



## Evaluation of modified mineral performance for chromate sorption from aqueous solutions

A.G. Thanos<sup>a</sup>, E. Katsou<sup>b,\*</sup>, S. Malamis<sup>b</sup>, K. Psarras<sup>a</sup>, E.A. Pavlatou<sup>a</sup>, K.J. Haralambous<sup>a</sup>

<sup>a</sup> School of Chemical Engineering, National Technical University of Athens, Zographou Campus, GR-15773 Athens, Greece

<sup>b</sup> Department of Biotechnology, University of Verona, Strada Le Grazie 15, I-37134 Verona, Italy

### HIGHLIGHTS

- ▶ HDTMA-Br modified minerals can effectively remove Cr(VI) from aqueous solutions.
- ▶ The modification process conditions impact on the subsequent adsorption efficiency.
- ▶ Langmuir was the best isotherm equation for all minerals except attapulgite.
- ▶ Zeta potential values were used to determine the adsorption efficiency of minerals.

### ARTICLE INFO

#### Article history:

Received 2 May 2012

Received in revised form 23 August 2012

Accepted 23 August 2012

Available online 1 September 2012

#### Keywords:

Hexavalent chromium

HDTMA-Br modified minerals

Adsorption

Modification

Isotherms

Kinetics

### ABSTRACT

The removal of Cr(VI) from aqueous solutions was investigated using various minerals, such as zeolite (clinoptilolite), bentonite, exfoliated vermiculite and attapulgite. These minerals were modified using hexadecylammonium bromide (HDTMA-Br). The parameters under investigation were the HDTMA-Br concentration (0.36–8 g L<sup>-1</sup>), the pH (3–9) at which the modification process was conducted, the pH (3–9) of the adsorption solution, the modified mineral type and its concentration (1.5–10 g L<sup>-1</sup>), the mineral–metal contact time, the chromium initial concentration (10–500 mg L<sup>-1</sup>) and the system equilibrium time with respect to chromate adsorption. FTIR, SEM-EDX, XRD and electrokinetic zeta measurements were conducted for the natural and modified minerals which confirmed the modification of the minerals. The optimum pH for Cr(VI) adsorption was 4, in all the examined cases. The maximum adsorption capacity followed the order vermiculite (27 mg g<sup>-1</sup>) > bentonite (24 mg g<sup>-1</sup>) > attapulgite (15 mg g<sup>-1</sup>) > zeolite (13 mg g<sup>-1</sup>). Freundlich was the isotherm that provided the best fit to the experimental data when attapulgite was employed, while Langmuir was the most suitable one when the other three minerals were employed. Kinetics examination revealed a rapid adsorption of the metal during the initial stages. The pseudo-second-order equation fitted well to the experimental data.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Chromium compounds are widely used in industrial activities such as metal surface finishing, steel production, leather tanning, paint manufacturing, electric and electronic components, and pulp processing [1–5]. Chromium mainly occurs in the trivalent and hexavalent oxidation states. Cr(III) is usually not toxic at low and medium concentrations, whereas Cr(VI) is highly toxic, a suspected carcinogenic agent, that is highly soluble and mobile in the aquatic environment [1,6–10]. Cr(VI) forms that dominate in the environment are diprotic chromic acid H<sub>2</sub>CrO<sub>4</sub>, monovalent HCrO<sub>4</sub><sup>-</sup>, divalent CrO<sub>4</sub><sup>2-</sup> and dichromate Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, whose prevalence depends on the concentration of Cr(VI) and the pH [1,11]. Apart from its mainly

anthropogenic formation Cr(VI) can naturally occur through Cr(III) oxidation due to rock corrosion at concentrations up to 0.073 mg L<sup>-1</sup> in ground and surface waters [12].

Several treatment processes such as chemical reduction, precipitation, ion exchange, membrane separation and adsorption have been applied to remove Cr(VI) from wastewater [13]. During the last decade attention has been given to treatment processes involving adsorption of Cr(VI) on low-cost materials. Natural zeolite and clay minerals are low-cost crystalline aluminosilicate materials, which exhibit significant cation exchange capacities due to their negatively charged framework structure [1,3,7,14,15]. However, these materials have little affinity for anion groups [2]. The treatment of water and wastewater contaminated with Cr(VI) using low-cost adsorbents is a feasible process, provided that the adsorbents have received adequate pre-treatment. The modification of the negatively charged surface of minerals with cationic surfactants can effectively remove inorganic anions such as hexavalent

\* Corresponding author. Tel./fax: +39 045 8027965.

E-mail address: [ekatsou@yahoo.gr](mailto:ekatsou@yahoo.gr) (E. Katsou).