static situation. When stirred at 300 rpm, a 95% reduction occurs within 30 min. However, at static conditions, a 9% reduction is observed. An initial rate of Cr(VI) removal in a stirred reaction of 140 μM/10 min. was calculated while the initial rate for static was 8 μM/10 min. The fast initial rate is likely due to a more efficient diffusion of chromate into the porous cavities of A that is required for contact with the borohydride species.

### CONCLUSIONS

Synthetic water, containing very high levels of Cr(VI), can be effectively and quickly remediated with the use of two polymer-supported reagents. The reagents attached to the insoluble beads, borohydride and a mild base, reduce Cr(VI) to Cr(III). The water, after filtration of the reagents, will contain only Cr(III) ions and any purification of remediation-based chemicals is not required.

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**Notes**
The authors declare no competing financial interest.

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