

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/44599271>

Comment on "Adsorption and Desorption of Oxytetracycline and Carbamazepine by Multiwalled Carbon Nanotubes"

ARTICLE in ENVIRONMENTAL SCIENCE AND TECHNOLOGY · JUNE 2010

Impact Factor: 5.33 · DOI: 10.1021/es100684f · Source: PubMed

CITATIONS

5

READS

25

2 AUTHORS:



Tung Xuan Bui

Nippon Koei Vietnam International Co., Ltd.

6 PUBLICATIONS 191 CITATIONS

SEE PROFILE



Heechul Choi

Gwangju Institute of Science and Technology

156 PUBLICATIONS 4,352 CITATIONS

SEE PROFILE

Comment on "Adsorption and Desorption of Oxytetracycline and Carbamazepine by Multiwalled Carbon Nanotubes"

Recently, Oleszczuk et al. (1) has reported the adsorption–desorption of two pharmaceuticals including oxytetracycline (OTC) and carbamazepine (CBZ) on multiwalled carbon nanotubes (MWCNT). We would like to comment on several issues, as discussed below.

First, the author mistyped the properties of two pharmaceuticals: OTC ($\log K_{ow} = 2.45$, $pK_a = 7$) and CBZ ($\log K_{ow} = -1.22$, $pK_a = 3.27, 7.32, 9.11$), which should be OTC ($\log K_{ow} = -1.22$, $pK_a = 3.27, 7.32, 9.11$) (2, 3) and CBZ ($\log K_{ow} = 2.45$, $pK_a = 7$). As such, the pK_a value of CBZ is still questionable. CBZ can be characterized with two pK_a values which can be named as pK_{a1} for the equilibrium $RCONH_3^+ \rightleftharpoons RCONH_2 + H^+$ (1) and pK_{a2} for the equilibrium $RCONH_2 \rightleftharpoons RCONH^- + H^+$ (2). pK_{a1} value of CBZ was reported as 1 (4) or 2.3 (5), whereas pK_{a2} was 13.9 (6, 7). We further confirmed the values by calculation using SPARC v4.5 (8) and ACDLab v12.0. pK_{a1} and pK_{a2} were determined as -1.30 and 15.37 using SPARC and -0.49 ± 0.2 and 13.9 ± 0.2 using ACDLab, respectively. Therefore, it was reasonable to ascribe CBZ having $pK_{a1} < 2.3$ and $pK_{a2} \geq 13.9$.

Second, the author used a pK_a of 7 for CBZ, so they deduced that CBZ is in cationic form at $pH < 7$ and suggested an electrostatic interaction occurring between CBZ and MWCNT at this pH. Actually, CBZ with $pK_{a1} < 2.3$ and $pK_{a2} \geq 13.9$ exists entirely as neutral charged in the pH range of $1.9–11.9$, as calculated by ACDLab. Hence, an electrostatic interaction between CBZ and MWCNT is not possible in the case. The higher desorption of CBZ at pH 8 in the study (1) might be only resulted from the change of MWCNT properties.

Third, we agree with the authors that the interaction between OTC and MWCNT can be responsible by $\pi-\pi$ electron-donor–acceptor interaction. Accordingly, $\pi-\pi$ interactions also can be formed between benzene rings of CBZ and the surface of MWCNT (9). To explain a higher sorption of OTC on MWCNT than CBZ, therefore, cation- π bonding between the protonated amino group of OTC and the graphene π electrons of MWCNT should be taken into account (10). However, $\pi-\pi$ interaction and cation- π bonding would be suppressed as pH increase (10), which seems to oppose with the fact that the desorption of OTC is lower at higher pHs (1). Probably another mechanism takes responsible for these phenomena. Actually, the authors neglected the role of Ca^{2+} in the solution. Ca^{2+} may form complex with OTC in the solution (11). Besides, it can act as a cation bridge between negatively charged OTC and negative charges of clay surface (3, 12) in the adsorption of OTC to clays. Hence, we suggest that a part of the adsorption of OTC on MWCNT may occur with the participant of Ca^{2+} . Ca^{2+} may simultaneously bind with negatively charged OTC and make an interaction either with negative charges of MWCNT (13) or with the graphene π electrons of MWCNT via a cation- π bonding (10). As pH is increased, both MWCNT and OTC become more negatively charged, which probably interacts more strongly with Ca^{2+} , and consequently, leading a lower desorption of OTC. This hypothesis could be further verified by studying the desorption of OTC in the presence of NaCl, instead of $CaCl_2$.

Fourth, there are several other mistakes in the article as well. Although the authors mentioned that the characterization of the adsorbents were presented in ref 7 therein, the ref (13) described only the characteristics of two adsorbents (MWCNT10 and MWCNT 100). As a result, the characterization of MWCNT20, MWCNT40, and MWCNT60 was missed. Besides, refs 8 and 9 in the article are identical. Moreover, the meaning of the sentence "Thus, interaction between OH groups of OTC & MWCNT can be explained by $\pi-\pi$ electron-donor-acceptor interaction between the electron-depleted surfaces of carbon nanotubes and π -electron-rich aromatic rings of OTC" is not clear. In the paragraph between the page of 9169 and 9170: "OTC has many more functional groups... and π -electron-rich aromatic rings of OTC (9)", ref 9 should be replaced by ref 10, which is more appropriate to the content cited.

Literature Cited

- Oleszczuk, P.; Pan, B.; Xing, B. Adsorption and desorption of oxytetracycline and carbamazepine by multiwalled carbon nanotubes. *Environ. Sci. Technol.* **2009**, *43* (24), 9167–9173.
- Kulshrestha, P.; Giese, R. F.; Aga, D. S. Investigating the molecular interactions of oxytetracycline in clay and organic matter: Insights on factors affecting its mobility in soil. *Environ. Sci. Technol.* **2004**, *38* (15), 4097–4105.
- Figuerroa, R. A.; Leonard, A.; MacKay, A. A. Modeling tetracycline antibiotic sorption to clays. *Environ. Sci. Technol.* **2004**, *38* (2), 476–483.
- Stein, K.; Ramil, M.; Fink, G.; Sander, M.; Ternes, T. A. Analysis and sorption of psychoactive drugs onto sediment. *Environ. Sci. Technol.* **2008**, *42* (17), 6415–6423.
- Nghiem, L. D.; Schafer, A. I.; Elimelech, M. Pharmaceutical retention mechanisms by nanofiltration membranes. *Environ. Sci. Technol.* **2005**, *39* (19), 7698–7705.
- Trenholm, R. A.; Vanderford, B. J.; Holady, J. C.; Rexing, D. J.; Snyder, S. A. Broad range analysis of endocrine disruptors and pharmaceuticals using gas chromatography and liquid chromatography tandem mass spectrometry. *Chemosphere* **2006**, *65* (11), 1990–1998.
- Jones, O. A.; Voulvoulis, N.; Lester, J. N. Aquatic environmental assessment of the top 25 English prescription pharmaceuticals. *Water Res.* **2002**, *36* (20), 5013–22.
- SPARC v4.5 website. <http://ibmlc2.chem.uga.edu./sparc/> (accessed March 3, 2010).
- Chen, W.; Duan, L.; Zhu, D. Adsorption of polar and nonpolar organic chemicals to carbon nanotubes. *Environ. Sci. Technol.* **2007**, *41* (24), 8295–8300.
- Ji, L.; Chen, W.; Duan, L.; Zhu, D. Mechanisms for strong adsorption of tetracycline to carbon nanotubes: A comparative study using activated carbon and graphite as adsorbents. *Environ. Sci. Technol.* **2009**, *43* (7), 2322–2327.
- Lunestad, B. T.; Goksoyr, J. Reduction in the antibacterial effect of oxytetracycline in sea water by complex formation with magnesium and calcium. *Dis. Aquat. Org.* **1990**, *9*, 67–72.
- Pils, J. R. V.; Laird, D. A. Sorption of tetracycline and chlortetracycline on K- and Ca-saturated soil clays, humic substances, and clay-humic complexes. *Environ. Sci. Technol.* **2007**, *41* (6), 1928–1933.
- Lin, D.; Xing, B. Adsorption of phenolic compounds by carbon nanotubes: role of aromaticity and substitution of hydroxyl groups. *Environ. Sci. Technol.* **2008**, *42* (19), 7254–7259.

Tung Xuan Bui and Heechul Choi

Department of Environmental Science and Engineering,
Gwangju Institute of Science and Technology (GIST),
261 Cheomdan-gwagiro, Buk-gu, Gwangju 500-712,
Republic of Korea

ES100684F