



# Adsorption of caesium from aqueous solution on binary mixture of iron pillared layered montmorillonite and goethite

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## ABSTRACT

Caesium adsorption was carried out on two materials namely iron pillared layered montmorillonite (Fe-PILM) and goethite ( $\alpha$ -FeOOH), and their mixture (Fe-PILM;  $\alpha$ -FeOOH).

The characteristics of these two adsorbents were determined by using X-ray diffraction, Fourier transform infrared spectrum. A set of experiments was done to estimate cation exchange capacities and zero point of charge  $pH_{zpc}$  of used materials. Adsorption of Cs as a function of pH, mass fraction of goethite in the mixture, initial concentration and ionic strength was investigated. The kinetic study showed that sorption followed pseudo-first-order kinetics with a good correlation coefficient ( $R^2 = 0.997$ ). Optimal Cs ions elimination was favoured at the pH range 5–9. The obtained results revealed that the maximum adsorption of 93%, took place at 20% composition of goethite in the mixture. The Cs sorption data onto optimal mixture were described using Freundlich, Langmuir and Dubinin–Radushkevich (D–R) models. The thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  for the Cs adsorption were determined by using four temperatures (288, 308, 338 and 360 K). Results show that the adsorption process was exothermic and favoured at low temperature.

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## 1. Introduction

The development of industrial and military activities, using radioactive materials led to the release of caesium radioisotopes in the environment [1].  $^{137}\text{Cs}$  and  $^{134}\text{Cs}$  are important radionuclides in radioactive waste for several reasons: they exhibit high solubility, have long half-life, and Cs can be easily incorporated into terrestrial and aquatic organisms (because of its chemical similarity to K). The bioavailability of Cs depends mainly on sorption properties of the solid phases [2].

In the deep geological repository of high-level nuclear waste, the interaction of carbon steel (Fe) overpack container and the back-fill clay mineral, montmorillonite, is an important issue to be clarified in view of the long-term performance of clay mineral as an engineered barrier. Montmorillonite interaction with the steel container in the geological conditions is of major concern. Indeed, the corrosion of steel can alter the clay mineral to some extent. In this context, many studies focus on the alteration of montmorillonite in contact with metallic iron and/or iron oxides at different conditions of pH, temperature, iron (oxide)/clay ratio, redox or fluid chemistry, etc., both experimental and simulated conditions [3].

Clays or modified clays are used worldwide as adsorptive media for several heavy metals [4], organic contaminants [5] or bacteria [6]. Chemical modifications on the surface of the clays with acids, bases, cationic surfactants and some poly hydroxyl cations were also conducted to improve their sorption capacities. It was reported that the intercalation of some metal oxides on 2:1 clay minerals significantly led to an increase in the sorption capacity [7].

Over the last decade iron oxides have been recognized as being solid phases, which exert a significant effect on the behaviour of a large range of environmentally relevant substances particularly heavy metals and other toxic elements, eutrophication compounds, and organic xenobiotics. Currently, these substances are inevitable constituents of most compartments of the earth's ecosystems. Iron oxides indirectly affect the environment by influencing the fate (mobility, decomposition, etc.) of the substances listed above. In another way, they can immobilise pollutants by surface adsorption or by incorporation [8].

Fe-PILM and goethite are used here as adsorbents to evaluate the difference in the basic properties, mainly diffusion of pollutants with respect to the basic materials such as montmorillonite. The association of goethite to Fe-PILM was done for three main reasons (i) after pillaring montmorillonite, a possible excess of iron ions may be transformed by neoformation to iron oxides, (ii) due to its high thermodynamic stability, goethite is by far the most common iron oxide in soils and (iii) iron oxides may occur as products of corrosion processes.

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In this study, an iron polycations were used to intercalate an algerian montmorillonite. This is designed to assess the effectiveness of Fe-PILM and goethite in the removal of caesium from aqueous solutions.

In fact, this type of material provides a texture and rigidity in favour of the investigation on dynamic adsorption contrary to the basic materials that block the liquid flow by clogging phenomenon.

## 2. Materials and methods

### 2.1. Reagents

All chemicals were of analytical grade and used without further purification. Radiotracer  $^{134}\text{Cs}$  solution was prepared by neutron irradiation of 3.6 mg of CsCl (Panreac QUIMICA) at Essalam Research Reactor CRNB (Centre de Recherche Nucléaire de Birine-Algeria) followed by dissolution of irradiated CsCl in deionised water (North Star ULTRA system: resistivity 1 M $\Omega$  cm).

### 2.2. Iron pillared montmorillonite

The starting material was a sample of bentonite from Maghnia (Algeria) supplied by ENOF "Entreprise Nationale des Matériaux non Ferreux" whose chemical composition is: 69.4% SiO<sub>2</sub>, 14.7% Al<sub>2</sub>O<sub>3</sub>, 1.2% Fe<sub>2</sub>O<sub>3</sub>, 1.1% MgO, 0.3% CaO, 0.5% Na<sub>2</sub>O, 0.8% K<sub>2</sub>O, 0.2% TiO<sub>2</sub>, 0.05% As and 11% loss on ignition [9]. The <2  $\mu\text{m}$  montmorillonite fraction was converted into Na<sup>+</sup> saturated form by washing several times, first with 0.1 M NaCl solution (Riedel-de Haën) and then with deionised water until the supernatant was free of chlorides. The obtained product was designated hereafter as Na-montm. Iron pillaring agent was prepared as follows: a 0.75 M NaOH solution (Riedel-de Haën) was slowly added drop by drop (0.6 mL  $\text{mn}^{-1}$ ) to 0.43 M FeCl<sub>3</sub>·6H<sub>2</sub>O solution (Riedel-de Haën) with vigorous stirring (using an agitator with glass rod) to obtain a final solution with an OH/Fe molar ratio equal to 2 and a final concentration of 0.2 M. The pillaring agent, named hereafter (PCBF), was left to age for 10 days at room temperature. After aging, the resulting solution was reacted with 0.5% aqueous suspension of Na-montm at a ratio of 5 mmol  $\text{g}^{-1}$  of clay [9], and left to react under vigorous stirring at room temperature. After filtration and washing several times with deionised water, obtained solid was dried at 40 °C for at least 72 h, ground, and sheltered from light. The modified clay was designated hereafter by Fe-PILM.

### 2.3. Goethite preparation

Goethite was prepared using a method based on that of Schwertmann and Cornell [8]. 0.1 M FeCl<sub>3</sub>·6H<sub>2</sub>O was slowly titrated with 5 M NaOH with purging N<sub>2</sub> gas to exclude CO<sub>2</sub> until the pH reached 12. The resulting suspension was aged for 60 h at 70 °C. The precipitate was dialyzed three times in deionised water and dried at 60 °C for 24 h, ground for homogenisation, and sheltered from light.

### 2.4. Solids characterization

X-ray diffraction patterns were recorded on a Philips PW1710 diffractometer using Cu K $\alpha_1$  radiation, ( $\lambda = 1.54060 \text{ \AA}$ ). Oriented specimens were prepared by spreading 2 mL of montmorillonite suspension on 3  $\times$  2.5 cm<sup>2</sup> glass slide and drying at room temperature. This method is recommended in order to obtain a strong basal reflection [10].

Infrared spectra were recorded over the 400–4000  $\text{cm}^{-1}$  range with a 4  $\text{cm}^{-1}$  resolution using a Infracal FT-02 (Alumex)-IR Fourier transform spectrometer. 1 mg of the sample was finely ground and mixed to 300 mg of KBr previously dried at 110 °C for 24 h.

The cation exchange capacity (CEC) was measured using the copper complex method (Gaboriau, 1991). 600 mg of sample were suspended for 12 h in 25 mL of a 0.02 N ethylene di-amine copper complex solution (Sigma–Aldrich). After centrifugation, the Cu concentration in solution was measured using an A-Analyst 400 atomic absorption spectrometer from PerkinElmer Inc. The adsorbent CEC value (in meq 100  $\text{g}^{-1}$ ) was calculated as the difference between the initial and final concentrations of Cu ions in the solutions.

The zero point charge (pH<sub>ZPC</sub>) is defined as the pH of the suspension at which the surface charge density  $\sigma_0 = 0$ . pH<sub>ZPC</sub> measurements are based on mass titration method [11]. It is to put increasing amounts of solid in a given volume of aqueous solution. When the amount of solid increases, the pH changes and tends to a constant value, it corresponds to the point of zero charge of the solid. The mass titration experiments were performed at 17 °C by introducing increasing amounts of solid in 10 mL of 0.1 M NaNO<sub>3</sub> solution (Sigma–Aldrich) in Teflon vessels in order to obtain the following mass concentrations: 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1%, 3%, 5%, 7% and 10%. Then, the vessels are subjected to N<sub>2</sub> gas (instead of argon) flow to maintain an inert atmosphere and placed in agitation using magnetic stirrer for 24 h. The pH of the suspensions was then measured using a Consort 831 pH meter. The uncertainty on the measured pH value is about 0.2 units.

### 2.5. Adsorption experiments

The batch experiments were carried out in 250 mL conical flasks where 0.1 g of mixture (mass ratio Fe-PILM/goethite = 1) is added to 50 mL of 13.3 mg L<sup>-1</sup> caesium solution. This final solution was traced by few drops (constant volume) of radiotracer solution. After attaining equilibrium, the solution is centrifuged and the supernatant is filtered through a 0.45  $\mu\text{m}$  cellulose nitrate membrane filter.  $\gamma$  activity is measured with high purity germanium (hpGe) detector combined with Gamma spectrometry system. The activities related to the loss by adsorption onto flask walls were subtracted by using blank experiments.  $\gamma$  spectrum for each sample was collected for 1000seconds.

The percentage adsorption  $R$  (%) and the distribution coefficient ( $K_d$ ) were calculated using the following equations, respectively:

$$R(\%) = \frac{A_i - A_f}{A_i} \times 100 \quad (1)$$

$$K_d(\text{mL g}^{-1}) = \frac{A_i - A_f}{A_f} \times \frac{v}{m} \quad (2)$$

where  $A_i$  and  $A_f$  are initial and final activity, respectively;  $v$  is the volume of the solution (mL) and  $m$  the adsorbent mass (g).

The effects of some parameters such as, mass fraction of goethite in the mixture (varied from 0 to 1), pH (from 2 to 11), initial concentration (from 1 to 133 mg L<sup>-1</sup>) and ionic strength (from 10<sup>-4</sup> to 10<sup>-1</sup> M NaCl solution) were studied. All experiments were conducted at 15–17 °C.

## 3. Results and discussion

### 3.1. Characterization of sorbents

XRD patterns of all samples are shown in Fig. 1. The obtained data for Na-montm showed characteristic d-spacing of 1.68, 2.53 and 4.41  $\text{\AA}$  indicates that the sample used in this work is bentonite. The peak appeared at 4.41  $\text{\AA}$  further implies the 2:1 mineral type. The original Na-montm has a d-spacing of 15.3  $\text{\AA}$  which increased to around 17  $\text{\AA}$  upon pillaring with iron. The increase in d-spacing was as expected since the pillaring causes an expansion in the interlayer spacing.

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