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SORPTION OF COMPLEX ORGANIC MIXTURES FROM RIVER WATERS ON LAYERED MONTMORILLONITES

Hadi DEBIH[a,*] and Istvan GEBEFÜGI[b]

[a] Faculty of Sciences, University Mohamed Boudiaf - M'sila, Laboratory of materials valorization and structurals mechanic, 28000 Algeria
[b] Institute of Ecological Chemistry, Helmholtz Zentrum München, German Research, Center for Environmental Health (GmbH) Ingolstädter Landstraße 1, D-85764 Neuherberg, Germany

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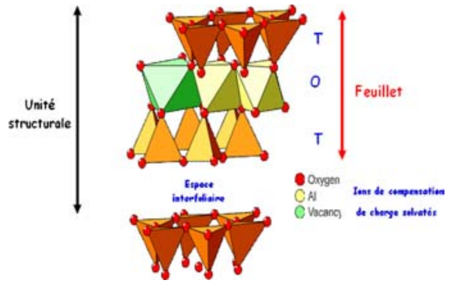
This paper analyses the impact of the increased use of natural organic materials (NOMs) from Suwannee River (USA). Aqueous solutions were contacted with clays materials to study their specific adsorption and/or possible alteration by combined high resolution ICR-FT (soluble NOMs) and FTIR (sorbed NOMs). The present study aims at initializing research with ICR on the effect of clays and three-dimensional porous materials in selectively sorbing molecules and fragments contained in various NOMs. In the presence of clays minerals, new techniques have been developed to study NOM interaction behaviour with clays. When soluble NOMs are in contact with natural clay minerals or with selected (meso-) porous synthetic materials, they are often selectively adsorbed in these substrates, so that their analysis before and after contact may help to understand the complex natural processes and further give hints for possibilities to use similar or other synthetic inorganic surfaces to monitor and control such modifications in relation to their bio-active significance. While clays retain aromatic molecules through an original mechanism, materials adsorb less bulky compounds, due to their shape and selective properties.



INTRODUCTION

NOM is present in several environmental areas such as soils, sediments fresh water, air etc. It appears after organic matter decomposition. The environmental fate of natural organic materials including interactions with xenobiotics contributes to a better understanding of the global biogeochemical organic matter cycle. The molecular level analysis of complex systems such as aquatic fulvic acids and related NOMs in natural waters could be elegantly investigated by ion cyclotron resonance ICR, since it was shown that this technique can constitute an indispensable tool at the core of molecular-level analysis of complex systems.[1-3] The measured several tenths of thousands of exact masses allowed the calculation of sum formulas of soluble NOMs and their visualization in Van Krevelen diagrams.[4] Here we illustrate these effects by measuring with ICR (ion cyclotron resonance) extremely accurately the exact mass of the numerous compounds from the SuwaFA

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[*] Corresponding author: debimah@yahoo.fr

(Suwannee River fulvic acid) used as a standard, before and after sorption. Compositional changes are visualized in Van Krevelen diagrams derived from FT-ICR spectra.[5]

RESULTS

The used clays are from north-west of Algeria: montmorillonite 1 or (MtMagh-) from Roussel Maghnia Region, montmorillonite 2 or (MtMost-) and bentonite (Bent-) from the deposit of M'zila – both from Mostaghanem region. Each clay was purified and exchanged with Na^+. The protocol of exchange was: raw crushed clay is primarily treated with $Na_2S_2O_4$ solution aluminum oxides eliminated by ion chelating reactions. For the second treatment method, the obtained product is treated with H_2O_2 at 60°C to clean it from organic matter. Third treatments contribute to eliminate carbonates by HCl 0.1M solution washing during one hour. At least, H^+- clay is poured in NaCl 1M solution three times during one day to exchange ions and washed with distilled water until Cl^- ions disappears. Tables 1 and 2 give mineralogical and elementary analysis of the clays. MtMagh- shows crystallites corresponding to SiO_2 aggregates or trace of ion oxides and alkaline metals. For MtMost- and Bent-, the same peaks appears, however the proportion is lower, the ratio SiO_2/Al is close to 1.5.

Concerning C.E.C. measurement (Table 3), CTAC surfactant solution was used, which adsorbs on colloidal particles and changes the clay charges from negative to positive and leads to specific adsorption on clay surface. Knowing surfactants equivalent charge (312.5 meq/100g) of CTAC, C.E.C. can be calculated. Results are given in Table 3.

Table 1

Clay mineralogical composition with EDX equipment (Kevex apparatus; Quantum model)[6]

Clays	Illite	Montmorillonite	Quartz	Calcite	Feldspar	Crystallinity
MtMagh-	-	93%	7%	-	Traces	MyC*
MtMost-	4%	78%	13%	5%	Traces	MyC
Bent-	-	90%	10%	-	Traces	MyC

*MyC: moderately crystallized

Table 2

Quantification and mass ratios using the technique EDX (Kevex apparatus; Quantum model)[6]

Clays	O	Na	Mg	Al	Si	Cl	K	Fe
MtMagh-	49.7	4.6	2.0	11.0	28.1	0.6	3.5	0.6
MtMost-	50.4	2.8	2.0	9.0	32.2	0.5	2.1	1.2
Bent-	49.3	2.9	2.0	8.9	31.8	0.4	2.8	1.9

Table 3

Measurement results of the specific surfaces of various clays[6]

Clays	Specific surface (m^2/g)	Micropores volume (cm^3/g)	$V_{a\mu pores}$ (cm^3/g)	$a_{\mu pores}$* (m^2/g)	C.E.C (meq-/100g)
MtMagh-	210.65	32.91	0.0002	0.31	30.1
MtMost-	83.78	9.13	0.0013	0.23	68.5
Bent-	80.75	8.12	0.0011	0.21	65.1

*$a_{\mu pores}$ means the slope which is also the surface of micropores or mesopores surface; $V_{a\mu pores}$ means the micropore volume or volume of mesopores corresponding to $a_{\mu pores}$.

FTICR (Fourier Transform Ion Cyclotron Resonance) was very helpful in detecting global theoretical C-H-O combinations. This matter is present wide world and in the global climate cycle. Aqueous solutions of natural organic materials from Suwannee River (recommended IHSS reference) were analysed before and after being exposed to clays by ICR Molecular masses could be computed from the ICR data with an accuracy allowing us to identify each mass isomer of all adsorbed molecules with an unrivalled accuracy.[7-9]

Concerning organic substance, we have chosen NOM fraction considered as a standard reference molecule SuwFA, fulvic acid fraction from Suwannee river of Georgia in USA. For the first time, different research groups from Helmholtz center have determined the maximum number of chemical compositions from carbon, hydrogen and oxygen atoms in organic matter (Fig. 1).

The H/C versus O/C ratios for all mass isomers could be visualized on Van Krevelen diagrams in which the numbers of chemically relevant isomers for a given molecular composition $C_xH_yO_z$ of a single nominal mass are provided and contrasted by statistical methods.

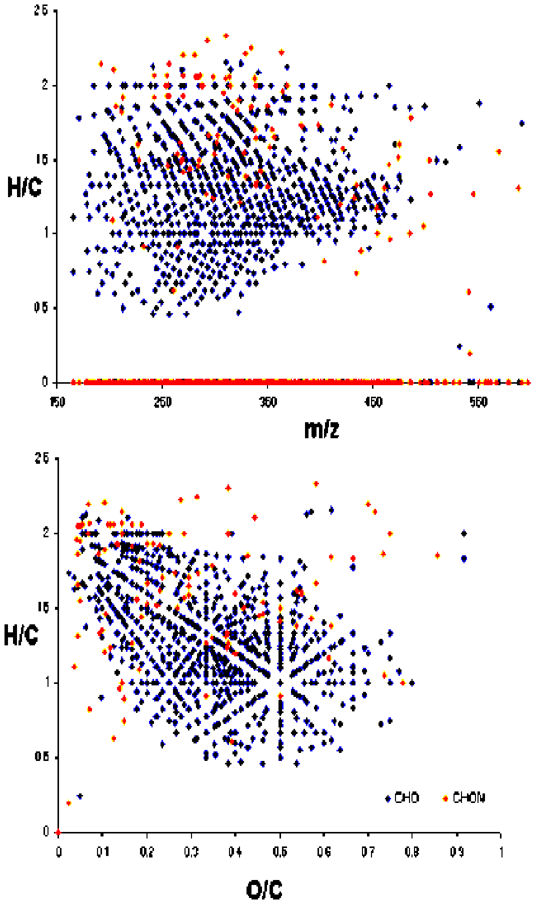

Fig. 1 – Van Krevelen diagram visualization of NOM molecules from fulvic acid from Suwannee River (SRFA).

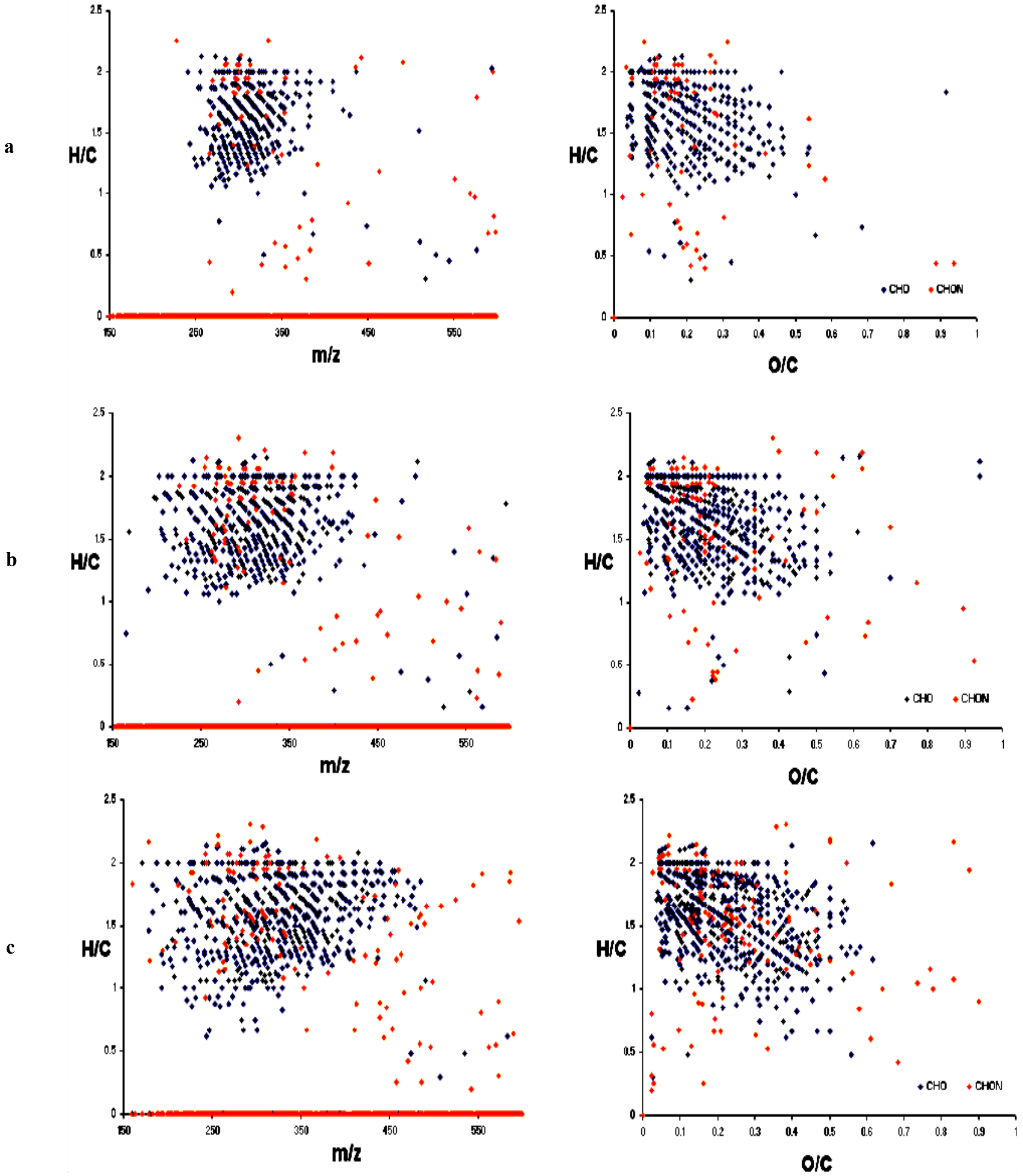

Fig. 2 – Van Krevelen diagram visualization of the changes induced by adsorption of some NOM molecules from fulvic acid from Suwannee River (SRFA) after contact with montmorillonites: a) MtMagh-, b) Bent-, c) MtMost-.

DISCUSSION

Differences between C.E.C. values are related to clay structure and composition. MtMost- clay, compared to MtMagh- and Bent-, shows agglomerated particles leading to smaller value of C.E.C. and smaller values of the specific area. Structural study of clays shows acceptable values of BET specific surface area (80 to 840 m²/g).[10]

Clays adsorb several NOM components in different ways that could be related to their specific void space and composition (selective molecular interactions with various framework atoms or groups such as hydroxyls). In the typical example of SRFA (Fig. 2), the lower H/C and higher O/C ratios after sorption demonstrate their preferential retention and bonding within MtMost- void space, while each clay shows a specificity in adsorbing selected families of aromatic molecules.

Table 4

Results of determination of the adsorbed amounts for different clays in contact with some NOM molecules from fulvic acid from Suwannee River (SRFA)

Clays	$C_{equilibrium}$ (g/L)	$C_{adsorbed}$ (g/L)	$C_{adsorbed}$ (mg/g)	Γ (mg/m^2)	$S_{(BET)}$** (m^2/g)
MtMagh-	0.113	0.387	21.15	0.099	210.65
MtMost-	0.024	0.476	26.01	0.31	83.78
Bent-	0.079	0.421	23.00	0.28	80.75

** The experiments were performed on an ASAP 2000 apparatus from Micromeritics.[6]

UV spectrophotometer technique was used for the measurement of fulvic acid and clay solutions when equilibrium concentration was evaluated. Knowing the initial concentration, the adsorbed quantity can be calculated (Table 4).

In Table 4, we can see SRFA adsorbed quantities on MtMagh- with high C.E.C. and specific surface is lower than those on MtMost- and Bent- clays.

If we analyze the values of specific surface areas and pore volumes (Table 4), we conclude that the more montmorillonite in the mixture, the better adsorption and the higher selectivity to aromatics. This selectivity is impressive for this sample (MtMost-). The graph also shows that in both experiments individual molecules underwent defined alterations, yielding new molecules or fragments readily released in the supernatant solution after contact with clay materials.[5,11,12]

EXPERIMENTAL

A 12 Tesla Apex-Q Fourier transform ion cyclotron mass spectrometer (Bruker, Bremen, Germany) using flow injection mode and electrospray (ESI) infusion ionizations, described in detail in literature,[1] was used to analyze the probes. Aqueous NOM samples extracted by reverse osmosis from Suwannee river water collection standards (SRFA) provided by the International Humic Substances Society (IHSS), were stirred at ambient temperature for 48 h with layered aluminosilicates, to study structure-specific sorption phenomena.[12,13]

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CONCLUSIONS

This new developed analysis method with high resolution allows the better understanding of structural chemistry of this unique material. Montmorillonites materials show significantly different results in terms of selectivity of the sorbed molecules. MtMost-retain more organic compounds than the other two. The adsorption order is:

MtMost- > Bent- > MtMagh-

In particular, it was demonstrated that aromatic molecules are adsorbed within the clay sheets and undergo, after substantial sheet swelling, polymerization. As a typical example, benzene readily yielded poly-paraphenylene cations sorbed on Cu^{2+} exchanged montmorillonite, and adsorption of asphaltenes onto clays made from water-saturated toluene. In that respect, Suwannee River involves relatively young NOMs with no contact with naturally occurring minerals (clays), so that our preliminary laboratory experiments could be extended on a larger scale, allowing one to obtain measurable effects regarding the whole NOM "inventory" of a system, in relation to its potential ecological applications and effects. The new method of high-resolution analysis newly developed allows now a much better understanding of the structural chemistry of this material ubiquitous natural.

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