



# Bidentate and Monodentate Binding of Chromium (VI) on the Acid Scavenger Exchange Resin, MP-Carbonate, as a Function of pH

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**Abstract** Hexavalent chromium or Cr (VI) is a serious health risk that has been identified in drinking water and generally originates as industrial by-products and hazardous waste sites, although natural sources have been reported. Common methods to remove Cr (VI) employ adsorption, filtration, ion exchange technologies, and redox reactions. We report on a macro porous polystyrene anion exchange resin, a solid-supported equivalent of tetra-alkyl ammonium carbonate (Biotage® MP-Carbonate), to effectively remove Cr (VI) from synthetic wastewater with bidentate or monodentate binding modes of chromate, depending on the pH environment. Sorption capacity is pH dependent with 332, 161, and 163 mg CrO<sub>4</sub><sup>2-</sup> per gram of MP-Carbonate adsorbed at pH 2, 6.8, and 10, respectively. Experimental data indicate an exergonic and endothermic adsorption process. Static vs. dynamic reaction conditions are discussed. Density functional theory calculations parallel the Gibbs free energy results of the bidentate binding of the large chromate ion compared to carbonate with the ammonium ions. These studies identify the potential uses of MP-Carbonate in the remediation of Cr (VI) wastewater unrelated to the pH of the water source.

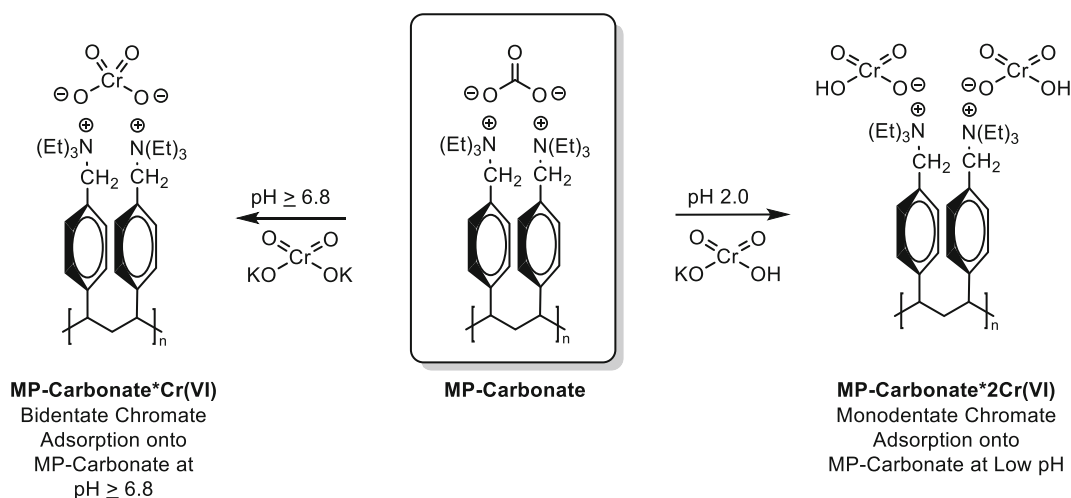
**Keywords** Chromium (VI) · Adsorption · Anion exchange resin · MP-Carbonate · Density functional theory calculations · pH independence

## 1 Introduction

Chromium (VI), or hexavalent chromium, is a well-known health risk in drinking water (Paine 2001). In response, the US Environmental Protection Agency (EPA) set a standard of the maximum containment level goal (MCLG) of 0.1 mg/L, or 0.8 μM, of total chromium ions - Cr (VI) and Cr (III). (US-EPA) The World Health Organization recommends safe levels to be less than 0.05 mg/L, or 0.04 μM (World Health Organization 2003). Cr (VI) is found naturally in ground water (Ball and Izbicki 2004; Robertson and Hexavalent 1975; Ku et al. 1978) and as by-products of many industrial processes such as metal plating, metal welding, alloy manufacturing, cooling tower blowdown, electroplating, and leather tanning (Owlad et al. 2009; McNeill et al. 2012). In aqueous solution hexavalent chromium exists in different ionic forms depending on pH (Beattie and Haight 1972). At values below 1, the dominant species is H<sub>2</sub>CrO<sub>4</sub> and can serve as a strong oxidizing reagent of organic alcohols and aldehydes. Between 1 and 6.5, the HCrO<sub>4</sub><sup>1-</sup> ion is the main form and will dimerize to form the dichromate dianion (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) at concentrations above 10 mM. Above pH 6.5 the major ion is CrO<sub>4</sub><sup>2-</sup>.

Physical methods of Cr (VI) removal are widely applied at contamination sites (Palmer and Wittbrodt 1991), water treatment facilities (Pradhan et al. 2017; Johnson et al. 2008; Fu et al. 2014), and some point of use applications (Korngold et al. 2003). These approaches generally rely on adsorption (Pakade et al. 2019; Pakade and Chimuka 2013), with zirconium-

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**Fig. 1** Proposed binding of chromate to a represented drawing of MP-Carbonate in a bidentate orientation at pH 7–10 and in a monodentate fashion at pH 2

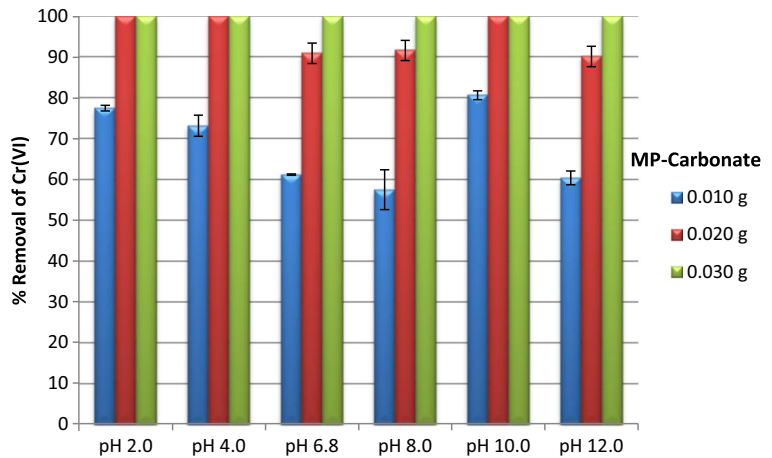
organic frameworks (Yang et al. 2019; Zou et al. 2019; Sun et al. 2018), filtration or ion exchange technologies using weakly or strongly basic anionic polymeric exchange resins (Korngold et al. 2003; Pehlivan and Cetin 2009; Shi et al. 2009; Galán et al. 2006; Rengaraj et al. 2001) to remove Cr (VI). The inherent limitation of resins containing  $\text{Cl}^-$  as the counter ion is the low pH requirements needed for the most efficient reduction of Cr (VI) levels. A chromate ion exchange resin in weakly alkaline media (Sengupta et al. 1986) has been described. Our work to adsorb Cr (VI) across a wide pH range relies on a macro porous polystyrene anion exchange resin that is a solid-supported equivalent of tetra-alkyl ammonium with  $\text{CO}_3^{2-}$  as the counter ion. Biotage® MP-Carbonate is primarily utilized in organic synthesis as a base to quench reactions or scavenge acidic organic molecules such as carboxylic acids or phenols from reaction mixtures (Ley and Massi 2000). The carbonate ion ( $\text{CO}_3^{2-}$ ) is generally believed to be coordinated between two tetra-alkyl ammonium ions on the polystyrene surface (represented as Fig. 1). We reasoned that ions such as  $\text{CrO}_4^{2-}$  might effectively bind to the resin surface at neutral and above pH values in a bidentate fashion (Korngold et al. 2003) and monodentate in acidic environments. To test this hypothesis MP-Carbonate was treated with solutions of 200 and 500  $\mu\text{M}$   $\text{K}_2\text{CrO}_4$  at pH values from 2.0 to 12.0. From these experiments, loading values, rates of reactions, and thermodynamic properties were determined. Molecular modeling and semi-empirical

calculation studies using density functional theory were employed to confirm the preferential binding mode at neutral pH of chromate ion vs. carbonate.

## 2 Experimental Procedures

Biotage® MP-Carbonate, a macro-porous poly(styrene-co-divinylbenzene) triethylammonium methylpolystyrene carbonate resin (Fig. 1), was purchased from Biotage USA and used without further purification. The specifications are as follows: capacity 2.9 mmol/g; particle size 350–1250  $\mu\text{m}$ ; bulk density 500 g/L; water solubility none; color off-white or buff colored with slight odor. Potassium chromate was purchased from Fisher Scientific. Deionized water is employed throughout. Spectroscopic measurements of the chromate concentrations were measured on a Metash Model V-5000 Visible Spectrophotometer at 372 nm (Fournier-Salaün and Salaün 2007; Sanchez-Hachair and Hofmann 2018) using standard calibration curves of Cr (VI) concentrations from 5.0 to 300  $\mu\text{M}$  at the indicated pH value. Stirring was conducted with a 12 cm  $\times$  9 cm  $\times$  9 cm magnetic stir bar at the indicated rpm on a Corning Hot Plate Stirrer. The temperatures were controlled on the Corning Hot Plate Stirrer with the Cr (VI) and MP-Carbonate in a 50-mL beaker immersed in a 500-mL beaker of water that was either heated to the specified temperature, cooled in ice, or at ambient temperature. Averages of duplicate or triplicate

**Fig. 2** Removal of 20 mL of 200 μM Cr (VI) with 0.010–0.030 g of MP-Carbonate at pH 2.0–12.0 after 120 min



experiments, and the range, of chromate reductions are reported. Aqueous HCl or NaOH was used to adjust pH values that were measured on a Denver Instrument Model UB-10 pH/mV Meter.

A typical procedure for the removal of Cr (VI): To a solution (20 mL) of aqueous K<sub>2</sub>CrO<sub>4</sub> (200 μM) in a 50-mL beaker was added MP-Carbonate (0.020 g). The mixture is stirred between 500 and 700 rpm at ambient temperature and an aliquot is removed for spectroscopic analysis. The percent Cr (VI) removal was calculated according to Eq. (1)

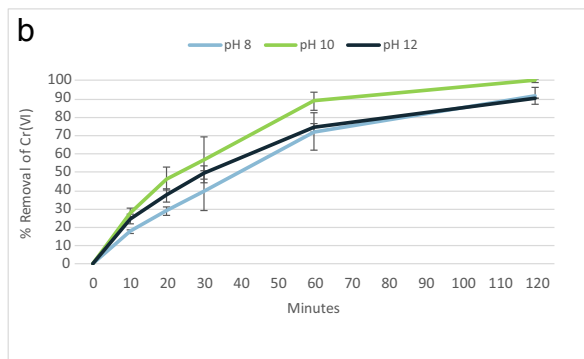
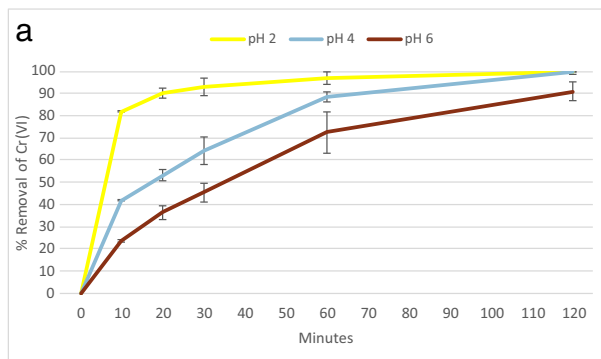
$$\% \text{Removal of Cr(VI)} = \frac{\lambda_{\max}[\text{stock}] - \lambda_{\max}[\text{sample}]}{\lambda_{\max}[\text{stock}]} \times 100\% \quad (1)$$

where λ<sub>max</sub> [stock] is the light absorption at 372 nm of the stock solution of Cr (VI) at the given pH. The λ<sub>max</sub> [sample] is the UV absorption at 372 nm of the sample treated with MP-Carbonate. Visually, the yellow CrO<sub>4</sub><sup>2-</sup> solution fades to clear and the surface of the off-white

MP-Carbonate beads changes to bright yellow during the adsorption process.

To ascertain the loading capacity of MP-Carbonate for Cr (VI), a solution of 500 μM K<sub>2</sub>CrO<sub>4</sub> (175 mL) at pH 2.0 and 200 μM K<sub>2</sub>CrO<sub>4</sub> (175 mL) at pH 6.8 and pH 10 and 0.020 g of MP-Carbonate were kept under static conditions for 7 days in a sealed beaker. The concentration of remaining Cr (VI) was determined from standard calibration curves. The breakthrough values at each pH were calculated from the amount of adsorbed Cr (VI) per gram of MP-Carbonate as shown in Eq. (2).

$$\begin{aligned} [\text{Cr(VI)}]_{\text{in}} - [\text{Cr(VI)}]_{\text{re}} &= [\text{Cr(VI)}]_{\text{ad}} \times 10^{-6} \\ &\times 0.175L \times 136 \frac{\text{g}}{\text{mol}} \times 50 \\ &= \text{Cr(VI)} \left[ \frac{\text{g}}{\text{g}} \right] \text{MP-Carbonate} \quad (2) \end{aligned}$$



**Fig. 3** **a** Acidic environment for Cr (VI) removal (20 mL of 200 μM K<sub>2</sub>CrO<sub>4</sub>) with MP-Carbonate (0.020 g). **b** Basic environment for Cr (VI) removal (20 mL of 200 μM K<sub>2</sub>CrO<sub>4</sub>) with MP-Carbonate (0.020 g)

**Table 1** Initial rates,  $R_{in}$ , (zero to 10 min) of Cr (VI) removal with MP-Carbonate at different pHs

	pH 2.0	pH 4.0	pH 6.8	pH 8.0	pH 10.0	pH 12.0
Conc. of Cr (VI) after 10 min. ( $\mu\text{M}$ )	$36.2 \pm 0.83$	$116.3 \pm 0.83$	$152.8 \pm 0.82$	$164.2 \pm 4.83$	$143.8 \pm 5.11$	$151.2 \pm 2.12$
$R_{in}$ of $\text{CrO}_4^{2-}$ adsorbed ( $\mu\text{M min}^{-1}$ )	16.4	8.4	4.7	3.6	5.6	4.9
Amt. of $\text{CrO}_4^{2-}$ removal ( $\text{mg CrO}_4^{2-} \text{ min}^{-1} \text{ g MP-Carbonate}^{-1}$ )	1.90	0.971	0.548	0.415	0.652	0.566

Removal of chromate from 20 mL of a 200  $\mu\text{M}$   $\text{K}_2\text{CrO}_4$  solution with 0.020 g of MP-Carbonate under stirring conditions. See “Experimental Procedures”

where  $[\text{Cr (VI)}]_{in}$  is the initial concentration of chromate,  $[\text{Cr (VI)}]_{re}$  the remaining concentration of Cr (VI), and  $[\text{Cr (VI)}]_{ad}$  the concentration of chromate adsorbed. Conversion of  $[\text{Cr (VI)}]_{ad}$  to grams of Cr (VI) adsorbed/g of MP-Carbonate is indicated.

Initial rate values ( $R_{in}$ ) were calculated using Eq. (3), where  $[\text{Cr (VI)}]_{t_1}$  and  $[\text{Cr (VI)}]_{t_2}$  are the initial and final concentrations at time zero and 10 or 20 min.

$$R_{in} = \frac{d[\text{Cr(VI)}]}{dt} = - \left[ \frac{[\text{Cr(VI)}]_{t_2} [\text{Cr(VI)}]_{t_1}}{t_2 - t_1} \right] \quad (3)$$

Values for thermodynamic parameters, such as free energy change ( $\Delta G^0$ ), enthalpy change ( $\Delta H^0$ ), and changes in entropy ( $\Delta S^0$ ), were calculated from Eqs. (4)–(6) (Khan and Singh 1987) using Van't Hoff relationships.  $K_c$  is the equilibrium constant,  $C_{Ae}$  is the equilibrium concentration (mg/L) of chromate on MP-Carbonate, and  $C_e$  is the equilibrium concentration (mg/L) in the reaction mixture.  $\Delta H^0$  and  $\Delta S^0$  were obtained from the Van't Hoff plot of  $\log K_c$  vs.  $1/T$  from Eq. (6) where the  $Y$ -intercept =  $\Delta S^0/2.303R$  and the slope of the line =  $-\Delta H^0/2.303R$ .

$$K_c = \frac{C_{Ae}}{C_e} \quad (4)$$

$$\Delta G^0 = -RT \ln K_c \quad (5)$$

$$\log K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad (6)$$

All calculations for the binding of  $\text{CO}_3^{2-}$  and  $\text{CrO}_4^{2-}$  to MP-Carbonate were geometry optimized and were performed at the  $\omega 97d/6-31G^*$  level of theory using the Spartan '18 software package (Wavefunction Inc n.d.). All molecular energies do not include a dielectric constant representation of the aqueous environment and, hence, its possible effects. Specifically, the quantum chemical electronic energy calculations of each reactant and product aggregate were executed at the above level of theory. To quantify the results  $\Delta E$ , the quantum mechanical calculation of the energy change of products minus reactants at 0 K and in vacuo is reported.

### 3 Results and Discussion

The use of MP-Carbonate (Fig. 1) has been restricted to organic synthesis serving as an insoluble base to quench acidic reactions or scavenge acidic by-products, such as carboxylic acids or phenols from reaction mixtures, thereby bypassing the need for aqueous extractions (Ley and Massi 2000). To examine the usefulness of

**Table 2** Breakthrough values of MP-Carbonate

	pH 2.0	pH 6.8	pH 12.0
Conc. ( $\mu\text{M}$ ) of $\text{K}_2\text{CrO}_4$ with 0.020 g MP-Carbonate	500	200	200
Volume (mL) of $\text{K}_2\text{CrO}_4$ solution	175	175	175
Conc. ( $\mu\text{M}$ ) of remaining $\text{CrO}_4^{2-}$	220	65	63
Conc. ( $\mu\text{M}$ ) of adsorbed $\text{CrO}_4^{2-}$	280	135	137
Grams $\text{CrO}_4^{2-}$ adsorbed per 0.020 g MP-Carbonate	0.00664	0.00321	0.00326
Grams $\text{CrO}_4^{2-}$ adsorbed per g MP-Carbonate	0.332	0.161	0.163

Removal of  $\text{CrO}_4^{2-}$  with 0.020 g of MP-Carbonate under static conditions after 6 days. See “Experimental Procedures”

**Table 3** Initial rates (zero to 20 min) of Cr (VI) removal with MP-Carbonate at different temperatures at pH 6.8

	0 °C	25 °C	50 °C
Conc. of $\text{CrO}_4^{2-}$ after 20 min. ( $\mu\text{M}$ )	142.3	102.9	62.7
Rate of $\text{CrO}_4^{2-}$ removal ( $\mu\text{M min}^{-1}$ )	2.9	4.9	6.9
Amt. of $\text{CrO}_4^{2-}$ removal ( $\text{mg CrO}_4^{2-} \text{ min}^{-1} \text{ g MP-Carbonate}^{-1}$ )	0.34	0.55	0.80

Removal of  $\text{CrO}_4^{2-}$  from 20 mL of a 200  $\mu\text{M}$   $\text{K}_2\text{CrO}_4$  solution with 0.020 g of MP-Carbonate under stirring conditions at pH 6.8. See “Experimental Procedures”

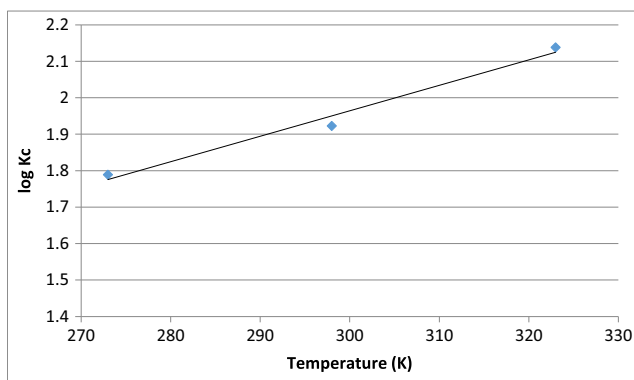
MP-Carbonate as a heavy metal adsorbent, varying amounts were added to 20 mL of a 200  $\mu\text{M}$   $\text{K}_2\text{CrO}_4$  solution at pH values from 2.0–12.0. As shown in Fig. 2 with 0.010 g of MP-Carbonate, partial chromate removal (57–79%) was achieved. When the amount of adsorbent was increased to 0.020 g, nearly complete elimination (90–100%) was observed. At 0.030 g of MP-Carbonate, the complete removal of Cr (VI) was accomplished in 2 h among all pH conditions.

Figure 3 a and b show the chromate adsorbent profiles of MP-Carbonate (0.020 g in 20 mL of 200  $\mu\text{M}$   $\text{K}_2\text{CrO}_4$ ) at pH values from 2.0–12.0. Reduction of  $\text{CrO}_4^{2-}$  levels at low pH value is in keeping with the optimum environment of recent reports of ion exchange resins (Pehlivan and Cetin 2009; Shi et al. 2009; Galán et al. 2006). However, the near equally effective removal of chromate under higher pH value conditions (Sengupta et al. 1986) can afford additional versatility during water remediation processes (McNeill et al. 2012).

To establish the kinetics of Cr (VI) adsorption by MP-Carbonate, the initial rates were calculated from Fig. 3 a and b and are shown in Table 1. From zero to 10 min, chromate adsorption occurs rapidly at pH 2.0

(16.4  $\mu\text{M min}^{-1}$ ) compared with pH 4.0 (8.4  $\mu\text{M min}^{-1}$ ) and above (3.6–5.6  $\mu\text{M min}^{-1}$ ). The initial rapid rate reflects the ability of Cr (VI) to react with readily accessible carbonate/ammonium ions on or near the surface of the bead. From this we calculate that initially 1.90, 0.548, and 0.652 mg of Cr (VI) are adsorbed per minute per gram of MP-Carbonate at pH 2.0, 6.8, and 10.0, respectively. We propose that under HCl conditions the tetra-alkyl ammoniums' counter ion,  $\text{CO}_3^{2-}$ , is rapidly replaced by  $\text{Cl}^-$  and subsequently exchanges with the  $\text{HCrO}_4^{1-}$  ion, as shown in Fig. 1 as MP-Carbonate 2Cr(VI). The increased rate suggests a faster displacement of the  $\text{Cl}^-$  leaving group coupled with a doubling of the available ammonium sites on the adsorbent. At values at or above neutral pH,  $\text{CO}_3^{2-}$  exchanges with  $\text{CrO}_4^{2-}$  for adsorption. Support for this is seen in the increase from pH 6.8 to pH 7.5 of a Cr (VI) solution after MP-Carbonate (0.02 g) has been statically exposed to chromate (120 mL of 200  $\mu\text{M}$   $\text{K}_2\text{CrO}_4$  solution). Taken together, the data suggests the displacement of chloride ion by  $\text{HCrO}_4^{1-}$  at low pH values is the most facile process. Nevertheless, the slightly slower adsorption rate—carbonate replaced by  $\text{CrO}_4^{2-}$ —at neutral or basic conditions provides for good adsorption without a significant effect on time. It is of interest to note that the rate of Cr (VI) absorption at pH 10.0 is faster than other values, except pH 2.0. We surmise in this pH range the equilibrium binding dynamics of  $\text{CO}_3^{2-}$  vs.  $\text{OH}^-$  with ammonium ions is favorably affecting displacement by  $\text{CrO}_4^{2-}$ .

To identify the maximum chromate adsorption capacity of MP-Carbonate, a solution of  $\text{K}_2\text{CrO}_4$  at pH values of 2.0, 6.8, and 10.0 was added to 0.020 g of MP-Carbonate and kept under static conditions for 7 days. Higher concentrations (500  $\mu\text{M}$ ) of Cr (VI) were used at pH 2 due to the larger adsorption capacity of MP-

**Fig. 4** Comparison of  $K_c$  at different temperatures

**Table 4** Thermodynamic parameters for the adsorption of  $\text{CrO}_4^{2-}$  on MP-Carbonate

$\Delta H^0$ (kJ mol <sup>-1</sup> )	$\Delta S^0$ (kJ mol <sup>-1</sup> )	$\Delta G^0$ (kJ mol <sup>-1</sup> )		
		T = 0 °C	T = 25 °C	T = 50 °C
5.073	0.0333	-9.351	-10.971	-13.222

See “Experimental Procedures” for calculations

Carbonate in an acidic environment. The concentration of non-adsorbed Cr (VI) was calculated from standard calibration curves and the breakthrough values established. As seen in Table 2, the calculated maximum  $\text{CrO}_4^{2-}$  loading capacity per gram of MP-Carbonate at pH 2.0, 6.8, and 10.0 is 330, 161, and 163 mg, respectively. We reason, as shown in Fig. 1, that under HCl conditions the bidentate coordination of  $\text{CO}_3^{2-}$  with two tetra-alkyl ammonium ions is initially replaced by two  $\text{Cl}^-$  ions which are subsequently exchanged with two  $\text{HCrO}_4^{1-}$  ions in a monodentate binding fashion (Fig. 1, MP-Carbonate+2Cr(VI)). The arrangement allows for maximum utilization of the tetra-alkyl ammonium ions in MP-Carbonate to bind with  $\text{HCrO}_4^{1-}$  and accounts for the doubling of the adsorption capacity at low pH solutions compared with neutral and above. At pH values near neutral and above,  $\text{CO}_3^{2-}$  exchanges with  $\text{CrO}_4^{2-}$  in a bidentate arrangement with the tetra-alkyl ammonium ions, as shown as MP-Carbonate+Cr (VI) in Fig. 1. At these pH levels, a pair of tetra-alkyl ammonium ions is required for  $\text{CrO}_4^{2-}$  adsorption, hence with a lower breakthrough value compared with pH 2.

In separate experiments, we sought to correlate changes to Cr (VI) adsorption with varying temperatures. Towards this goal, initial rates were measured (zero to 20 min to allow sufficient Cr (VI) adsorption to occur at 0 °C) at pH 6.8 at temperatures of 0 °C, 25 °C, and 50 °C. As seen in Table 3, the initial rate increases from 2.9  $\mu\text{M min}^{-1}$  at 0 °C to 6.9  $\mu\text{M min}^{-1}$  at elevated temperatures (50 °C).

The effects of temperature change on the thermodynamic sorption properties at pH 6.8 of Cr (VI) by MP-Carbonate were calculated (see “Experimental

Procedures”). As shown in Fig. 4, the equilibrium constant ( $\log K_c$ ) increases as temperature increased from 273 K (0 °C) to 323 K (50 °C). The thermodynamic values (Khan and Singh 1987) of free energy change ( $\Delta G^0$ ), enthalpy change ( $\Delta H^0$ ), and changes in entropy ( $\Delta S^0$ ) values are summarized in Table 4. The negative  $\Delta G^0$  indicates an exergonic adsorption process. The positive  $\Delta H^0$  value, representing an endothermic reaction, supports the observation that by increasing the temperature of the adsorption process the  $K_c$  values and initial rate also increase. The relatively small  $\Delta S^0$  value suggests the replacement of  $\text{CO}_3^{2-}$  on MP-Carbonate with  $\text{CrO}_4^{2-}$  does not significantly alter the net amount of ordered water molecules associated with chromate or carbonate solutions.

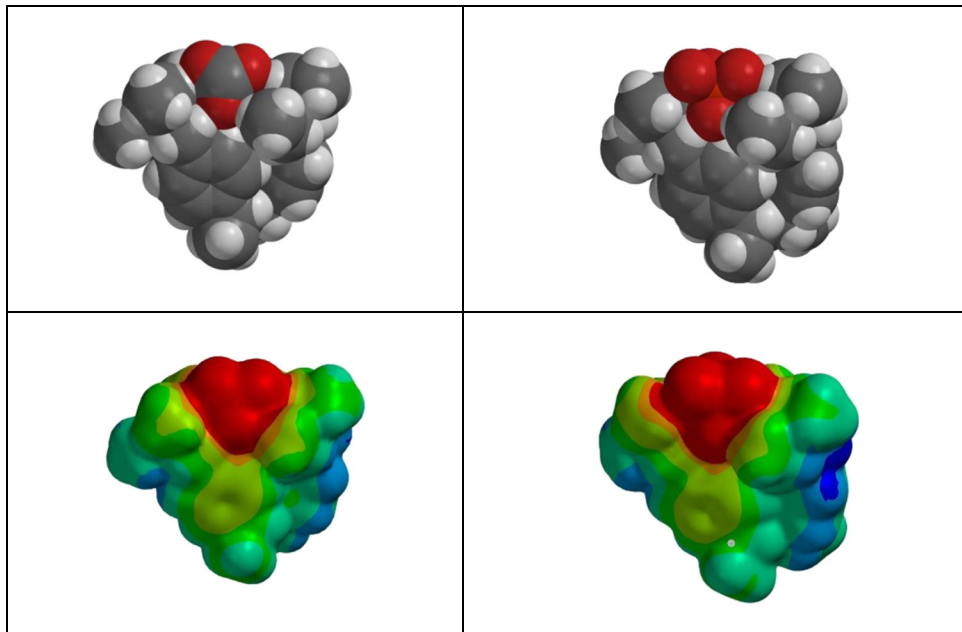
We have previously observed that the fluid dynamics of resin-based Cr (VI) removal agents, specifically Cr (VI) reduction to Cr (III), contributed to the efficiency of the remediation (Regan et al. 2019). Specifically, heterogeneous solutions containing resins that were in motion (stirring) were more efficient than static conditions due to a faster diffusion rate of chromate into the porous cavities. To confirm this observation with adsorption of Cr (VI) with MP-Carbonate, we varied the speed in which the water was stirred. Table 5 shows that in a static environment Cr (VI) removal is negligible at pH 6.8. Increasing stirring speeds accelerates the efficiency (Kocaoba and Akcin 2003) of adsorption of Cr (VI) suggesting that need for extensive diffusion of solvent throughout the macro porous resin for optimal sorption. At very high stirring speed (1100 rpm), the adsorption is nearly complete after 60 min.

**Table 5** Effects of solution dynamics on Cr (VI) reduction after 60 min

Stirring (rpm)	0	60	350	700	1100
% removal of $\text{CrO}_4^{2-}$ at 60 min	< 5	11.4 ± 3.6%	28.2 ± 0.5%	57.1 ± 2.8%	95.3 ± 3.5%

Removal of  $\text{CrO}_4^{2-}$  from 20 mL a 200  $\mu\text{M}$   $\text{K}_2\text{CrO}_4$  solution at pH 6.8 with 0.020 g of MP-Carbonate under static or stirred conditions. See “Experimental Procedures”





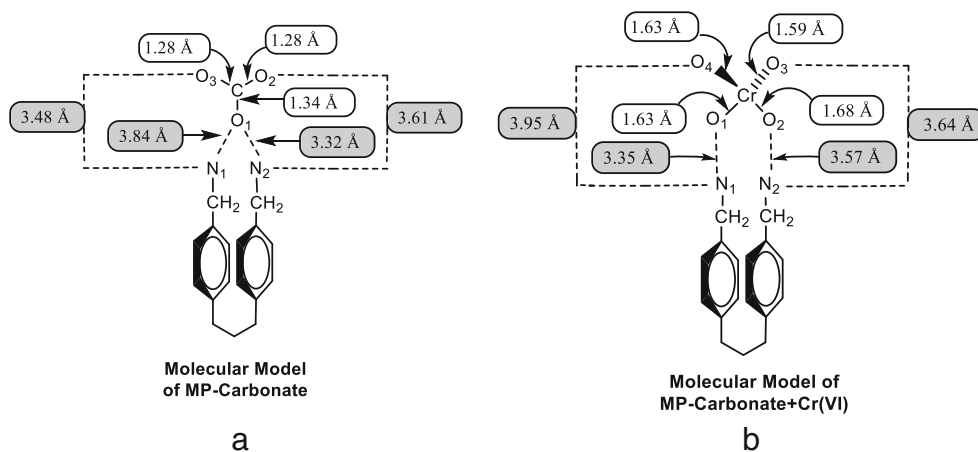
**Fig. 5** Space filling and electrostatic potential (EP) maps of MP-Carbonate (a) and MP-Carbonate + Cr (VI) (b) from molecular modeling calculations of the binding of  $\text{CO}_3^{2-}$  and  $\text{CrO}_4^{2-}$  to MP-Carbonate performed at the semi-empirical level of theory. Hydrogen atoms are pictured as light gray, carbon as dark gray, and

oxygen as red in space filling models. EP maps show intermediate potentials of the materials and are assigned colors according to standard color spectrum: red (most negative) < yellow < green < light blue < dark blue (more positive)

The characteristic loss of efficacy of Cr (VI) sorption by exchange resins using chloride as the counter ion at high pH (Pehlivan and Cetin 2009; Shi et al. 2009; Galán et al. 2006; Rengaraj et al. 2001; Sengupta et al. 1986; Meshram et al. 2018) is likely due to  $\text{Cl}^-$  displacement by  $\text{OH}^-$ . Under these scenarios,  $\text{CrO}_4^{2-}$  is less able to replace

$\text{OH}^-$  from the tetra-alkyl ammonium ion and withstands adsorption. However, with MP-Carbonate, the counter ion  $\text{CO}_3^{2-}$  is likely in equilibrium with  $\text{OH}^-$  in a basic environment thereby facilitating  $\text{CrO}_4^{2-}$  adsorption.

To verify the preferred energy of binding of  $\text{CrO}_4^{2-}$  with tetra-alkyl ammoniums ions compared with  $\text{CO}_3^{2-}$ ,



**Fig. 6** Molecular modeling representations of MP-Carbonate and MP-Carbonate + Cr (VI) with bidentate binding. The alkyl groups on nitrogen have been removed for visual clarity. Solid or broken lines (—) represent covalent bonds and dashed lines (---)

indicate ionic bonds. **a** Calculated orientation of trigonal planar  $\text{CO}_3^{2-}$  and bond lengths in MP-Carbonate. **b** Calculated orientation of tetrahedral  $\text{CrO}_4^{2-}$  and bond lengths in MP-Carbonate + Cr (VI). See “Experimental Procedures” for details

**Table 6** Molecular modeling data for MP-Carbonate (a) and MP-Carbonate + Cr (VI) (b)

MP-Carbonate (a)	Bond length	Bond angle	MP-Carbonate+Cr (VI) (b)	Bond length	Bond angle
C–O <sub>1</sub>	1.34 Å	118.6°	Cr–O <sub>1</sub>	1.63 Å	110.2°
C–O <sub>2</sub>	1.28 Å	121.2°	Cr–O <sub>2</sub>	1.68 Å	107.7°
C–O <sub>3</sub>	1.28 Å	122.4°	Cr–O <sub>3</sub>	1.59 Å	106.2°
CO <sub>1</sub> –N <sub>1</sub>	3.32 Å	106.3°	Cr–O <sub>4</sub>	1.63 Å	112.7°
CO <sub>1</sub> –N <sub>2</sub>	3.84 Å	90.1°	CrO <sub>1</sub> –N <sub>1</sub>	3.35 Å	103.7°
CO <sub>2</sub> –N <sub>2</sub>	3.48 Å	108.6°	CrO <sub>2</sub> –N <sub>2</sub>	3.57 Å	94.7°
CO <sub>3</sub> –N <sub>1</sub>	3.65 Å	94.1°	CrO <sub>3</sub> –N <sub>2</sub>	3.64 Å	62.8°
			CrO <sub>4</sub> –N <sub>1</sub>	3.95 Å	92.9°

See “Experimental Procedures” and Fig. 6 a and b for details

calculations were performed using density functional theory (Wavefunction Inc n.d.). The calculated  $\Delta E$  (products minus reactants) is  $-82.16$  kJ/mol and parallels the thermodynamic parameters of Cr (VI) adsorption by MP-Carbonate (Table 4). Molecular modeling depictions of the adsorption process are shown in Fig. 5 with space filling and electrostatic potential energy maps of MP-Carbonate (Fig. 5a) and MP-Carbonate+Cr (VI) in Fig. 5b. The covalent bond lengths and ionic bonding distances of  $\text{CO}_3^{2-}$  compared with  $\text{CrO}_4^{2-}$  with ammonium ions are shown in Fig. 6 a and b and summarized in Table 6. The molecular geometry of  $\text{CO}_3$  (US-EPA n.d.) has trigonal planar symmetry (point group  $D_{3h}$ ) (Fortes et al. 2014) with bond angles of  $118$ – $122^\circ$ . Chromate adopts a tetrahedral molecular orientation with bond angles between  $106$  and  $112^\circ$  (McGinnety 1972). A 4.6% longer C–O<sub>1</sub> bond is observed compared with C–O<sub>2</sub> and C–O<sub>3</sub> (Fig. 6a) and may signify an optimization of the ionic interactions between the oxygen anion and the two ammonium ions. The Cr–O bond lengths are within normal ranges (McGinnety 1972). The distance between the ammonium ions in each case is  $6.42$  Å indicating that the scaffold in the model (see Fig. 6) did not undergo molecular movement to accommodate the larger chromate ion during the sorption process.

Details of the ionic bond distances of the carbonate oxygen ion and the two ammonium ions, CO<sub>1</sub>–N<sub>1</sub> and CO<sub>1</sub>–N<sub>2</sub>, are seen in Fig. 6a with distances of  $3.84$  Å and  $3.32$  Å. The other carbonate oxygen ions and the two ammonium ions bonds, CO<sub>2</sub>–N<sub>2</sub> and CO<sub>3</sub>–N<sub>1</sub>, have ionic bond distances of  $3.48$  Å and  $3.65$  Å, respectively.

The chromate oxygen ionic bond lengths, CrO<sub>1</sub>–N<sub>1</sub> and CrO<sub>4</sub>–N<sub>1</sub>, are  $3.35$  Å and  $3.64$  Å while the CrO<sub>2</sub>–N<sub>2</sub> and CrO<sub>3</sub>–N<sub>2</sub> are  $3.57$  Å and  $3.95$  Å (Fig. 6b). This data shows that the ionic bond distances between the oxygen ions of carbonate and chromate and the ammonium ions remain nearly identical, but are generally longer than those seen with carboxylate and ammonium ions (Oxton et al. 1977; Debiec et al. 2014). This may reflect the sterically congested environment around each ammonium ions by the three ethyl groups attached to it and thereby preventing shorter ionic distances. Nevertheless, the ionic binding of four chromate oxygen anions with two ammonium ions of MP-Carbonate is a key factor in the  $\Delta E = -82.97$  kJ/mol calculation compared with three carbonate oxygen anions with two ammonium ions.

#### 4 Conclusion

MP-Carbonate has been shown to be an effective adsorbent of synthetic Cr (VI) wastewater ( $200$  and  $500$   $\mu\text{M}$   $\text{K}_2\text{CrO}_4$ ) at pH values from  $2.0$ – $12.0$ . Initial chromate adsorption occurs rapidly at pH 2 and slows somewhat at a higher pH environment. Specifically,  $1.90$ ,  $0.548$ , and  $0.652$  mg of Cr (VI) are adsorbed per minute per gram of MP-Carbonate at pH  $2.0$ ,  $6.8$ , and  $10.0$ , respectively. The loading capacity is also pH dependent:  $332$ ,  $161$ , and  $163$  mg  $\text{CrO}_4^{2-}$  per gram MP-Carbonate at pH  $2.0$ ,  $6.8$ , and  $10.0$ , respectively. At low pH environments, the binding of chromate forms a monodentate composition with the tetra-alkyl ammonium ions while at neutral and higher pH values, binding occurs in a monodentate assembly. The  $\text{CO}_3^{2-}$  counter ion is believed to contribute to the sorption effectiveness of Cr (VI) by MP-Carbonate at high pH levels. Based on thermodynamic calculations, the adsorption is a spontaneous (negative  $\Delta G^0$ ) and endothermic (positive  $\Delta H^0$ ) process. The rate of Cr (VI) adsorption is dependent on fluid dynamics and temperature. Stirring solutions were more effective at chromate removal than static conditions due to the improved solvent diffusion efficiencies. During the adsorption process, the tetrahedral  $\text{CrO}_4^{2-}$  ion replaces the trigonal planar  $\text{CO}_3^{2-}$  ion on MP-Carbonate with similar ionic bond lengths to the ammonium ions. In the case of MP-Carbonate, three oxygen ions bind to two ammonium ions, whereas, for chromate sorption, four oxygen ions bind to two ammonium ions and contribute to the calculated  $\Delta E = -82.97$  kJ/mol



value for the adsorption process. Taken together, the results show the potential usefulness of MP-Carbonate in the remediation of Cr (VI) wastewater, regardless of the pH of the water source.

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#### Compliance with Ethical Standards

**Conflict of Interest** The authors declare that they have no conflict of interest.

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