

Priority communication

# A characterization study of some aspects of the adsorption of aqueous $\text{Co}^{2+}$ ions on a natural bentonite clay

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## Abstract

The natural bentonite used in this study contained montmorillonite in addition to low cristobalite. The uptake of aqueous  $\text{Co}^{2+}$  ions was investigated as a function of time, concentration, and temperature. In addition, the change in the interlayer space of montmorillonite was analyzed using XRPD, and the distribution of fixed  $\text{Co}^{2+}$  ions on the heterogeneous clay surface was recorded using EDS mapping. The sorbed amount of  $\text{Co}^{2+}$  appeared to closely follow Freundlich isotherm, with the sorption process showing apparent endothermic behavior. The relevance of the apparent  $\Delta H^{\circ}$  values is briefly discussed. Analysis of the Co-sorbed bentonite samples using SEM/EDS showed that the montmorillonite fraction in the mineral was more effective in  $\text{Co}^{2+}$  fixation than the cristobalite fraction. XRPD analysis demonstrated that the interlayer space of montmorillonite was slightly modified at the end of sorption.

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## 1. Introduction

$^{60}\text{Co}$  ( $t_{1/2} = 5.27$  yr) is an important radioisotope of Co that is extensively used in medicine for cancer treatment and sterilization. This radioisotope is produced by nuclear activation of  $^{59}\text{Co}$  in nuclear power plants. Due to its relatively long half-life and strong  $\gamma$  radiation ( $E_{\gamma} = 1173.2, 1332.5$  keV),  $^{60}\text{Co}$  is an important radionuclide to watch for from the viewpoint of environmental safety, in particular if this element is present in its aqueous ionic form, which facilitates its migration within terrestrial systems.

Bentonite is the name of the rock that contains the montmorillonite type of clay minerals. Compared with other clay types, montmorillonite has excellent sorption properties and possesses sorption sites available within its interlayer space as well as on the outer surface and edges. Montmorillonite belongs to the 2:1 clay family, the basic structural unit of which is composed of two tetrahedrally coordinated sheets of silicon ions surrounding

a sandwiched octahedrally coordinated sheet of aluminum ions. The binding force between the stacked layers of basic units is mainly the weak van der Waals type of force, which facilitates change in the interlayer space size depending on the humidity conditions and/or the type of material encountered within the interlayer spacing of the clay. Montmorillonite is usually subjected to isomorphous substitution (e.g., substitution of  $\text{Mg}^{2+}$  for  $\text{Al}^{3+}$ ), thus leading to the development of a negative charge on the entire structure.

According to our literature survey results, a limited number of studies regarding the sorption of  $\text{Co}^{2+}$  on bentonite are available. The reported studies have addressed the effects of various parameters on the extent and nature of uptake of  $\text{Co}^{2+}$  by bentonite (or montmorillonite). The effects of pH and chelating agents were investigated and they were reported to substantially affect the retarded  $\text{Co}^{2+}$  ions [1,2]. Thermodynamic aspects of  $\text{Co}^{2+}$  retention by bentonite have also been discussed in other works [3,4]. These studies reported concentration-dependent sorption that is nonlinear and of an endothermic nature. Another study has noted that  $\text{Co}^{2+}$  sorption is time-dependent and highly irreversible [5]. High affinity of Na-activated bentonite for  $\text{Co}^{2+}$  was reported and the effect of solid/liquid ratio on the

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sorption process was discussed in another work [6]. The analytical applicability of bentonite in the preconcentration of  $\text{Co}^{2+}$  contained in waste water (prior to analysis by atomic absorption spectroscopy) was verified [7].

In this study, various aspects of the sorption behavior of  $\text{Co}^{2+}$  on this clay were examined. Part of the experiments were performed using  $^{60}\text{Co}$  as a radiotracer, while in the other part only stable Co isotopes were applied, with the bulk concentration of cobalt in this part determined using atomic absorption spectroscopy (AAS). The investigated sorption parameters were the effects of time, concentration, and temperature. Characterization of the natural and Co-loaded bentonite samples was done using scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM/EDS) in addition to X-ray powder diffraction (XRPD). SEM/EDS was applied to reveal the distribution of  $\text{Co}^{2+}$  across the heterogeneous bentonite surface, while XRPD analysis aimed at studying any structural changes in the bentonite matrix upon  $\text{Co}^{2+}$  sorption.

## 2. Experimental

The bentonite samples originated from the Giresun region, located on the Black Sea coast of Turkey. The samples were dry-sieved and the fractions with particle size  $<38\ \mu\text{m}$  were used in the experiments. Throughout the study, the batch method was applied. To each of a set of 50-mg bentonite samples placed in preweighed tubes, 5.0 ml of  $\text{Co}^{2+}$  solution (prepared from cobalt nitrate salt) containing an appropriate amount of  $^{60}\text{Co}$  radiotracer was added. The initial concentrations of  $\text{Co}^{2+}$  solution used in these experiments were 100, 500, 1000, and 2500 mg/L. Tubes were shaken at temperatures of  $25\ ^\circ\text{C}$  for time periods of 10 min, 30 min, 2 h, 4 h, 7 h, 24 h, 48 h, and 4 days. The experiments were then repeated at  $55\ ^\circ\text{C}$  for the initial concentrations 750, 1000, 1500, and 2500 mg/L. Shaking was done in a temperature-controlled environment using a Nuve ST 402 water bath shaker equipped with a microprocessor thermostat. The samples were then centrifuged and 4.0-ml portions of the supernatant were counted for 1000 s using a  $35\text{-cm}^3$  HPGe detector connected to a multichannel PGT analyzer. Duplicate samples were used in each measurement.

The pH of the cobalt solutions in contact with bentonite varied between 4.2 and 6.4, with the pH decreasing as the initial concentration was increased. The chemical speciation analysis of cobalt ions in aqueous solution under different pH conditions was performed using visual MINTEQ software. The data were generated based on the initial concentration, temperature, pH, and ionic strength, all of which were defined in an input file. According to this analysis, up to pH values of 8–9, the dominant chemical form of Co in aqueous media is  $\text{Co}^{2+}$ . Beyond pH 9, other forms of Co (such as  $\text{CoOH}^+$  and  $\text{Co}(\text{OH})_2(\text{aq})$ ) become increasingly effective. Based on this analysis, it is clear that within the experimental conditions of this study, the dominant form of cobalt in aqueous media is  $\text{Co}^{2+}$ .

In the Co-loaded bentonite samples that were characterized by surface techniques, no radioactive cobalt was used. The SEM/EDS analysis was started by sprinkling the solid samples

onto adhesive carbon taps supported by circular metallic disks. The samples were then analyzed using a Philips XL-30S FEG type SEM/EDS instrument. Images of the sample surfaces were recorded at different magnifications. EDS elemental analysis was performed at several different points of the surface in order to minimize any possible anomalies arising from the heterogeneous nature of the analyzed surface.

The natural and Co-sorbed bentonite samples were also characterized using XRPD. For this purpose, the powders were first ground, mounted on rectangular glass holders, and then introduced to a Rigaku miniflex instrument for X-ray diffraction analysis.  $\text{CuK}\alpha$  radiation was used as a source. X-rays were generated in a tube operating at 30 kV and 15 mA. Spectra were recorded with  $2\theta$  values ranging from  $2$  to  $35^\circ$  in steps of  $0.02^\circ$  and dwell times of 10 s per step.

## 3. Results and discussion

The XRPD pattern of natural bentonite is given in Fig. 1a. The figure indicates that the clay is composed primarily of montmorillonite, with the characteristic features at  $d_{001} = 15.15\ \text{\AA}$  and  $d_{020} = 4.50\ \text{\AA}$ , in addition to low cristobalite (a polymorph of quartz), marked by its main reflection at  $d_{101} = 4.05\ \text{\AA}$ . The heterogeneous nature of the natural clay is demonstrated in the SEM image given in Fig. 1b. The elemental composition of bentonite obtained using EDS showed that the atomic percentages are 57.3 (O), 31.1 (Si), 8.1 (Al),

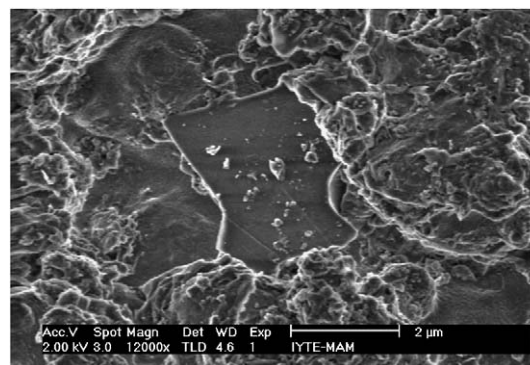
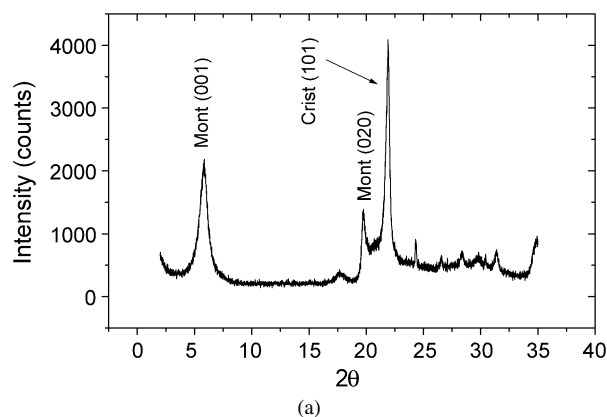


Fig. 1. (a) XRPD pattern of bentonite mineral applied in this study; (b) a typical SEM image of the surface of the same mineral.

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