



**HAL**  
open science

# COMBINATION OF SURFACTANT MICELLE AND ORGANOCLAY FOR THE ADSORPTION OF DICLOFENAC

Régis Guégan, Tiago de Oliveira, Mohammed Boussafir, Claude Le Milbeau,  
Fabrice Muller, Mikael Motelica-Heino

► **To cite this version:**

Régis Guégan, Tiago de Oliveira, Mohammed Boussafir, Claude Le Milbeau, Fabrice Muller, et al..  
COMBINATION OF SURFACTANT MICELLE AND ORGANOCLAY FOR THE ADSORPTION  
OF DICLOFENAC. 8th International Workshop on Contaminant Bioavailability in the Terrestrial  
Environment, Oct 2015, Nankin, China. insu-01334063

**HAL Id: insu-01334063**

**<https://insu.hal.science/insu-01334063v1>**

Submitted on 20 Jun 2016

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# COMBINATION OF SURFACTANT MICELLE AND ORGANOCLAY FOR THE ADSORPTION OF DICLOFENAC

RégisGuégan, Tiago De Oliviera, Mohammed Boussafir, Claude Le Milbeau, Fabrice Muller, Mikael Motelica-Heino

Institut des Sciences de la Terre d'Orléans, CNRS-The University of Orléans, Orléans, France

regis.guegan@univ-orleans.fr

## Introduction

Among pharmaceutical products (PPs) that are commonly found in aquatic environments, Diclofenac sodium (DCF) was identified as a recalcitrant compound to conventional wastewater treatments showing a low biodegradability. Indeed, the removal percentage of this non-steroidal pharmaceutical substance during wastewater treatment processes typically ranges from 21% to 40% [6], which explains its presence in surface water, groundwater and even in drinking water [1-3]. DCF is, together with the synthetic hormone 17 $\alpha$ -ethinylestradiol, one of the few pharmaceutical compounds that had proven to be ecotoxic, and it affects both aquatic and terrestrial ecosystems [4-5].

Adsorption is the most appropriate easy way to remove both inorganic and organic micropollutants. Clay minerals were for a long time known for their outstanding adsorption properties. However, although being used in drinking water treatment, these layered materials turn out to be ineffective for the sequestration of persistent nonpolar hydrophobic contaminants and/or negatively charged organic species such as DCF [6-8]. Surfactants used as chemical modifier for the preparation of organoclays or as micelle in solution generate an appropriate hydrophobic environment for the adsorption of emerging micropollutants. Indeed, the intercalation of cationic surfactants, through ion exchange with the inorganic cations, switches the chemical nature of the starting layered material from hydrophilic to hydrophobic. Moreover, the resulting organoclay composite layered materials show a wide opening of their interlayer space that significantly improve the adsorption of numerous organic compounds [8]. Nevertheless, the improvement of the sequestration mainly depends on both the chemical nature and the structural organization of the intercalated surfactants. Thus, surfactants showing a long alkyl chains such as hexadecyltrimethylammonium (HDTMA) create an appropriate organic environment within the inorganic frame for the adsorption of alkanes whereas modifiers such as benzyl decyltrimethylammonium (BDTA) show an excellent affinity with aromatic compounds [8]. The aim of this work is to study the adsorption of DCF onto different organoclays showing different arrangements and chemical nature under several temperature and pH environmental conditions and with the use as well of surfactant micelle organoclay complexes.

## Methods

A Na exchanged montmorillonite (Mt) was used as a starting layered material for the preparation of organoclays synthesized with BDTA and HDTMA cationic surfactants. The adsorption of the surfactants was performed at amount of 0.4, 1 and 4 times the cation exchange capacity (CEC), leading to the intercalation of a lateral monolayer, lateral bilayers and paraffin (or normal bilayer) surfactant arrangement within the interlayer space of BDTA-Mt and HDTMA-Mt organoclays. The environmental adsorption properties for DCF of the whole prepared absorbents (including the starting Na-Mt) as well as organoclay and cationic surfactant micelle complexes were characterized by a set of complementary techniques: X-ray diffraction (XRD), gas chromatography coupled with mass spectroscopy (GC/MS), Fourier transform infrared (FTIR) spectroscopy.

## Results and discussion

The equilibrium adsorption isotherms obtained by GC/MS and the derivative data determined through the fitting procedure by using Langmuir, Freundlich and Dubinin-Radushkevitch equation models explicitly highlight that the magnitude of the adsorption of DCF was correlated to the density of surfactant. The supplementary FTIR and XRD results support the proper adsorption and intercalation of DCF within the interlayer space of the organoclays. However, as expected for the starting raw clay mineral, no or traces of DCF adsorption was observed due to the antagonist charges of both DCF and Na-Mt. In contrast, organoclay composite layered materials show in one hand a sufficient hydrophobic environment and on another hand once surfactant is intercalated at high concentration (i.e. > 1 CEC), display an excess of positively charged surfactant sites that contribute to the adsorption of DCF. In other words, DCF could be adsorbed through two mechanisms: weak molecular interaction with the hydrocarbon chains of surfactants and due to strong electrostatic interaction with surfactants for organoclays prepared with surfactants at 4 times the CEC. Moreover, positively charged micelle surfactants form with DCF ionic complexes in solution that could be totally intercalated through molecular interaction into organoclays, which is confirmed by both XRD and FTIR results.

## Conclusion

Organoclay showed their particular adsorption properties for DCF. The adsorption was enhanced as the density of surfactant was increased within the interlayer space of the hybrid materials highlighting electrostatic interaction between DCF and surfactant. The combination of both organoclay and surfactant micelle in solution allowed a total adsorption of DCF and may represent a powerful way for the treatment of wastewater.

## References

- [1] L.H.M.L.M. Santos, A.N. Araújo, A. Fachini, A. Pena, C. Delerue-Matos, M.C.B.S.M. Montenegro, *J. Hazard. Mater.* 175 (2010) 45–95.
- [2] M. Stumpf, T.A. Ternes, R. Wilken, S.V. Rodrigues, W. Baumann, *Sci. Total Environ.* 225 (1999) 135–141.
- [3] M. Antunes, V. I. Esteves, R. Guégan, J. S. Crespo, A. N. Fernandes, M. Giovanela *Chem. Eng. J.* 192 (2012) 114–121.
- [4] J.L. Oaks, M. Gilbert, M.Z. Virani, R.T. Watson, C.U. Meteyer, B.A. Rideout, H.L. Shivaprasad, S. Ahmed, M.J.I. Chaudhry, M. Arshad, S. Mahmood, A. Ali, A.A. Khan, *Nature* 427 (2004) 630–633.
- [5] R. Triebkorn, H. Casper, A. Heyd, R. Eikemper, H.-R. Köhler, J. Schwaiger, *Aquat. Toxicol.* 68 (2004) 151–166.
- [6] T. Thiebault, R. Guégan, M. Boussafir, *J. Colloid Interface Sci.* 453 (2015) 1-8.
- [7] Y. Park, G.A. Ayoko, R.L. Frost, *J. Colloid Interface Sci.* 354 (2011) 292-305.
- [8] R. Guégan, M. Giovanela, M. Motelica-Heino, *J. Colloid Interface Sci.* 437 (2015) 71-79.