J Therm Anal Calorim (2010) 101:775–778
DOI 10.1007/s10973-010-0920-8

Sorptive and thermal properties of red clay in relation to Cr(VI)

**A. Gładysz-Płaska · M. Majdan · D. Sternik ·
S. Pikus · E. Zięba**

IVMTT2009 Special Chapter

Abstract The results of Cr(VI) adsorption on the red clay modified by hexadecyltrimethylammonium bromide are given. The adsorption isotherm of Cr(VI) is determined based on the Langmuir–Freundlich model and exhibits the adsorption capacity of 0.0005 mol/g in relation to Cr(VI). The study of the pH effect showed that the optimal pH range corresponding to the Cr(VI) adsorption maximum on this clay is 2–6.5. Thermal analysis of the modified adsorbent, i.e., Na/HDTMA-clay, shows two DTG peaks at 58–61 and 241 °C. The first one is a consequence of dehydration of the modified clay sample. The other DTG peak results from evaporation and pyrolysis of HDTMA adsorbed on the clay. In the case of Na/HDTMA-Cr-clay three peaks appear at: 64, 232, and 340 °C. The third DTG peak is related to the oxidation of surfactant. Moreover, the raw mineral shows the peak at 543 °C attributed to the clay dehydroxylation.

Keywords HDTMA · Red mud · Clay · Adsorption · Chromate

Introduction

The pollution of water with different toxic substances, especially heavy metals, aromatic compounds, and dyes is a serious problem for the environment at present and dangerous for humans. Heavy metals, especially Cr(VI), appeared as pollutants in the 20th century. Higher concentrations of Cr(VI) can be found in wastewaters from many industries including metal finishing and corrosion control, leather tanning, textile dyeing, wood preserving, drilling, as well as in the manufacturing of inks, pigments, glass, ceramics, and glues.

The presence of Cr(VI) ions in the environment is a serious threat because of their carcinogenic, mutagenic, and teratogenic character.

The admissible concentration of Cr(VI) is 0.5 ppm in water and 5 ppm in soil. The lethal dose is 5 g for soluble chromates and 1–2 g for chromic(VI) acid.

It is necessary to devise effective ways of Cr(VI) disposal from the environment applying such methods as extraction, ion exchange, or adsorption on active carbons and natural sorbents, e.g., zeolites, clays (kaolinite, bentonite, illite, etc.), fly ashes, manure, and slags.

There are different ways of Cr(VI) elimination from aqueous solutions by adsorbents:

1. adsorption on the external and internal surfaces of adsorbents;
2. reduction of Cr(VI) to Cr(III) and consecutive Cr(III) adsorption on the external surface of the adsorbent;
3. adsorption of Cr(VI) by adsorbents modified in different ways, e.g., by cationic surfactants or metallic hydroxypolycation [1, 2].

The aim of this study is to prepare and describe natural red clay modified by hexadecyltrimethylammonium bromide

A. Gładysz-Płaska (✉) · M. Majdan · D. Sternik · S. Pikus
Faculty of Chemistry, Maria Curie-Skłodowska University,
pl. M. C. Skłodowskiej 2, 20-031 Lublin, Poland
e-mail: aglad@op.pl

M. Majdan
e-mail: majdan.marek@gmail.com

E. Zięba
Zoology and Ecology Department, SEM Laboratory, Catholic
University of Lublin, Kraśnicka St. 102, 20-718 Lublin, Poland

(HDTMA-Br) and to check its applicability in the elimination of chromates from aqueous solutions. We have intentionally selected the modified clay as adsorbent for Cr(VI) taking into account the evident increase of organoclays application, especially montmorillonite, in environmental remediation [3–6].

Experimental

The clay used in this study comes from the Pałęga clay pit in the vicinity of Kielce. Its chemical composition is: SiO_2—64.79%, Al_2O_3—16.26%, Fe_2O_3—7.22%, TiO_2—0.91%, MnO—0.09%, MgO—2.38%, CaO—0.40%, K_2O—2.68%. The mineralogical composition is: illite 23–37%, kaolinite 6–12%, chlorite 3–5%, quartz 30–45%, hematite 3–6%.

Modified clay preparation

Clay loaded with HDTMA-Br was prepared in the following way. To ensure that there is an excess of sodium ion concentration in the relation to the cation exchange capacity (CEC) the 5 g sample of clay was contacted with 100 mL of 1 M NaCl (Sigma-Aldrich, min 99.5%) for 24 h. The sodium form of red clay was washed several times with water to remove the sodium chloride remains. The presence of chlorides in the washing solution was checked argentometrically. After filtration the solid residue was dried in air. In the next stage, the 1 g sample of sodium-clay was equilibrated for 4 h using a mechanical shaker with 100 mL of HDTMA-Br (Sigma-Aldrich, 99% purity) with the concentration of 0.0005, 0.001, and 0.005 M at 60 °C. The time of equilibration seemed to be enough to replace the majority of sodium by alkylammonium ions in the clay sample [7]. In the next stage, the solution was filtered through the paper filter and the solid residue dried in air was used in further experiments.

The modified clay loaded with chromates was prepared in the following way. The 1 g sample of Na/HDTMA-clay was equilibrated for 4 h with 100 mL of 0.005 M $K_2Cr_2O_7$ (Polish Chemical Reagents). After filtration of the solution, washed twice with water, the solid residue (Na/HDTMA-Cr-clay) was dried in air and used in further experiments.

Equilibrium study

The adsorption isotherms of Cr(VI) were registered through 4-h equilibration of 0.1 g samples of HDTMA-clay with 100 mL of $K_2Cr_2O_7$ (Polish Chemical Reagents) of Cr(VI) concentration ranging from 0.0001 to 0.001 M. After 4 h the solutions were filtered using paper filter (Filtrak 390, Polish Chemical Reagents) and centrifuged at 10,000 rpm for 10 min. The initial and equilibrium concentrations of Cr(VI) were determined spectrophotometrically using diphenylcarbazide [8].

The concentration of Cr(VI) in the clay phase was found from the equation:

$$c_{\mathrm{ads}} = \left(c_{\mathrm{in}} - c_{\mathrm{eq}}\right) V/m \qquad (1)$$

where c_{ads}, c_{in}, c_{eq} denote the concentrations of Cr(VI) in the clay phase, as well as in the initial and equilibrium solutions. The symbols V and m relate to the volume of solution in cm^3 and to the sample mass in mg. The pH values of the equilibrium solutions were controlled using a combined glass electrode (Sigma Chemical Co.) connected to the pH-meter (CX-731 type, Elmetron Co.).

Thermal analysis

The thermal decomposition spectra of the red clay samples were recorded via the TG/DTG/DTA technique, using a derivatograph Q-1500D (produced by MOM Hungary). The following conditions were maintained: platinic crucible, heating rate—10°/min, air atmosphere, mass sample—200 mg, reference—Al_2O_3.

Results and discussion

Equilibrium study

Figure 1a reveals the kinetics of chromates adsorption on the HDTMA-red clay. The following conditions were maintained during the experiment: the initial concentration of Cr(VI) = 0.0001 M, the volume of the aqueous phase = 100 mL, the mass of the solid phase = 0.2 g. The equilibrium was established within 120 min, so from the practical viewpoint the kinetics was fast. The specific rate constant of Cr(VI) anions adsorption was determined using the following formula:

$$\ln\left[\left(c_{\mathrm{t}} - c_{\mathrm{eq}}\right)/\left(c_{\mathrm{o}} - c_{\mathrm{eq}}\right)\right] = -kt \qquad (2)$$

where c_{o}, c_{t}, and c_{eq} are the concentrations of Cr(VI) anions in the solution: initial, at time t and at equilibrium, respectively, and k refers to the rate constant. The linear relationship was found between $\ln[(c_{\mathrm{t}} - c_{\mathrm{eq}})/(c_{\mathrm{o}} - c_{\mathrm{eq}})]$ (Fig. 1b) and t, which results from the fact that the adsorption reaction is the first order in respect to Cr(VI) ions. The adsorption rate constant k is 0.033/min.

The isotherms of chromates adsorption on the HDTMA-red clay at different temperatures are given in Fig. 2. They refer to the constant equilibrium pH conditions (6.5–6.7 range). The Cr(VI) adsorption on the red clay is well described by the Langmuir–Freundlich isotherm. The parameters of the isotherm: a, K, n (adsorption maximum,

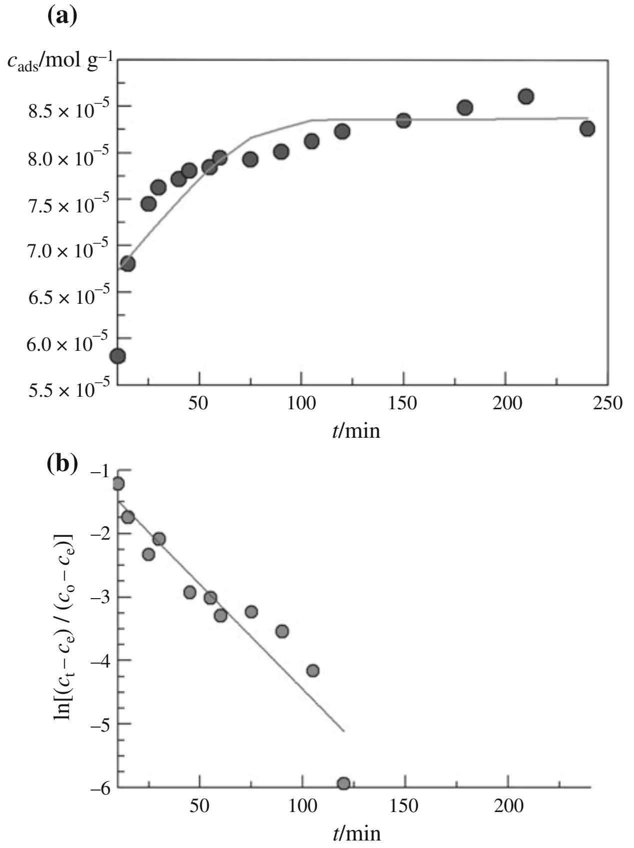

Fig. 1 **a**, **b** Kinetics of adsorption of Cr(VI) on the HDTMA-red clay; c_{ads} denotes the equilibrium concentrations of Cr(VI) in the clay phase

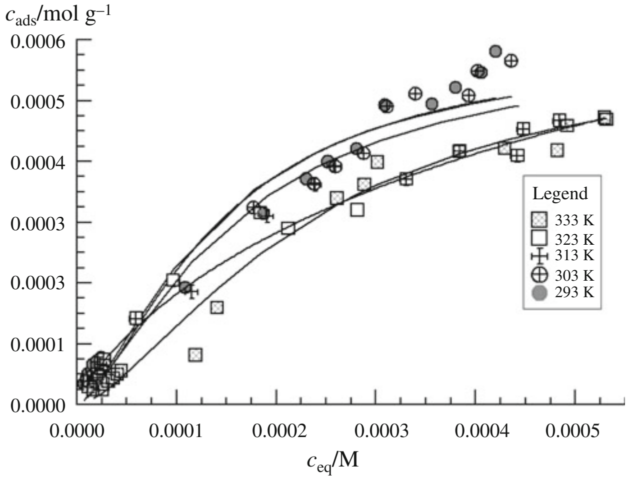

Fig. 2 The adsorption isotherms of Cr(VI) on the HDTMA-red clay for different temperatures

adsorption constant, heterogeneity parameter of the surface) are taken from the Langmuir–Freundlich equation [9]:

$$c_{ads} = a\left(Kc_{eq}\right)^n / \left[1 + \left(Kc_{eq}\right)^n\right] \tag{3}$$

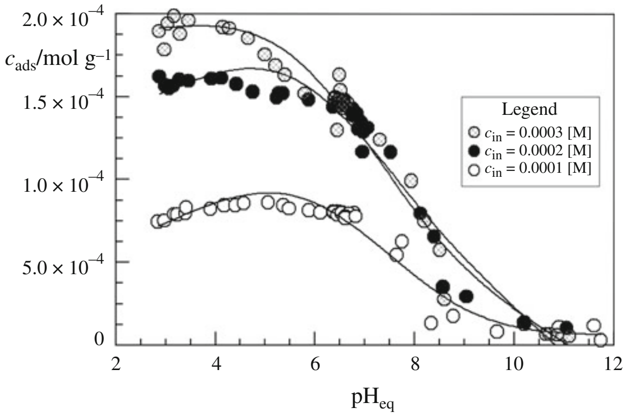

Fig. 3 The influence of pH on the Cr(VI) concentration on the red clay phase for different initial concentrations (c_{in}) of Cr(VI)

There is a slight decrease of the concentration of Cr(VI) in the clay phase with the temperature increase. Exothermicity of the adsorption results from the strong electrostatic interaction on the negatively charged Cr(VI) ions with the positively charged alkylammonium ions HDTMA$^+$. The solid lines on the plots refer to the "best fit" found from the Langmuir–Freundlich equation. The heterogeneity parameters n are: 1.52, 1.47, 1.27, 1.44, and 1.55 for 293, 303, 313, 323, and 333 K, respectively, so one can conclude about the strong interaction between alkyl chains of the surfactant cation, which is independent of the temperature.

The study of the pH effect showed that the optimal range corresponding to the Cr(VI) maximum adsorption on this clay is pH 2–6.5 (Fig. 3). Beginning from pH 6.5 a sudden drop of the chromates concentrations in the adsorbent phase appears, which results probably from the concurrent formation of alkylammonium hydroxide HDTMA(OH), according to reaction [10]:

$$\mathrm{HDTMAHCrO_4} + \mathrm{OH^-} \leftrightarrow \mathrm{HDTMAOH} + \mathrm{HCrO_4^-} \tag{4}$$

Moreover quick decrease of chromates adsorption at higher pH values can be justified after taking into account different forms of Cr(VI) anions present in the aqueous phase. In the pH range: 2–7 the dominant forms of Cr(VI) are $Cr_2O_7^{2-}$ and $HCrO_4^-$ ions; for higher pH values ions CrO_4^{2-} prevail in the solution [11]. The affinity of these ions for the modified clay is probably lower than that of $Cr_2O_7^{2-}$ and $HCrO_4^-$ ions.

Thermal spectra

The results of thermal analysis of the Na/HDTMA-clay and Na/HDTMA-Cr-clay samples are given in Fig. 4. In the case of Na/HDTMA-K three DTG peaks occur. The first is located around 60 °C and corresponds to dehydration of

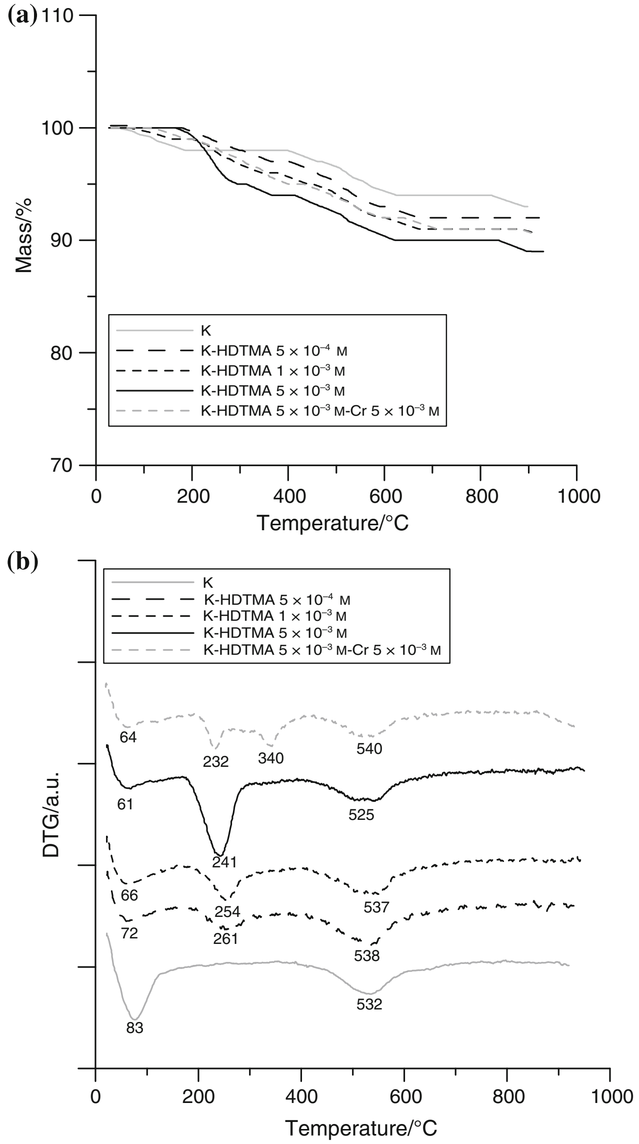

Fig. 4 The TG (**a**) and DTG (**b**) spectra of Na/HDTMA-K, Na/HDTMA-Cr–K, where K denotes clay

the adsorbent. Its position is slightly changed to higher temperature, i.e., 83 °C for raw clay. The second peak is observed at 241, 254, 261 °C for the initial HDTMA concentrations: 0.005, 0.001, 0.0005 M and results from the pyrolysis and evaporation of HDTMA adsorbed on the clay. For the highest concentration of HDTMA, i.e., for 0.005 M, its position is at the lowest temperature. This fact is probably due to of higher contribution of Van der Waals forces in the mutual interaction of HDTMA cations and in their interaction with the surface of the clay The third peak is located at 525, 537, 538 °C and is related to the dehydroxylation of the clay.

In the case of Na/HDTMA-Cr-K four peaks appear at: 64, 232, 340, and 540 °C. The third DTG peak (at 340 °C) is related to the oxidation of the surfactant [5].

Conclusions

1. The red clay from Pałęga pit modified by HDTMA is potentially useful in chromates removal from aqueous solutions with respect to fast kinetics, high efficiency of adsorption and a wide range of pH values of the aqueous phase: 2–6.5.
2. The results of thermal analysis show, that modification of the clay by HDTMA should be performed at a temperature below 232 °C to avoid the surfactant decomposition.

References

1. Mohan D, Pittman ChU Jr. Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. J Hazard Mater. 2006;B137:762–811.
2. Shanker AK, Cerrvantes C, Loza-Tavera H, Avudainayagam S. Chromium toxicity in plants. Environ Int. 2005;31:739–53.
3. Hrachova J, Billik P, Fajnor VS. Influence of organic surfactants on structural stability of mechanochemically treated bentonite. J Therm Anal Calorim. doi:10.1007/s 10973-009-0575-5.
4. Lu L, Cai J, Frost RL. Desorption of stearic acid upon surfactant adsorbed montmorillonite. A thermogravimetric study. J Therm Anal Calorim. 2010;100:141–4.
5. Zidelkheir B, Abdelgoad M. Effect of surfactant agent upon the structure of montmorillonite X-ray diffraction and thermal analysis. J Therm Anal Calorim. 2008;94(1):181–7.
6. Hoyo C, Dorado C, Rodriguez-Cruz MS, Sanchez-Martin MJ. Physico-chemical study of selected of surfactant—clay mineral systems. J Therm Anal Calorim. 2008;94(1):227–34.
7. Krishna BS, Murthy DSR, Parakash BS. Thermodynamics of chromium(VI) anionic species sorption onto surfactant modified montmorillonite clay. J Colloid Interface Sci. 2000;229:230–6.
8. Marczenko Z, Balcerzak M. Spektrofotometryczne metody w analizie nieorganicznej. Warszawa: Wydawnictwo Naukowe PWN SA; 1998.
9. Majdan M, Pikus S, Kowalska-Ternes M, Gładysz-Płaska A, Staszczuk P, Fuks L, Skrzypek H. Equilibrium study of selected divalent d-electron metals adsorption on A-type zeolite. J Colloid Interface Sci. 2002;262:321–30.
10. Majdan M, Maryuk O, Pikus S, Olszewska E, Kwiatkowski R, Skrzypek H. Equilibrium, FTIR, scanning electron microscopy and small wide angle X-ray scattering studies of chromates adsorption on modified bentonite. J Mol Struct. 2005;740:203–11.
11. Ramsey JD, Xia L, Kending MW, McCreery L. Raman spectroscopic analysis of the speciation of dilute chromate solutions. Corros Sci. 2001;43:1557–72.
12. Fosse N, Brohan L. Thermal and structural investigations of the bis-dihexadecyldimethylammonium dichromate. J Solid State Chem. 1999;145:655–67.