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Adsorption of chromate from aqueous solutions by HDTMA-modified clinoptilolite, glauconite and montmorillonite

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ABSTRACT

Adsorption of chromate on natural clinoptilolite (Cp), glauconite (Gl), and montmorillonite (Mt) treated with hexadecyl trimethylammonium (HDTMA) bromide at amounts equivalent to 1.0 and 2.0 of their cation-exchange capacities (CEC) was investigated by batch study. In the case of the Cp and Gl, adsorption of HDTMA took place on the zeolite and clay mineral surfaces only and thus relates to the external CEC (ECEC). The amount of chromate removed from the solution by the organo-silicates continuously decreased with increasing pH in the range 1.3–10. The highest values were obtained at pH between 1.3 and 6, and decreased rapidly above pH 6. At an initial chromate concentration of 6.25 mmol/L, its amounts bound to the Cp, Gl and Mt modified using 1.0 CEC loadings of the surfactant were 47, 102, and 168 mmol/kg, respectively. When amount of HDTMA used was equivalent to 2.0 CEC of the silicate, these values increased to 182, 240, and 285 mmol/kg, respectively. The results obtained suggest that the surfactant molecules, bound beyond the CEC to the external surfaces of the Cp and Gl, show a greater chromate adsorption ability in comparison with such molecules located in the interlayer spaces of the Mt. It is also evident that an excess of the surfactant, not adsorbed on the silicate surfaces, participated in the removal of chromate from the solution by formation of a precipitate of alkylammonium chromate.

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1. Introduction

Chromium most often exists in the environment as Cr(III) and Cr(VI), and the latter is harmful for people and animals. Reduction of Cr(VI) to Cr(III) occurring inside living cells and disturbing biochemical reactions of DNA synthesis may result in various mutations or activate cancerous processes, manifesting themselves as malignant tumors (ATSDR, 2000). Chromium is a common pollutant introduced into natural waters due to the discharge of a variety of industrial wastewaters. Moreover, chromium-based catalysts were also usually employed in various chemical processes, including selective oxidation of hydrocarbons.

The conventional treatment of chromate-rich effluent is to reduce Cr(VI) to Cr(III) and precipitate Cr(III) as chromium hydroxide or chromium iron hydroxide at high pH, followed by the disposal of the resulting dewatered sludge. The major drawback of the method is the high cost of chemicals used for the reduction of chromate (David et al., 1998). Extensive research was performed to find materials for chromate adsorption and immobilization. In numerous experiments, pure mineral phases, e.g. oxides or hydroxides of iron, aluminium, manganese, and activated carbons; in addition, natural or secondary polymineral mixtures like soils, claystones, coals, peats were used.

Other suitable adsorbents of chromate were organo-silicates. Clay minerals and zeolites modified with quaternary alkylammonium cations were frequently studied because of their potential application as environmental remediation materials (e.g. Bowman, 2003; Boyd et al., 1988; Chmielewska et al., 2003; Stockmeyer, 1991). Such adsorbents to remove chromate from liquid phases were prepared using smectite (Krishna et al., 2001; Li and Bowman, 1998; Majdan et al., 2005), kaolinite (Li and Bowman, 2001), illite (Li et al., 2002), palygorskite and sepiolite (Li et al., 2003). HDTMA surfactant was commonly applied for surface modification. Zeolites show a high cation-exchange capacity (CEC) reaching values from 100 to 200 meq/100 g (natural) to around 450 meq/100 g (synthetic). In contrast, adsorption of anions on the surfaces of these silicates is very limited. The anion exchange capacity (AEC) of zeolites can, however, be considerably improved by chemical modification of their surface properties using selected organic compounds. Such organo-zeolites (mainly organo-clinoptilolites) obtained using HDTMA-Br were frequently studied as adsorbents to remove chromates from aqueous solutions (Bajda and Kłapyta, 2006; Bowman, 2003; Haggerty and Bowman, 1994; Mozgawa et al., 2011).

The aim of the study reported here was to compare the chromate adsorption capacities of clinoptilolite, glauconite, and montmorillonite from selected Polish deposits modified with HDTMA-Br. The silicate modification procedure described in most papers included washing of the reaction products to remove excess organic salt. In our experiments, unwashed organo-silicates were used to test the role of unadsorbed surfactant in the chromate removal process.

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2. Materials and methods

Clinoptilolite (Cp) was separated by settling from the claystone located in the village of Dylągówka in the Outer Flysch Carpathians of Poland (Franus and Dudek, 1999; Wieser, 1969). The zeolite concentrate obtained consisted of about 95% Cp and 5% quartz (Q) and illite (Mozgawa and Bajda, 2005). Glauconite (Gl) was collected from Tertiary sands of the Lubartowska Lowland near Nowodwór (Poland). Its average content in these sediments varies between 20 and 30% (Franus et al., 2004). The sands were washed on a 63 μm sieve; then, from the Gl-Q concentrate left on the sieve the Gl was magnetically separated. Montmorillonite (Mt) was separated by sedimentation from a Tertiary (Miocene) bentonite located in Chmielnik (central Poland). The sample obtained contained an admixture of a few mass% of Q (Kulesza-Wiewióra, 1984). Exchange positions of the Mt were saturated with Ca^{2+} ions (Kulesza-Wiewióra, 1984; Tokarski, 1953; Waclawska, 1984).

The CEC values of the Cp, Gl, and Mt determined by adsorption of HDTMA ions were 16, 18, and 95 meq/100 g, respectively. In the case of the Cp and Gl, adsorption of the surfactant took place on the external exchange sites only. Thus, the measured CEC relates to the external CEC (ECEC) (Haggerty and Bowman, 1994; Ming and Dixon, 1987). In contrast, adsorption of these alkylammonium ions may be used for determination of the total (external and internal) CEC of smectites and swelling micas (Bergaya et al., 2006; Kłapyta et al., 2001).

The organo-silicates were obtained using the following procedure: 7 g of the sample was first dispersed in about 300 mL of deionized water, to which the desired amount of HDTMA-Br in water solution was slowly added. The amounts of HDTMA⁺ were equivalent to 1.0 and 2.0 CEC of the silicate. In the case of the Mt, 0.25 and 0.5 of its CEC loadings were additionally used. The mixtures were stirred for 2 h at 60 °C and then left for 24 h at 25 °C. The samples obtained without washing were dried at 100 °C and ground in an agate mortar. A similar methodology was used by Bowman et al. (2002); however, the authors did not investigate the role of the free surfactant in the chromium adsorption process.

The adsorption experiments were conducted in two sets, with and without the presence of the minerals. In the first set, the adsorption of chromate on the modified silicates was measured as a function of pH (1.3–10) at an initial concentration 2.11 mmol/L. The pH was modified using 1 M HCl and 1 M NaOH. The adsorption of chromate was also determined as a function of its initial concentration (0.02–14.2 mmol/L corresponding to 1–740 mg/L) at a starting pH of the solution equal to 3.0. The effect of HDTMA loading (1.0 and 2.0 CEC of the silicate, additionally 0.25 and 0.5 CEC in the case of Mt) on the adsorption of chromate was measured at initial concentrations of the pollutant in the range 0.1–2.0 mmol/L. 100 \pm 1 mg of the organo-silicate was placed in an 8 mL centrifuge polypropylene tube and 5 mL of potassium chromate solution was added. The pH was adjusted with 1 M HCl. The mixture was shaken for 24 h at 25 °C and centrifuged at 14,000 rpm for 15 min, until the washing solution was clear. Based on the previous studies it was found that 24 h is a sufficient period of time to reach the equilibrium state between chromate ions remaining in the solution and adsorbed on the organo-silicates (Haggerty and Bowman, 1994; Krishna et al., 2001; Li and Bowman, 1998). All the sorption experiments were done in duplicate for each chromate concentration. In the second set, chromate was reacted with HDTMA salt dissolved in redistilled water. 4 mL of HDTMA solutions justified to pH from 2 to 10 was injected with 1 mL of chromate solution so as to give a concentration of 2.11 mmol/L. The initial concentration of HDTMA corresponded to its amount in the organo-Mt sample used in the first set, obtained at a 1.0 CEC loading of the surfactant.

The chromate concentration in the supernatant was determined spectrophotometrically (UV–VIS Hitachi U-1800) using the biphenylcarbazide method (ASTM, 1992).

3. Results and discussion

3.1. Effect of pH on the adsorption of chromate

The amount of chromate removed from the solution with an initial concentration of 2.11 mmol/L decreased with increasing pH in the range 1.3–10 (Fig. 1A). Under these conditions, the chromate adsorption capacities of the organo-silicates obtained at amounts of HDTMA equivalent to 1.0 CEC of the silicate were widely different and equal to 103–16, 65–23, and 66–6 mmol/kg for the modified Mt, Gl, and Cp, respectively. The maximum values were obtained at a pH below 2. In the pH range of 1–3, the amounts of chromate adsorbed sharply decreased, and then remained relatively constant until pH 6. Between pH 6 and 8, it decreased suddenly, and above pH 8 was insignificant. In contrast, the amounts of chromate removed by all these minerals modified by

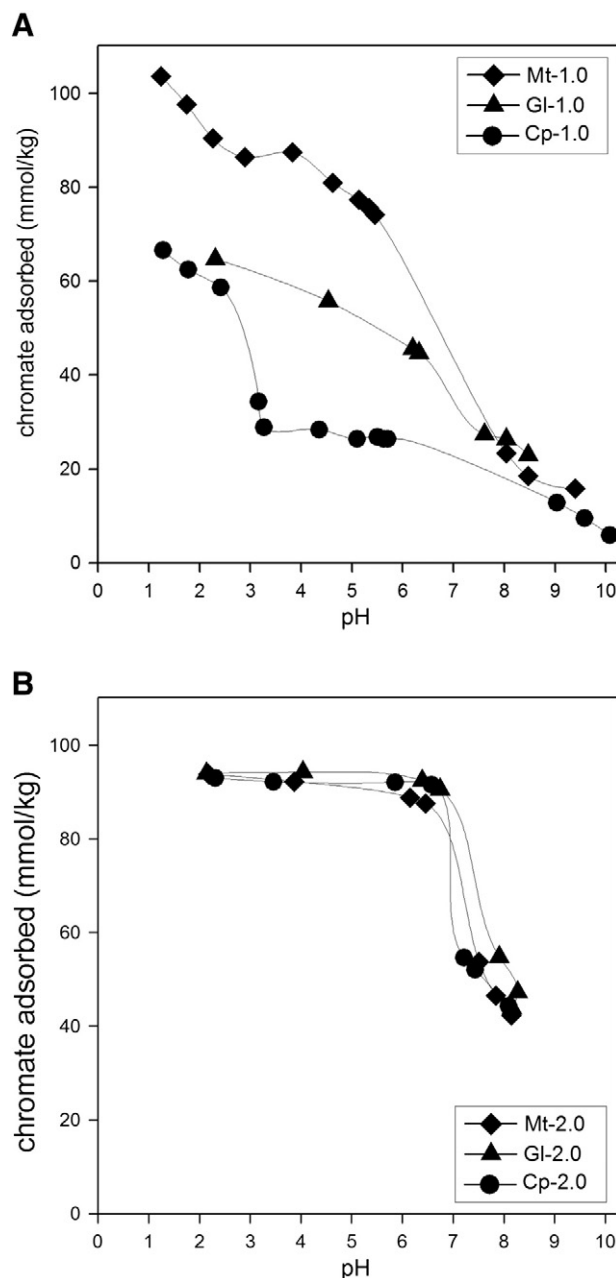


Fig. 1. Adsorption of chromate as a function of pH (1.3–10) on the organo-silicates obtained at HDTMA loadings of (A) 1.0 CEC and (B) 2.0 CEC of the silicate. Initial concentration of chromate: 2.11 mmol/L.

using 2.0 CEC loadings of the surfactant were similar (94–41 mmol/kg) (Fig. 1B), testifying that the adsorption capacity of each of the adsorbent used was sufficient to remove most of the chromate from the solutions. These values were constant between pH 2–6 and decreased above pH 6. Similar trends were observed by Li (2004) and Majdan et al. (2005) for adsorption of chromate on bentonite and zeolite modified with HDTMA.

For clarification of the role of HDTMA-Br not bound to the silicate surfaces in the chromate adsorption process, further investigations were carried out using the pure alkylammonium salt, without minerals. In Fig. 2, the reduction in chromate concentration (%) of the solution, measured at various pH, was compared for the organo-Mt obtained at a 1.0 CEC loading of HDTMA ions, and pure HDTMA-Br. The same amount of the surfactant was used in these two adsorption measurements. Surprisingly, the differences between the curves obtained are small, suggesting that the chromate removal mechanism in the above experiments was similar. The chromate species may be represented in the solution phase by various forms such as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , and CrO_4^{2-} , depending on the solution pH. Above pH 6, the dominant species is ion CrO_4^{2-} ; between pH 1 and 6, HCrO_4^- and dichromate ion $\text{Cr}_2\text{O}_7^{2-}$ are in equilibrium (Dickson et al., 1989). The amount of $\text{Cr}_2\text{O}_7^{2-}$ is only significant at very low pH and high concentrations of Cr. The adsorption of chromate in the experiments was the highest for each of the organo-silicates generally at pH between 2 and 6, while beginning from pH 6, a sudden drop in the chromate concentration in the adsorbents phase appears. This is due primarily to the dominant species of chromate which exist in water and the exchange capacity of the modified silicates for one species. At lower pH, the chromate species are mostly in the univalent form, HCrO_4^- , and thus require one exchange site for one molecule of chromate species at that pH. The HCrO_4^- anion displaces the surfactant counter ion from the exchange sites on the silicates forming (Majdan et al., 2005):



In contrast, at pH above 6, the divalent form of chromate species, CrO_4^{2-} , is mostly present and needs two exchange sites on the organo-silicate surface for the adsorption to occur:



Dependence of the chromate species on the amount of adsorbed chromate as described above is distinct especially in the case of silicates modified using a 2.0 CEC concentration of the alkylammonium ions (Fig. 1B). On their external surfaces, a part of HDTMA forms an admicelle surfactant configuration and reverses the surface charge to positive (Haggerty and Bowman, 1994). At low pH, a high concentration of protons influences the speciation of chromate, and additionally makes possible displacement of the HDTMA ions from the exchange sites of the silicate and their reaction with chromate ions to form a precipitate of alkylammonium chromate. The strong competition between Cr(VI) ions and OH^- and Br^- ions for HDTMA^+ ions is probably the reason why the amount of Cr(VI) adsorbed on the organo-silicates decreases rapidly in alkaline solutions (Hong et al., 2008).

3.2. Adsorption isotherms

The chromate adsorption capacities of the Cp, Gl, and Mt modified using 1.0 CEC loadings of the alkylammonium ions and the solution with an initial chromate concentration of 9.6 mmol/L were 62, 102, and 190 mmol/kg, respectively (Fig. 3A). Considerably higher values (262, 404, and 689 mmol/kg, respectively) were obtained for the organo-silicates prepared using 2.0 CEC loadings of the surfactant and an initial chromate concentration of 14.2 mmol/L (Fig. 3B). The amount of chromate bound generally depended on the quantity of HDTMA in the adsorbent, resulting from the CEC of the silicate. Thus, the removal

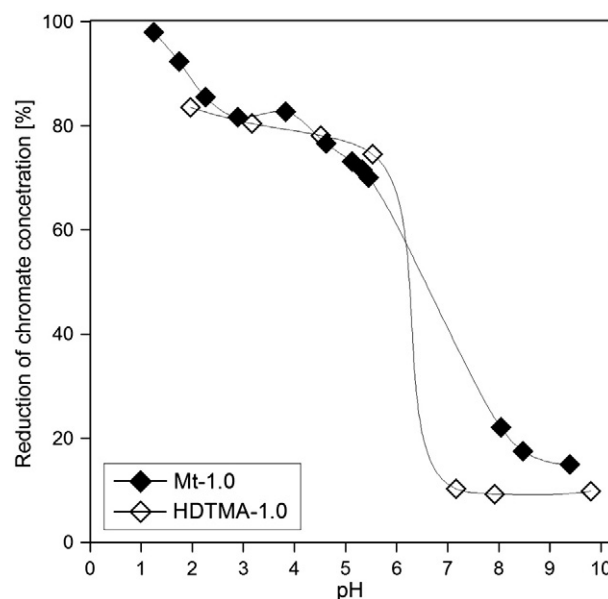


Fig. 2. Comparison of the reduction in chromate concentration of the solution by organo-Mt obtained at a 1.0 CEC loading of HDTMA and by the equivalent amount of pure HDTMA. pH: 1.3–10. Initial concentration of chromate: 2.11 mmol/L.

of the pollutant by the organo-Gls and organo-Cps was lower than that of the organo-Mts.

3.3. Effect of HDTMA loading on the chromate adsorption

The maximum amounts of chromate adsorbed from the solution with an initial concentration of 6.25 mmol/L on the organo-silicates prepared at 1.0 and 2.0 CEC loadings of HDTMA show two trends depending on the amount of the surfactant added to the silicate (Fig. 4). One of them represents this dependence for the modified Cp and Gl, and the second is characteristic of organo-Mts. This suggests that the surfactant molecules, added beyond the CEC to the Cp and Gl, show a greater ability to adsorb chromate in comparison with such molecules located in the interlayer spaces of the Mt, which are probably only in part available for the reaction with the pollutant.

The total quantities of the alkylammonium ions added to the silicates were used in calculating the chromate/HDTMA-Br molar ratio in the chromate–organo-silicate complexes resulting after adsorption of chromate from the solution with an initial concentration of 6.25 mmol/L. The values of 0.31 and 0.60, obtained for the organo-Cp and organo-Gl prepared at 1.0 CEC loadings of HDTMA ions, increased to 0.63 and 0.75 at 2.0 CEC. These molar ratios calculated for the organo-Mts obtained under the same experimental conditions at 1.0 and 2.0 CEC loadings were significantly lower (0.24 and 0.25).

Additional experiments were carried out using the organo-Mts prepared at HDTMA loadings between 0.25–1.0 CEC, and the solutions with initial chromate concentrations in the range of 0.1–2.0 mmol/L. When the surfactant amount increased in the order 0.25–0.5–1.0 CEC, the maximum adsorption of chromates increased in the order 5–10–73 mmol/kg (Fig. 5). The calculated chromate/HDTMA-Br ratios are 0.023, 0.025 and 0.104, respectively. These results testify that the organo-Mt prepared at a 1.0 CEC loading of HDTMA shows a four times greater ability to remove chromate from the solution than those of the adsorbents containing the surfactant in amounts equal to 0.25 and 0.5 CEC.

3.4. Adsorption mechanism

Bonding of anions, especially chromates, to clay minerals and zeolites modified with quaternary alkylammonium surfactants was described by most authors as the formation of a positively charged bilayer

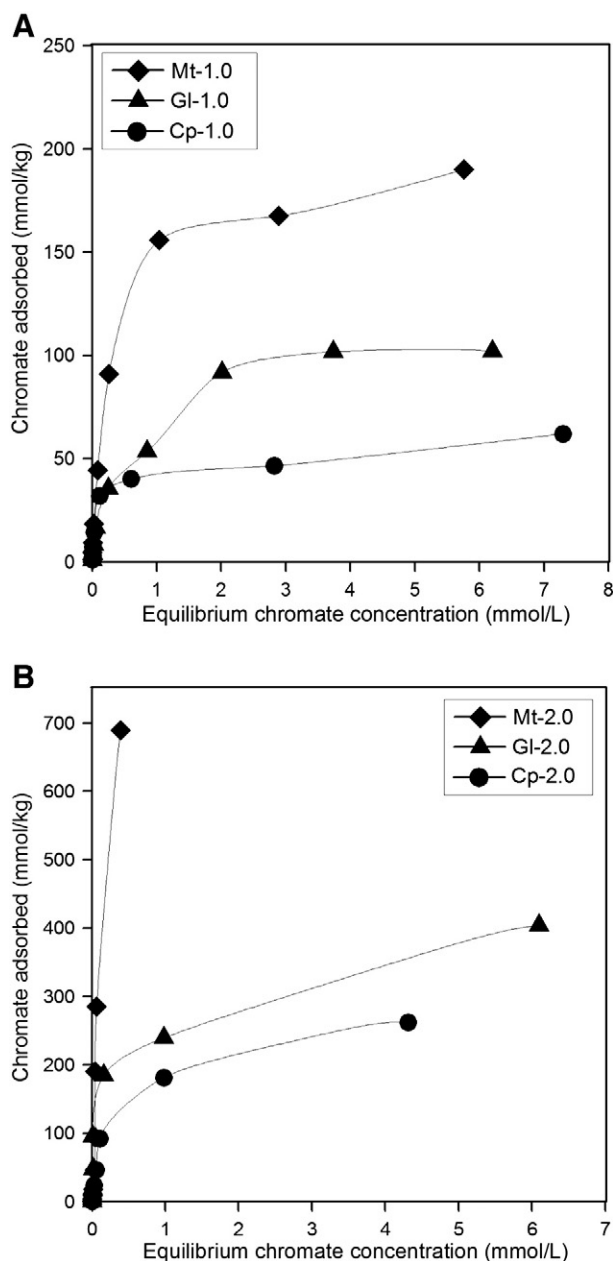


Fig. 3. Adsorption isotherms of chromate on the organo-silicates obtained at (A) 1.0 CEC and (B) 2.0 CEC loadings of HDTMA. Initial concentration of chromate: 0.02–9.60 and 0.02–14.2 mmol/L, respectively.

or patchy bilayer of these cations on the mineral surface, which attracts counter ions from the aqueous solution (Bowman et al., 2000; Haggerty and Bowman, 1994; Li, 2004; Li and Bowman, 1998). However, this explanation relates to the adsorbents prepared with a surfactant loading higher than the CEC of the starting minerals. In contrast, Krishna et al. (2001) investigated montmorillonite exchanged fully with HDTMA ions and found that the maximum adsorption of chromate, observed at $\text{pH} \leq 1$, was proportional to the amount of organic ions bound to the adsorbent. The authors suggested that under these conditions, chromate anions displaced the surfactant cations from the silicate exchange positions and formed a precipitate of alkylammonium chromate on the montmorillonite surface. They concluded that the exchange sites of the mineral are balanced by the protons present in the medium. Under acidic conditions, the high mobility and activity of protons in the solution and the strong affinity of chromate anions for HDTMA cations are the driving forces for desorption of these cations from the silicate exchange sites and their precipitation as alkylammonium chromates.

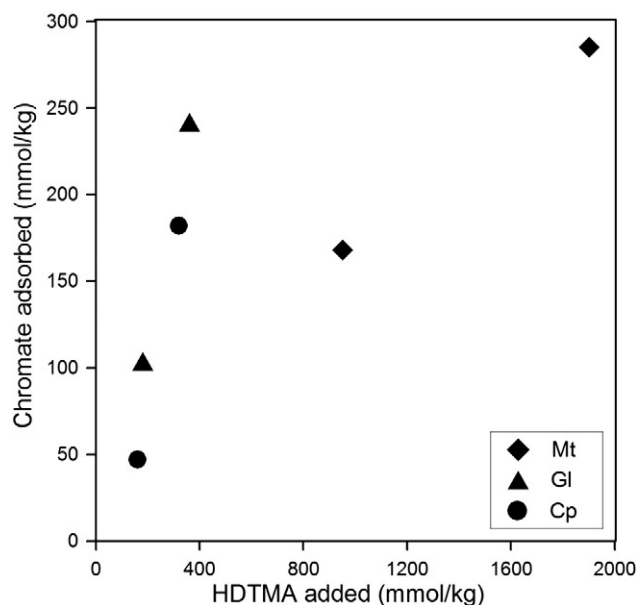


Fig. 4. Comparison of the maximum adsorption of chromate from its solution with an initial concentration of 6.25 mmol/L on the organo-silicates obtained at 1.0 and 2.0 CEC loadings of HDTMA.

As evidenced by Majdan et al. (2005), smectite with inorganic exchangeable cations only partially replaced by HDTMA ions also showed adsorption properties toward chromates. These authors confirmed that removal of chromate from its solution mainly proceeds via the formation of alkylammonium chromates. From the cited papers and our experiments it resulted that both the above processes are possible depending on the reaction conditions. Adsorption by admicelles is significant at a concentration of HDTMA higher than the CEC of the silicate, whereas formation of a precipitate with alkylammonium ions bound to the silicate surface may occur when these ions fully or only partially occupy the exchange sites. Yusof and Malek (2009) reported reduced adsorption of chromate on organo-silicates prepared at an excess of HDTMA beyond the CEC, probably due to the release of the surfactant

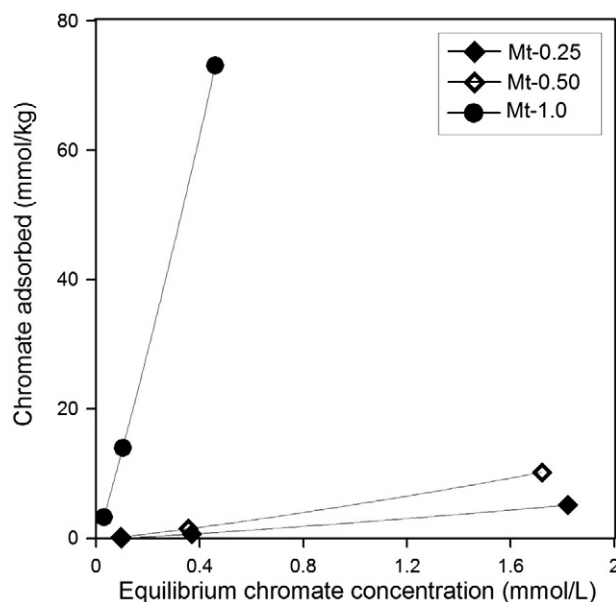


Fig. 5. Adsorption of chromate on the organo-Mts obtained at 0.25, 0.5, and 1.0 CEC loadings of HDTMA. Initial concentration of chromate: 0.1–2.0 mmol/L.

ions loosely bound on the silicate surface into the solution. These ions could compete for chromate anions with HDTMA ions bound to the silicate exchange sites. However, from our experiments it resulted that an excess of the surfactant molecules, not adsorbed on the silicate surface, react also with chromate anions forming a precipitate of alkylammonium chromate.

4. Conclusion

After modification with HDTMA surfactant, the Cp, Gl and Mt used in this work show significant ability to remove chromate from aqueous solutions. The amounts of chromate bound to the organo-silicates strongly depended on the pH of the solution. The highest values (262, 404 and 689 mmol/L, respectively) were obtained at pH between 1 and 6. Under these conditions, chromate species were in the univalent form which only need one exchange site from the organo-silicates (hence, more chromate species can be adsorbed by the modified minerals). Such large amounts of Cr(VI) ions bound were also reported for organo-montmorillonite (Krishna et al., 2001) and organo-rectorite (Hong et al., 2008) (795 and 400 mmol/kg, respectively). The maximum chromate uptake by the organo-silicates depended on the amount of HDTMA in the adsorbent. The results obtained suggest that the surfactant molecules added to the Cp and Gl in amounts higher than their ECEC show a greater chromate adsorption ability in comparison with such molecules located in the interlayer spaces of the Mt. The chromate/HDTMA-Br ratio calculated after adsorption of chromate on the organo-Cp, organo-Gl and organo-Mt obtained at 2.0 CEC loadings of the surfactant was 0.63, 0.75 and 0.25, respectively. It is also evident that an admixture of HDTMA not bound to the mineral surface participates in the removal of chromate from the solution by precipitation of alkylammonium chromate.

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