Applied Clay Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

# Investigation of adsorption of 5-Chlorouracil onto montmorillonite: An IR and Raman spectroscopic study

Sevim Akyuz*, Tanil Akyuz

*Physics Department, Istanbul Kultur University, Bakirkoy, 34156 Istanbul, Turkey*

ARTICLE INFO

*Keywords:*
Adsorption
Clays
5-Chlorouracil
FTIR
Raman

ABSTRACT

In this study, the adsorption of 5-Chlorouracil (5-ClU) on natural montmorillonite from Anatolia was investigated using FT-IR and Raman spectroscopy. The 5-ClU is a thymine antagonist and has some antitumor properties. The comparison of the vibrational spectra of the adsorbed 5-ClU with those of the free molecule provided data on the nature and characteristics of the clay organic complexes. The intercalation of 5-ClU within montmorillonite has been shown by X-ray diffraction to increase the interlayer spacing. Vibrational spectroscopy indicates that adsorbed 5-ClU molecules on montmorillonite are coordinated to exchangeable cations, directly or indirectly through water bridges.

## 1. Introduction

Uracil analogs with halogen substitution at the 5-position, represent an important class of compounds with regard to their mutagenic activity (Lindahl, 1993). The 5-fluorouracil (5-FU) analog is a well-known anti-cancer drug for treatment of human malignancies (Henderson et al., 2003). The 5-Chlorouracil (5-ClU) has a similar structure with thymine, which can replace the thymine in DNA, and therefore it can be used in the synthesis of antineoplastic and anti-inflammatory drugs with antimetabolic functions (Jiang et al., 2003; Henderson et al., 2003). It has antitumor activity in the complexes with some metal (II) ions (Ortiz et al., 2013; Narang et al., 1998; Singh et al., 1988; Singh et al., 1989), as cobalt (II) and nickel (II), and in the complexes with metal (III) ions (Narang et al., 1998). Other derivatives are potential anticancer/antiviral agents (Khan et al., 2001). de Benetoli et al. (2008) investigated the adsorption of uracil on bentonite and montmorillonite at a wide range of pH (2.0–7.2). It was reported that at pH 2.0 the interaction of uracil with the clays proposed to occur through positively charged, protonated groups. In our previous study (Akalin et al., 2007) we have investigated the adsorption of 5-FU into the layers of montmorillonite and saponite. As continuation of our studies, in this study, we investigated the interaction of 5-ClU with montmorillonite. Over the last decade, smectite clays with intercalated organic molecules have attracted great research interest, since they exhibit novel physical and chemical properties. The adsorption of bioactive molecules on clays has been studied not only for the sake of understanding their physical and chemical properties but also for their possible application in drug-delivery systems (Fraile et al., 2016; Jayrajsinh et al., 2017). Montmorillonite (Mt) is a smectite group of clay that has a layered structure. The adsorption properties of Mt are well documented in the scientific literature, with many examples of adsorption of organic materials (Theng, 1974; Atwood et al., 1991). In this study, the adsorption of 5-ClU on natural montmorillonite from Anatolia was investigated using FT-IR and Raman spectroscopy. The aim of this study was to investigate the sorption properties of 5-ClU by clays. Since 5-ClU has pharmacological activity, we hope to contribute to the explanation of the host-guest interaction through the study of the vibrational spectra of the pure and adsorbed species.

## 2. Experimental

The natural montmorillonite used was from the Cankiri region of Anatolia (Turkey). The chemical compositions of the montmorillonite is as follows (in wt%): $SiO_2$ (58.3), $Al_2O_3$ (16.0), CaO (3.5), Σ(FeO + $Fe_2O_3$) (3.0), MgO (2.5), $K_2O$ (1.1), $Na_2O$ (2.1), $TiO_2$ (0.6), $P_2O_5$ (0.1), loss on ignition (13.1). The clay was ground to an approximately 200-mesh size powder. Solid 5-ClU as reagent grade (Aldrich Chemicals) and was used as received. The 5-ClU treated clay was prepared by immersing the clay in aqueous solution of 5-ClU in a sealed bottle at room temperature for 2 days. The initial composition of 5-ClU to Mt was 30 wt%. After then clay organic suspension was washed and centrifuged at 7000*g* for 10 min.

The XRD spectra of the investigated samples were recorded on a Rigaku D/Max 2200 powder X-ray diffractometer using Cu $K_\alpha$ radiation.

The energy dispersive X-ray fluorescence analysis (EDXRF) were

* Corresponding author.
*E-mail address:* s.akyuz@iku.edu.tr (S. Akyuz).

http://dx.doi.org/10.1016/j.clay.2017.08.018
Received 2 March 2017; Received in revised form 8 August 2017; Accepted 16 August 2017

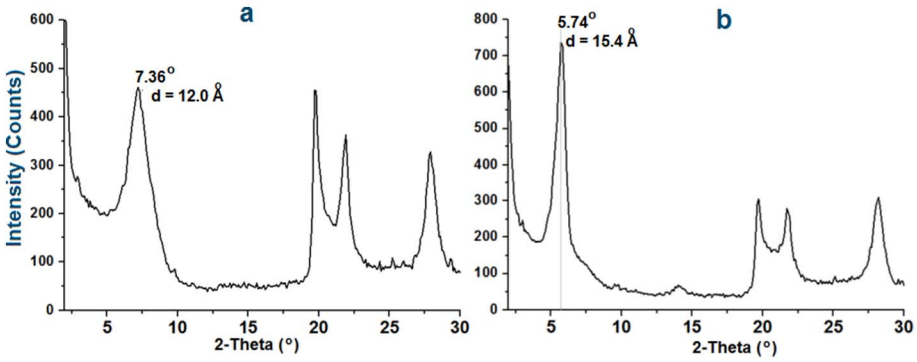


**Fig. 1.** The XRD patterns of montmorillonite, before (a) and after treatment with 5-ClU.

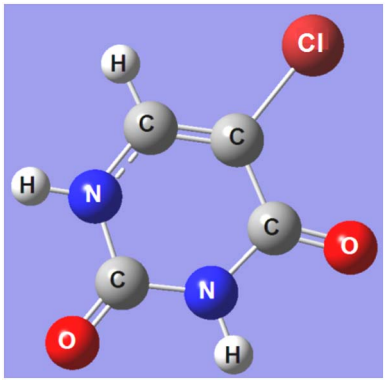


**Fig. 2.** Molecular model of 5-Chlorouracil.

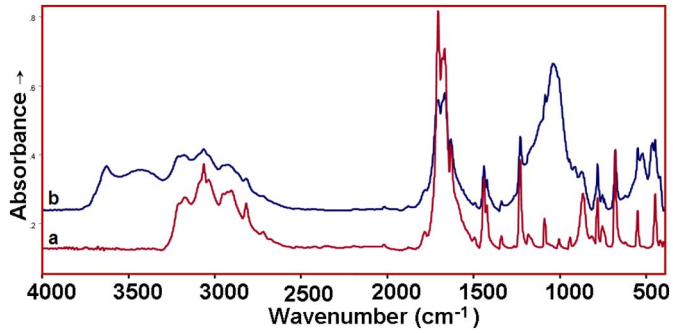


**Fig. 3.** The FT-IR spectra of solid 5-ClU (a) and 5-ClU treated Mt (b).

performed on a spectro iQ-II model spectrometer. The samples were analyzed for 300 s using an air cooled low power Pd end window X-ray tube (25–50 kV) combined with Highly Oriented Pyrolytic Graphite (HOPG) crystal for monochromatization and polarization of the primary tube spectrum. The orientation of HOPG crystal enables to focus Pd $L_\alpha$ line onto sample. A silicon Drift Detector (SDD) was used to collect the fluorescence radiation from the sample. The resolution of the SDD was better than 175 eV (for Mn $K_\alpha$ at an input count rate of 10,000 cps). During the measurement, the excitation area was flushed

**Table 1**
The IR and Raman wavenumbers of 5-ClU adsorbed on Mt and 5-ClU wavenumbers in solid state and in Ar-matrix.

| Assignment[a] | Ar-matrix[b] | Solid ref[a] | | Solid (this study) | | Adsorbed on Mt | |
|---|---|---|---|---|---|---|---|
| | IR | IR | Ra | IR | Ra | IR | Ra |
| νNH | 3472 | 3160 | 3155 | 3210<br>3166 | nm | 3208<br>3171 | nm |
| νNH | 3426 | 3060 | 3060 | 3088<br>3062 | nm | 3063 | nm |
| νC = O | 1764 | 1732 | 1735 | 1710<br>1703 | 1716 | 1718<br>1696[c] | 1715[c]<br>1701[c] |
| νC = O | 1729 | 1678 | 1700 | 1682<br>1666 | 1689[c]<br>1681<br>1670[c] | 1683<br>1669 | 1688[c]<br>1676 |
| νCC | 1641 | 1635 | | 1631 | 1630<br>1610[c] | 1639 | 1637<br>1624[c] |
| δNH | 1461 | 1505 | 1510 | 1493 | 1494 | 1490 | 1495 |
| δNH | 1387 | 1410 | 1410 | 1415 | 1415 | 1423 | 1425 |
| γNH | 657 | 860 | 880 | 866 | 870 | 884 | 879 |
| νring | – | 780 | 784 | 783 | 790 | 795 | 793 |

[a] Assignment and wavenumbers of solid 5-ClU are taken from (Ortiz et al., 2013).
[b] Wavenumbers of 5-ClU in a argon matrix is taken from (Dobrowolski et al., 2005), nm = not measured.
[c] Obtained by band component analysis.

with helium gas. The amount of adsorbed 5-ClU onto Mt was determined depending on the analysis of the chlorine content of the clays. The EDXRF analysis of the Mt before and after treatment with 5-ClU were performed in triplets and showed good reproducibility.

The FT-IR spectra (400–4000 $cm^{-1}$) of self-supporting films, prepared according to (Madejova, 2003), or KBr discs were recorded on a Bruker Tensor FT-IR spectrometer (1 $cm^{-1}$ resolution) based on averaging 200 scans.

The Raman spectra of the powdered sample was recorded on a Jasco NRS-3100 μ-Raman spectrometer (1200 lines/mm grating and high sensitivity cooled CCD). A 532 nm line of the diode laser was used as the excitation wavelength.

The GRAMS/AI 7.02 (Thermo Electron Corporation) software package was used to perform a comprehensive processing (baseline and smoothing corrections, derivative and band fitting procedures), visualization and reporting. For IR and Raman spectra, band component

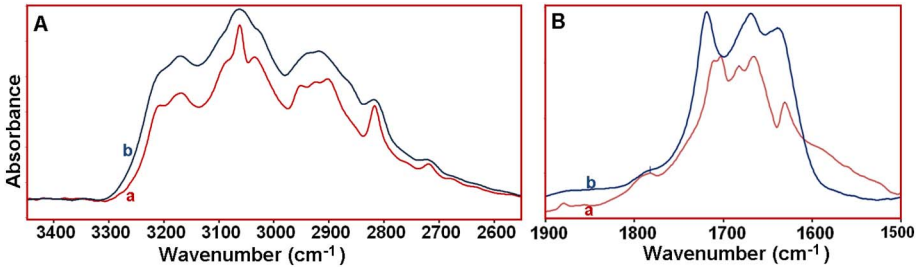


**Fig. 4.** The 3400–2600 $cm^{-1}$ (A) and 1900–1500 $cm^{-1}$ (B) regions of the FT-IR spectra of solid 5-ClU (a) and 5-ClU treated Mt after subtracting the vibrational bands of the natural clay (b).