Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology. This journal is © The Royal Society of Chemistry 2020

Supporting Information

Carbon Electrodes are Effective for the Detection

and Reduction of Hexavalent Chromium

in Water

Callie M. Stern, Darius W. Hayes, Lebogang O. Kgoadi, Noémie Elgrishi*

Department of Chemistry, Louisiana State University,

Baton Rouge, Louisiana, 70803, United States

*Correspondence to: noemie@lsu.edu

Index		Page
Impact of citric acid on voltammograms of 200 µM Cr(VI)		
Evolution of cathodic peak current vs citric acid concentration	Figure S1	SI-3
Evolution of cathodic peak potential vs citric acid concentration	Figure S2	SI-3
Evolution of pH vs citric acid concentration	Figure S3	SI-4
UV-vis spectra of K ₂ CrO ₄ and K ₂ Cr ₂ O ₇ at 100 µM total Cr(VI)		
UV-Vis spectra of K ₂ CrO ₄ and K ₂ Cr ₂ O ₇ in pH 5.00 citric acid buffer	Figure S4	SI-5
Impact of citric acid on UV-vis spectra of 200 µM Cr(VI)		
UV-Vis spectra of citric acid titration into 200 µM Cr(VI)	Figure S5	SI-6
Evolution of pH vs citric acid titration into 200 µM Cr(VI)	Table S1	SI-6
Impact of [Cr(VI)] on voltammograms of citric acid at pH 4.75		
Voltammogram of Cr(VI) titration in 0.1 M citric acid buffer	Figure S6	SI-7
Evolution of cathodic peak potential vs Cr(VI) concentration	Figure S7	SI-7
Effect of pH on Cr(VI) detection and reduction		
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 2.25	Figure S8	SI-8
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 2.50	Figure S9	SI-8
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 2.75	Figure S10	SI-9
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 3.00	Figure S11	SI-9
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 3.25	Figure S12	SI-10
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 3.50	Figure S13	SI-10
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 3.75	Figure S14	SI-11
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 4.00	Figure S15	SI-11
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 4.25	Figure S16	SI-12
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 4.50	Figure S17	SI-12
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 4.75	Figure S18	SI-13
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 5.00	Figure S19	SI-13
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 5.25	Figure S20	SI-14
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 5.50	Figure S21	SI-14
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 5.75	Figure S22	SI-15
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 6.00	Figure S23	SI-15
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 6.25	Figure S24	SI-16
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 6.50	Figure S25	SI-16
Voltammogram of 200 µM Cr(VI) in citric acid buffer at pH 6.75	Figure S26	SI-17
Cr(VI) detection in different water sources at pH 4.75		
Voltammogram of 200 µM Cr(VI) in Milli-Q water	Figure S27	SI-18
Voltammogram of 200 µM Cr(VI) in DI water	Figure S28	SI-18
Voltammogram of 200 µM Cr(VI) in Tap water	Figure S29	SI-19
Voltammogram of 200 µM Cr(VI) in University Lake water	Figure S30	SI-19
Voltammogram of 200 µM Cr(VI) in Mississippi River water	Figure S31	SI-20

Impact of citric acid on voltammograms of 200 µM Cr(VI)



Figure S1. Evolution of cathodic peak current with increasing citric acid concentration in the presence of 200 μ M K₂CrO₄ in 1 M KCl in water, pH not controlled. The slope of the linear fit is 1.12 μ A/dec with an adj. R² value of 0.985. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S2. Evolution of cathodic peak potential with increasing citric acid concentration in the presence of $200 \ \mu M \ K_2 CrO_4$ in 1 M KCl in water, pH not controlled. The slope of the linear fit is 0.123 V/dec with an adj. R² value of 0.971.



Figure S3. Evolution of pH with increasing citric acid concentration in the presence of 200 μ M K₂CrO₄ in 1 M KCl in water, pH not controlled. Concentration of citric acid from 0, 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5 mM.

UV-vis spectra of K₂CrO₄ and K₂Cr₂O₇ at 100 µM total Cr(VI)



Figure S4. UV-Vis spectra of 100 μ M K₂CrO₄ (grey) and 50 μ M K₂Cr₂O₇ (red) in aqueous solutions in the presence of a 0.1 M citric acid buffer at a pH of 5.00 and 1 M KCl.





Figure S5. Evolution of the UV-Vis spectrum of an aqueous solution of 200 μ M K₂CrO₄ with sequential 5.2 μ M additions of citric acid. Starting volume 2 mL and ending volume 2.027 mL. Data shown is corrected for dilution.

Citric Acid (µM)	рН
0	7.322
5.2	7.077
10.4	6.993
15.6	6.867
20.8	6.774
26.0	6.713
31.2	6.596
36.4	6.510
41.6	6.451
46.8	6.387
52.0	6.291
57.2	6.221
62.4	6.130
67.6	6.095

Citric Acid	рН
72.8	6.025
78.0	5.944
83.2	5.878
88.4	5.775
93.6	5.706
98.8	5.629
104.0	5.552
109.2	5.437
114.4	5.375
119.6	5.295
124.8	5.176
130.0	5.096
135.2	5.045
140.4	4.955

Table S1. Evolution of pH in an unbuffered aqueous solution of 200 μ M K₂CrO₄ with sequential 5.2 μ M additions (1 μ L) of citric acid.

Impact of [Cr(VI)] on voltammograms of citric acid at pH 4.75



Figure S6. Representative cyclic voltammograms of 0.025 to 12 mM K₂CrO₄ in a 0.1 M citric acid buffer at pH 4.75 with 1 M KCl as the supporting electrolyte. Concentration of Cr(VI) from red to purple: 0.025, 0.05, 0.1, 0.15, 0.25, 0.3, 0.5, 0.75, 1, 3, 5, 6, 7, 8, 10, 12 mM. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S7. Evolution of the cathodic peak potential for 0.025 to 12 mM K₂CrO₄ titrated in a 0.1 M citric acid buffer at pH 4.75 in water with 1 M KCl as the supporting electrolyte. Red lines added to guide the eyes and define the two regimes.

Effect of pH on Cr(VI) detection and reduction



Figure S8. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 2.25 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu$ M K₂CrO₄. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S9. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 2.50 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu\text{M}$ K₂CrO₄. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S10. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 2.75 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu$ M K₂CrO₄. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S11. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 3.00 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu\text{M}$ K₂CrO₄. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S12. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 3.25 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu\text{M}$ K₂CrO₄. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S13. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 3.50 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu\text{M}$ K₂CrO₄. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S14. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 3.75 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu M \, K_2 CrO_4$. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S15. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 4.00 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu$ M K₂CrO₄. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S16. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 4.25 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of 200 μ M K₂CrO₄. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S17. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 4.50 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu$ M K₂CrO₄. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S18. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 4.75 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu M \, K_2 CrO_4$. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S19. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 5.00 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu$ M K₂CrO₄. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S20. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 5.25 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu M \, K_2 CrO_4$. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S21. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 5.50 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu\text{M}$ K₂CrO₄. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S22. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 5.75 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu M \, K_2 CrO_4$. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S23. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 6.00 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu M \, K_2 CrO_4$. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S24. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 6.25 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu M \, K_2 CrO_4$. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S25. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 6.50 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu\text{M}$ K₂CrO₄. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S26. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 6.75 in water with KCl as the supporting electrolyte in the absence (black) or presence (blue) of $200 \,\mu M \, K_2 CrO_4$. Data collected on 3 mm diameter glassy carbon electrodes.

Cr(VI) detection in different water sources at pH 4.75



Figure S27. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 4.75 in Milli-Q water with KCl as the supporting electrolyte in the absence (black) or presence (red) of 200 μ M K₂CrO₄. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S28. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 4.75 in deionized water with KCl as the supporting electrolyte in the absence (black) or presence (red) of $200 \,\mu\text{M}$ K₂CrO₄. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S29. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 4.75 in building tap water with KCl as the supporting electrolyte in the absence (black) or presence (red) of 200 μ M K₂CrO₄. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S30. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 4.75 in University Lake water with KCl as the supporting electrolyte in the absence (black) or presence (red) of 200 μ M K₂CrO₄. Data collected on 3 mm diameter glassy carbon electrodes.



Figure S31. Representative cyclic voltammogram of 0.1 M citric acid buffer at pH of 4.75 in Mississippi River water with KCl as the supporting electrolyte in the absence (black) or presence (red) of 200 μ M K₂CrO₄. Data collected on 3 mm diameter glassy carbon electrodes.