Comment on “The multi-mechanisms and interlayer configurations of metoprolol uptake on montmorillonite”

Thomas Thiebault

► To cite this version:

Thomas Thiebault. Comment on “The multi-mechanisms and interlayer configurations of metoprolol uptake on montmorillonite”. Chemical Engineering Journal, 2019, 371, pp.378-379. 10.1016/j.cej.2019.04.059 . insu-02094825

HAL Id: insu-02094825

<https://hal-insu.archives-ouvertes.fr/insu-02094825>

Submitted on 15 Apr 2019

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.

Comment on “The multi-mechanisms and interlayer configurations of metoprolol uptake on montmorillonite”

Thomas Thiebault*

EPHE, PSL Research University, UMR 7619 METIS Sorbonne University, F-75005, 4 place Jussieu, Paris, France

*To whom correspondence should be addressed. E-mail: thomas.thiebault@ephe.psl.eu Phone: +33 (0) 1 44 27 59 97

Abstract

In the work “the multi-mechanisms and interlayer configurations of metoprolol uptake on montmorillonite”, published in Chemical Engineering Journal, montmorillonite are used as an adsorbent for the uptake of metoprolol under various experimental conditions. The results are interesting but the authors has made a mistake when assessing the speciation of metoprolol. This β -blocker is mostly neutral rather than zwitterionic for pH values up to pK_{a1} . This mistake may induce confusion and false conclusions for the readers of Chemical Engineering Journal unfamiliar with such organic contaminants, especially when assessing the impact of pH on the adsorption mechanisms of metoprolol onto clay minerals.

Keywords: Comment; Speciation; Metoprolol; Adsorption; Ion-dipole interaction

In a recent work published in Chemical Engineering Journal, Li and co-authors [1] reported the adsorption of metoprolol onto montmorillonite under various experimental conditions. Even if the scientific quality of this paper cannot be disclaimed, the presented speciation diagram of metoprolol and several consequent discussions presented in this article appear to be inappropriate.

As described in the manuscript (Section 2, Fig.1b), metoprolol displays two pK_a , $pK_{a1} = 9.67$ and $pK_{a2} = 14.09$ respectively [1]. However, when the equilibrium solution pH is between pK_{a1} and pK_{a2} , metoprolol is neutral rather than zwitterionic, as confirmed by numerous studies in the literature [2–5]. The zwitterionic charge state is indeed not possible for metoprolol because $pK_{a,base} < pK_{a,acid}$ [6]. Hence, the speciation diagram should be presented as described in Figure 1.

Figure 1: Speciation of metoprolol under different pH values

The consequences of this mistake are obvious in the sections dealing with the impact of pH and temperature on the adsorption capacity of metoprolol onto montmorillonite.

The adsorption capacity of metoprolol as a function of pH value displays a strong decrease for pH values up to 8.0. Hence, for pH values close or above pK_{a1} value, the uptake of metoprolol is strongly diminished as it is well-explained in the manuscript. However, this uptake drop cannot be presented as a shift from pure cation exchange (i.e. protonated form) to a mix between electrostatic interaction and ion-dipole interaction (i.e. zwitterionic form), because above pK_{a1} , metoprolol is mostly neutral. As a result, the decrease in the adsorption capacity should be understood through the shift from a protonated to a neutral form as the pH increase. Generally, the adsorption mechanisms of neutral organic compounds onto clay minerals are considered to be weak electrostatic interactions which not lead to high adsorption capacities or favorable adsorption behaviors [7,8]. As raised in the manuscript, at pH = 11, 7% of metoprolol is cationic whereas 93% is neutral. This indicates that even if the whole cationic species are sorbed, a significant part of neutral metoprolol is also adsorbed probably through weak electrostatic interactions.

This potential adsorption mechanisms of neutral metoprolol are also visible on the Fig.6 (Section 3.5.) of the manuscript, in which the impact of temperature on the uptake of metoprolol at different pH is presented. The uptake variation at pH 10 (i.e. cationic/neutral form) and pH 7 and 3 (i.e. cationic form) displays distinct patterns. Hence, at pH 3 and 7 the uptake increases as the temperature decreases and

the opposite pattern is observed at pH 10. Even if the impact of temperature on the cation exchange extent is still discussed [9,10], it is very surprising that the uptake of neutral metoprolol (i.e. pH = 10) is improved at higher temperatures, because such weak electrostatic interactions are generally considered to be more significant at lower temperatures [11]. However, the discussion of the adsorption mechanisms as a function of the temperature is not performed in the paper, except the modification of thermodynamic parameters. The shift from positive to negative enthalpy values at pH 10 and the two other values (i.e. 3 and 7) respectively, could be assume as an indicator of such modifications.

As a reminder, this comment was motivated by the willingness to confine the propagation of incorrect information in the literature rather than criticize estimated colleagues. The correction could therefore be published by the authors.

References:

- [1] Z. Li, P.-H. Chang, W.-T. Jiang, J.-S. Jean, The multi-mechanisms and interlayer configurations of metoprolol uptake on montmorillonite, *Chemical Engineering Journal*. 360 (2019) 325–333. doi:10.1016/j.cej.2018.11.230.
- [2] A. Niedbala, M. Schaffer, T. Licha, K. Nödler, H. Börnick, H. Ruppert, E. Worch, Influence of competing inorganic cations on the ion exchange equilibrium of the monovalent organic cation metoprolol on natural sediment, *Chemosphere*. 90 (2013) 1945–1951. doi:10.1016/j.chemosphere.2012.10.036.
- [3] G. Caron, G. Steyaert, A. Pagliara, F. Reymond, P. Crivori, P. Gaillard, P.-A. Carrupt, A. Avdeef, J. Comer, K.J. Box, H.H. Girault, B. Testa, Structure-Lipophilicity Relationships of Neutral and Protonated β -Blockers, Part I, Intra- and Intermolecular Effects in Isotropic Solvent Systems, *Helvetica Chimica Acta*. 82 (1999) 1211–1222. doi:10.1002/(SICI)1522-2675(19990804)82:8<1211::AID-HLCA1211>3.0.CO;2-K.
- [4] T.C.G. Kibbey, R. Paruchuri, D.A. Sabatini, L. Chen, Adsorption of Beta Blockers to Environmental Surfaces, *Environ. Sci. Technol.* 41 (2007) 5349–5356. doi:10.1021/es070152v.
- [5] M.A. Amirdehi, M. Pousti, F. Asayesh, F. Gharib, J. Greener, Solvent Effects on Acid–Base Equilibria of Propranolol and Atenolol in Aqueous Solutions of Methanol: UV-Spectrophotometric Titration and Theory, *J Solution Chem.* 46 (2017) 720–733. doi:10.1007/s10953-017-0595-x.
- [6] M. Schaffer, T. Licha, A guideline for the identification of environmentally relevant, ionizable organic molecule species, *Chemosphere*. 103 (2014) 12–25. doi:10.1016/j.chemosphere.2013.12.009.
- [7] T. Thiebault, M. Boussafir, R. Guégan, C. Le Milbeau, L. Le Forestier, Clayey–sand filter for the removal of pharmaceuticals from wastewater effluent: percolation experiments, *Environ. Sci.: Water Res. Technol.* 2 (2016) 529–538. doi:10.1039/C6EW00034G.
- [8] W. Zhang, Y. Ding, S.A. Boyd, B.J. Teppen, H. Li, Sorption and desorption of carbamazepine from water by smectite clays, *Chemosphere*. 81 (2010) 954–960. doi:10.1016/j.chemosphere.2010.07.053.
- [9] Y. Chen, A. Zhou, B. Liu, J. Liang, Tramadol hydrochloride/montmorillonite composite: Preparation and controlled drug release, *Applied Clay Science*. 49 (2010) 108–112. doi:10.1016/j.clay.2010.04.011.

- [10] T. Thiebault, R. Guégan, M. Boussafir, Adsorption mechanisms of emerging micro-pollutants with a clay mineral: Case of tramadol and doxepine pharmaceutical products, *Journal of Colloid and Interface Science*. 453 (2015) 1–8. doi:10.1016/j.jcis.2015.04.029.
- [11] T.M. Berhane, J. Levy, M.P.S. Krekeler, N.D. Danielson, A. Stalcup, Sorption–desorption of carbamazepine by palygorskite–montmorillonite (PM) filter medium, *Journal of Hazardous Materials*. 282 (2015) 183–193. doi:10.1016/j.jhazmat.2014.09.025.