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

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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 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 pKa, 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.

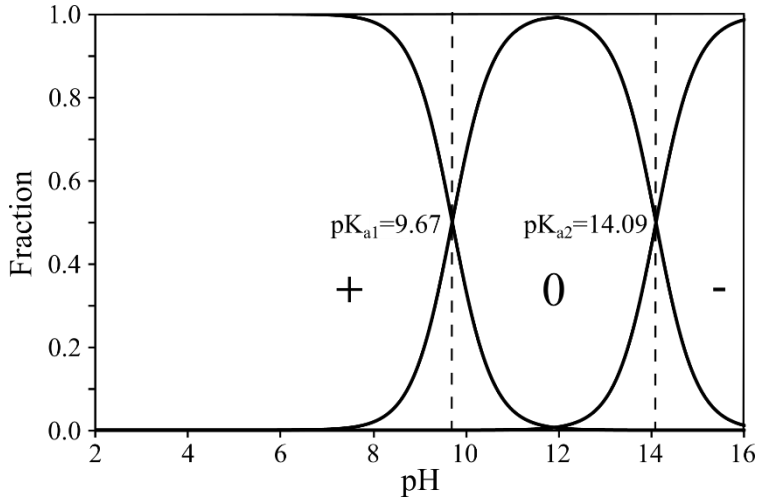

Figure 1: Speciation of metoprolol under different pH values

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.

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