



Letter to the Editor

Reply to the comments on “Facilely synthesized cobalt doped hydroxyapatite as hydroxyl promoted peroxymonosulfate activator for degradation of Rhodamine B” by Zuo et al.


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ABSTRACT

In a Co-HAP/PMS system, catalytic degradation process of RhB was accompanied by the gradual leaching of cobalt ion. The results of additional experiments showed that leached cobalt ion indeed contributed to active PMS for RhB degradation, which was not addressed in the previous study. The finding of the contribution from leached cobalt ion to PMS activation was reported due to the valuable comments of Zuo et al., what will be concerned in the future work. Importantly, Co-HAP still showed a significant contribution to PMS activation for RhB degradation at the initial stage. Fortunately, the release of Co^{2+} from Co-HAP was slow, the secondary pollution could not be addressed due to the slightly release of Co^{2+} ion that the Co^{2+} concentration is lower than the standard of the discharge wastewater. Furthermore, the mechanism of non-radical reaction in the Co-HAP/PMS system was reported to confirm the heterogeneous catalysis of a Co-HAP/PMS system.

We have received the comments from Zuo et al., and we are very grateful for the constructive comments on our original paper [1]. Indeed, a low concentration of leached Co can favor the RhB degradation as being described in the previous comments. For most cobalt-based PMS catalysts, cobalt leaching is inevitably observed during the PMS activation, but only a few studies considered the contribution of the dissolved cobalt ion to the degradation of organic compounds [2,3]. Also, it was unfortunately ignored in our previous study. In order to clearly report the contribution of Co^{2+} /PMS to RhB degradation in the Co-HAP/PMS system, additional experiments were further carried out to investigate the Co^{2+} leaching behavior in the Co-HAP/PMS system. Also, the contribution of leached Co^{2+} to PMS activity was reported to address the effect of leached Co^{2+} on the PMS activation for RhB degradation. The details of these experiments are described as follows:

Co-HAP-2 sample was synthesized using the method described in our previous work [1], in which the cobalt was exchanged into HAP by mixing with the cobalt (II) nitrate solutions in 25 mmol/L. The doses of Co-HAP-2 and PMS were 0.2 g/L and 0.4 mmol/L, respectively, in the work. The concentrations of RhB and cobalt ion were determined by a UV-vis spectro-photometer (UV-5500PC, Shanghai Metash Instruments) and an ICP-OES (ICP-OES-720, Agilent), respectively.

In our previous cyclic experiments, for the purpose of better collection of Co-HAP, the initial dosage of Co-HAP was set at 0.3 g/L which is higher than the typical dosage (0.2 g/L) in our previous study [1]. As can be seen in Table 1, at the first 4 min, the leached Co^{2+} was 0.30 mg/L, and the leached Co^{2+} increased to 0.55 mg/L at 12 min when the dosage of the Co-HAP-2 was 0.2 g/L, suggesting that Co^{2+} was released from Co-HAP gradually. Of note, the leached concentration of Co^{2+} remained below the standard of the China discharged wastewater (1 mg/L, GB 25467-2010). As shown in Fig. 1, the degradation efficiency of RhB reached 41.0 % within 4 min when the Co^{2+} was 0.3 mg/L, which is equal to the leached Co ion concentration at the 4th min when the dosage of Co-HAP-2/PMS was 0.2 g/L. Interestingly, 61.2 % of RhB

could be removed in the Co-HAP-2/PMS system within the 2 min, what is significantly higher than the activity of that in the presence of leached Co^{2+} . These results suggested that Co-HAP-2 showed a significant improvement on RhB degradation at the beginning of the reaction. As the reaction proceeded, the enhancement of RhB degradation by Co-HAP-2 decreased gradually.

As described in section 3.1 of our paper, Co-HAP-2 contained 2.0 wt % cobalt species. Hence, the total cobalt in the Co-HAP/PMS system was 6 mg/L when the dosage of Co-HAP-2 was 0.3 g/L. At the first run, 0.71 mg/L Co^{2+} was leached. After 4 runs, the total cobalt decreased to about 4.0 mg/L (from the theoretical calculation based on the data of our previous work [1]). About 2 mg/L of Co ion was leached in the four recycles. The leached Co^{2+} might lead to the reduction in the activity of Co-HAP on PMS activation, but the Co-HAP-2 remained a favorable contribution to PMS activation.

According to the previously reported paper, radical-driven degradation reactions, rather than non-radical reactions, were the main reaction route in a Co(II)/PMS system [4,5]. However, in our previous work, singlet oxygen was the dominant ROS generated in the Co-HAP-2/PMS system, suggesting that non-radical reaction was dominant during the RhB degradation. These results indicated that it is inappropriate to entirely ascribe the efficient RhB degradation to the Co^{2+} /PMS system.

Indeed, the homogeneous reaction made a contribution to the RhB degradation in the Co-HAP-2/PMS system, especially at the second half of RhB degradation. At first 2 min, Co-HAP-2 still showed a significantly enhanced effect on RhB degradation, suggesting that the heterogeneous catalytic performance of Co-HAP-2 was highly effective at the beginning of RhB degradation. Moreover, in our paper, the main conclusion points out that singlet oxygen played a leading role in the RhB degradation. This conclusion is still valid and also provides indirect evidence in the heterogeneous Co-HAP/PMS system.

To sum up, Co-HAP should be regarded as a slow-releasing Co-based

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Table 1

The concentration of leached cobalt ion in a dosage of 0.2 g/L of Co-HAP at different reaction time.

Reaction time (min)	Leached Co ²⁺ (mg/L)
4	0.30
8	0.50
12	0.55

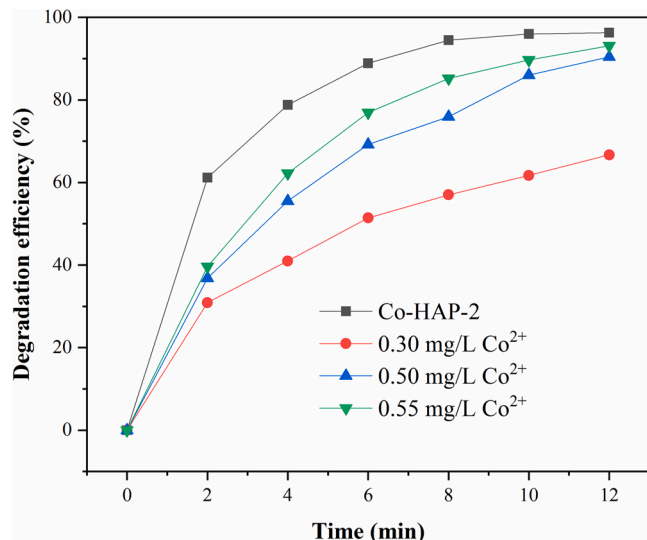


Fig. 1. Effect of Co-HAP-2 and leached Co²⁺ on RhB degradation during the PMS activation, Conditions: Co-HAP-2 = 0.2 g/L, [RhB] = 40 mg/L, initial pH = 5.5, [PMS] = 0.4 mmol/L.

PMS activator instead of an entire heterogeneous catalyst. Both leached Co and Co-HAP contributed to the PMS activation for RhB degradation. However, at the study conditions, the leached cobalt²⁺ was below the emission standard (1 mg/L, GB 25467-2010). Also, the Co-HAP could be reused four times at least. Hence, in our further work, we will explore other synthesized methods (such as solvothermal and hydrothermal method) to better stabilize the cobalt species on Co-HAP composite. Also, the contribution of the leached Co²⁺ to the PMS activation should be concerned in the future. Thanks for your constructive comments again.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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