Supporting Information for

The removal of Cd(II) by the UV/permanganate process: Role of continuous *in situ* formed MnO_2 and reactive species

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Submitted to:

Environmental Science: Water Research & Technology

Number of pages (including this page): 17

Number of Text: 1

Number of Figures: 14

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Text S1. Calculation method of concentration of $KMnO_4$ and in situ formed MnO_2.

$KMnO_4$ concentration can be determined by UV/vis spectrophotometery (TU-1900, Persee Co., China) at 418 and 525 nm simultaneously by Equation S4 derived from Equations S1 - S3, while MnO_2 was determined at 418 nm. Note that permanganate shows negligible absorbance at 418 nm.

$$A_t^{525} = [\text{Mn(VII)}]_t \varepsilon_{KMnO_4}^{525} + [MnO_2]_t \varepsilon_{MnO_2}^{525} \quad \text{(S1)}$$

$$[\text{Mn(VII)}]_t = (A_t^{525} - \varepsilon_{MnO_2}^{525}[MnO_2]_t)/\varepsilon_{KMnO_4}^{525} \quad \text{(S2)}$$

$$[\text{Mn(VII)}]_t = (A_t^{525} - \varepsilon_{MnO_2}^{525} A_t^{418}/\varepsilon_{MnO_2}^{418})/(A_0^{525}/[\text{Mn(VII)}]_0) \quad \text{(S3)}$$

$$[\text{Mn(VII)}]_t = (A_t^{525} - A_f^{525} A_t^{418}/A_f^{418})/(A_0^{525}/[\text{Mn(VII)}]_0) \quad \text{(S4)}$$

where A means the absorbance, the superscript means wavelength, and the sub-scripts 0, f, and t represent initial, final, and variable time. In this study, the $KMnO_4$ was irradiated by ultra-violet for 3 hours to completely transform to MnO_2 colloids and then immediately measure the final absorbance.

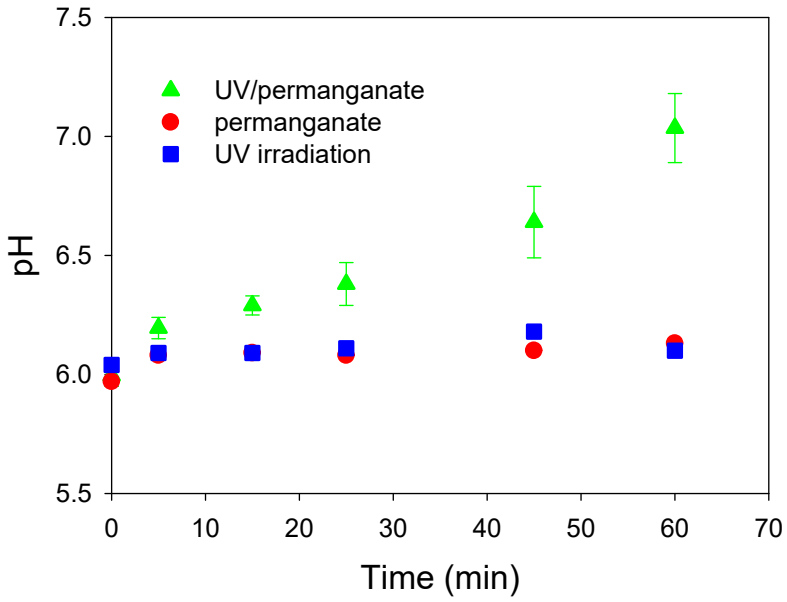

Figure S1. pH variation during Cd(II) removal by the UV/permanganate process at pH_0 6.0. Conditions: $[KMnO_4]_0$ = 100 μM, $[Cd(II)]_0$ = 20 μM.

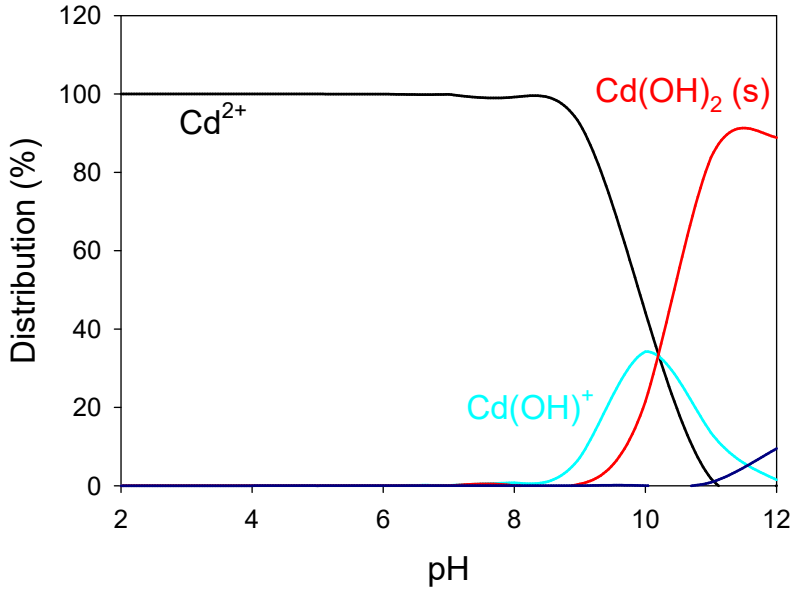

Figure S2. Distribution of Cd(II) species with pH variation.

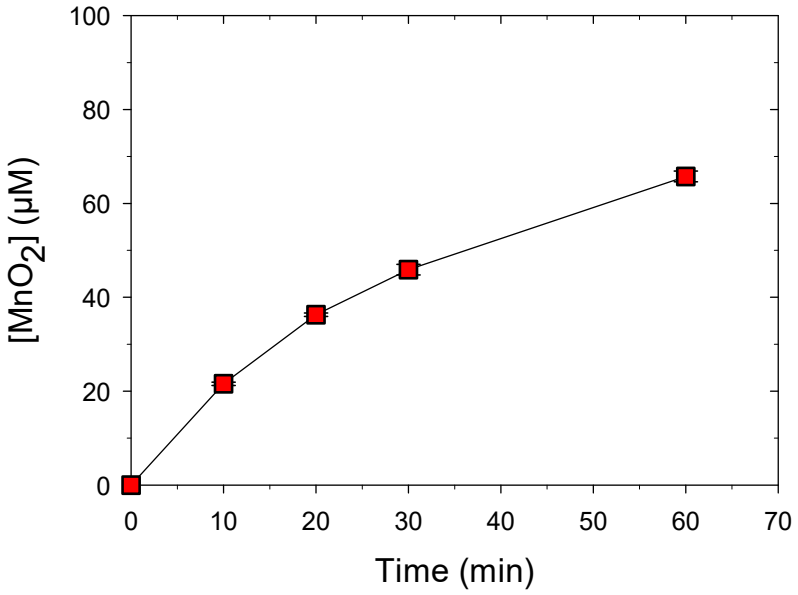

Figure S3. Time-dependent formation of MnO_2 during the Cd(II) removal by the UV/permanganate process at pH_0 6.0. Conditions: $[KMnO_4]_0$ = 100 μM, $[Cd(II)]_0$ = 20 μM.

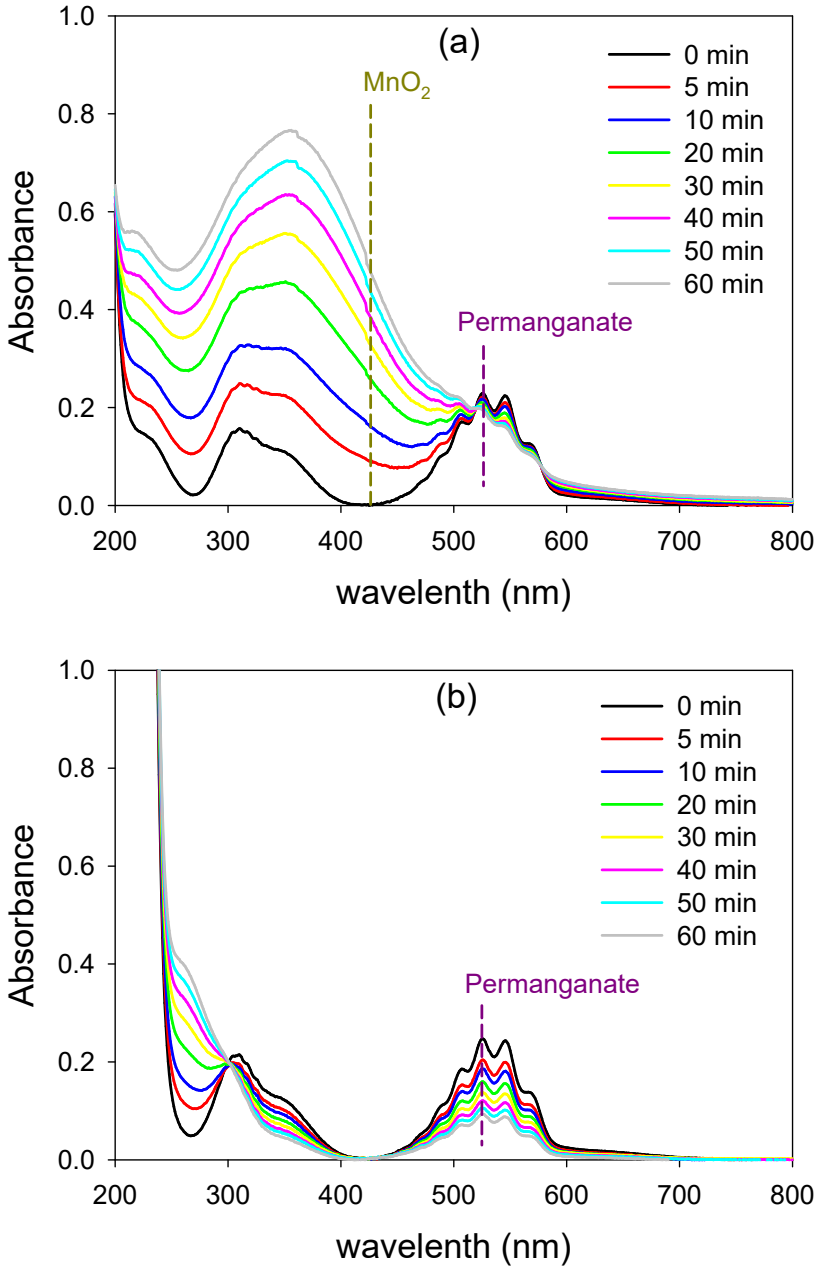

Figure S4. Time-dependent UV-vis spectra at the wavelengths of 200 - 800 nm in the UV/permanganate process with a permanganate dosage of 100 μM (a) in the absence of PP and (b) in the presence of 5 mM PP.

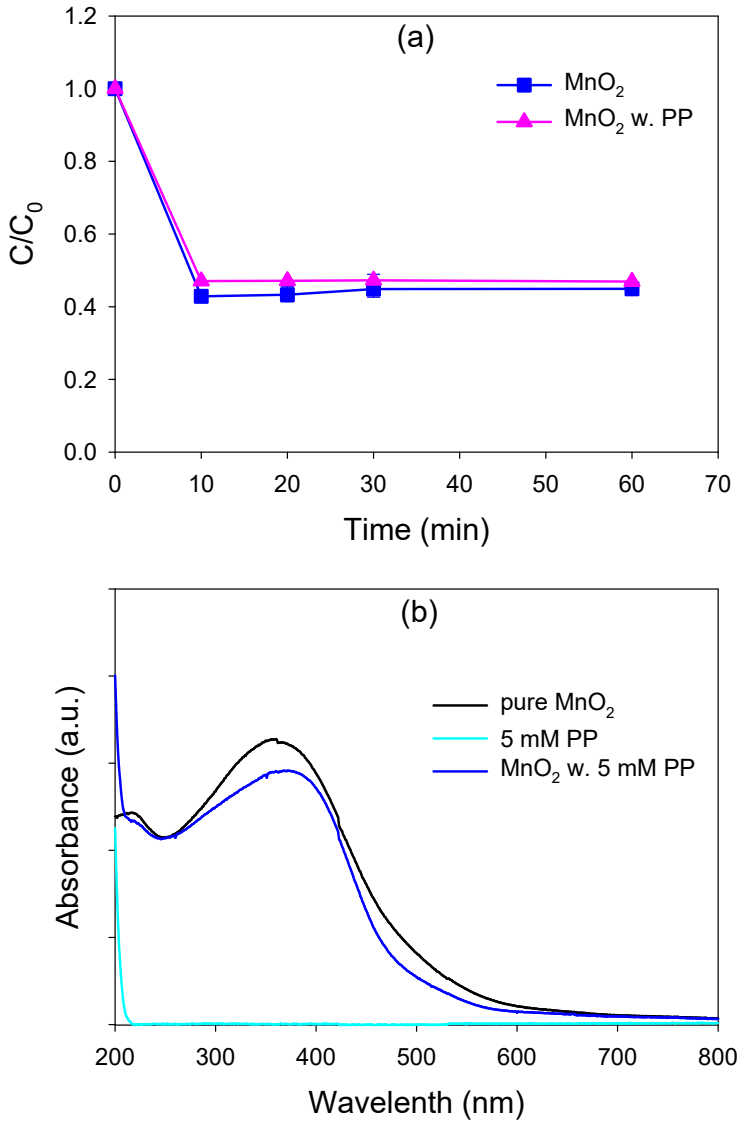

Figure S5. (a) The effects of PP on Cd(II) removal by prepared MnO_2. Conditions: pH = 6.0, $[MnO_2]_0$ = 65 μM, $[Cd(II)]_0$ = 20 μM, [PP] = 5 mM. (b) UV-vis spectra at the wavelengths of 200 - 800 nm of MnO_2 in the absence/presence of 5 mM PP. Conditions: pH = 6.0, $[MnO_2]_0$ = 65 μM, $[Cd(II)]_0$ = 20 μM, [PP] = 5 mM.

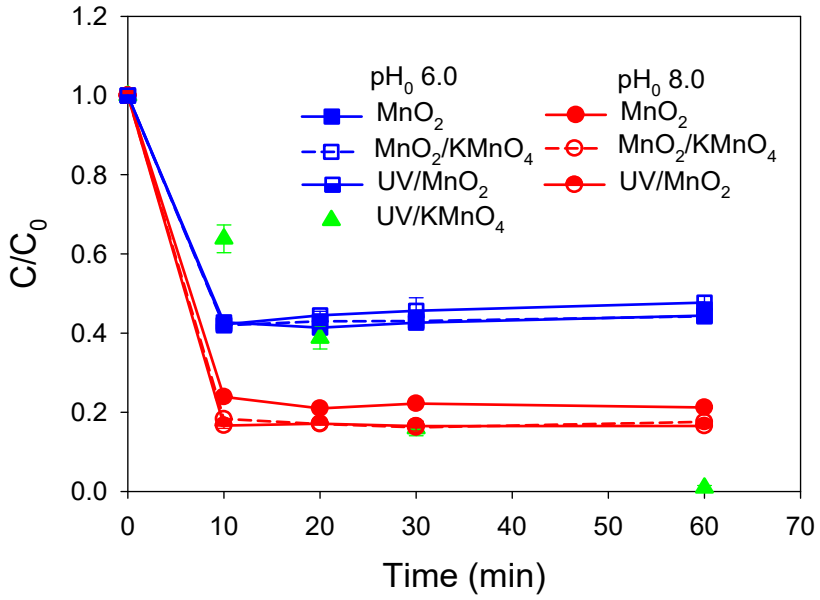

Figure S6. The kinetics of Cd(II) removal by the MnO_2/permanganate and UV/MnO_2 process. Conditions: pH_0 = 6.0 and 8.0, $[MnO_2]_0 = [KMnO_4]_0$ = 65 μM, $[Cd(II)]_0$ = 20 μM.

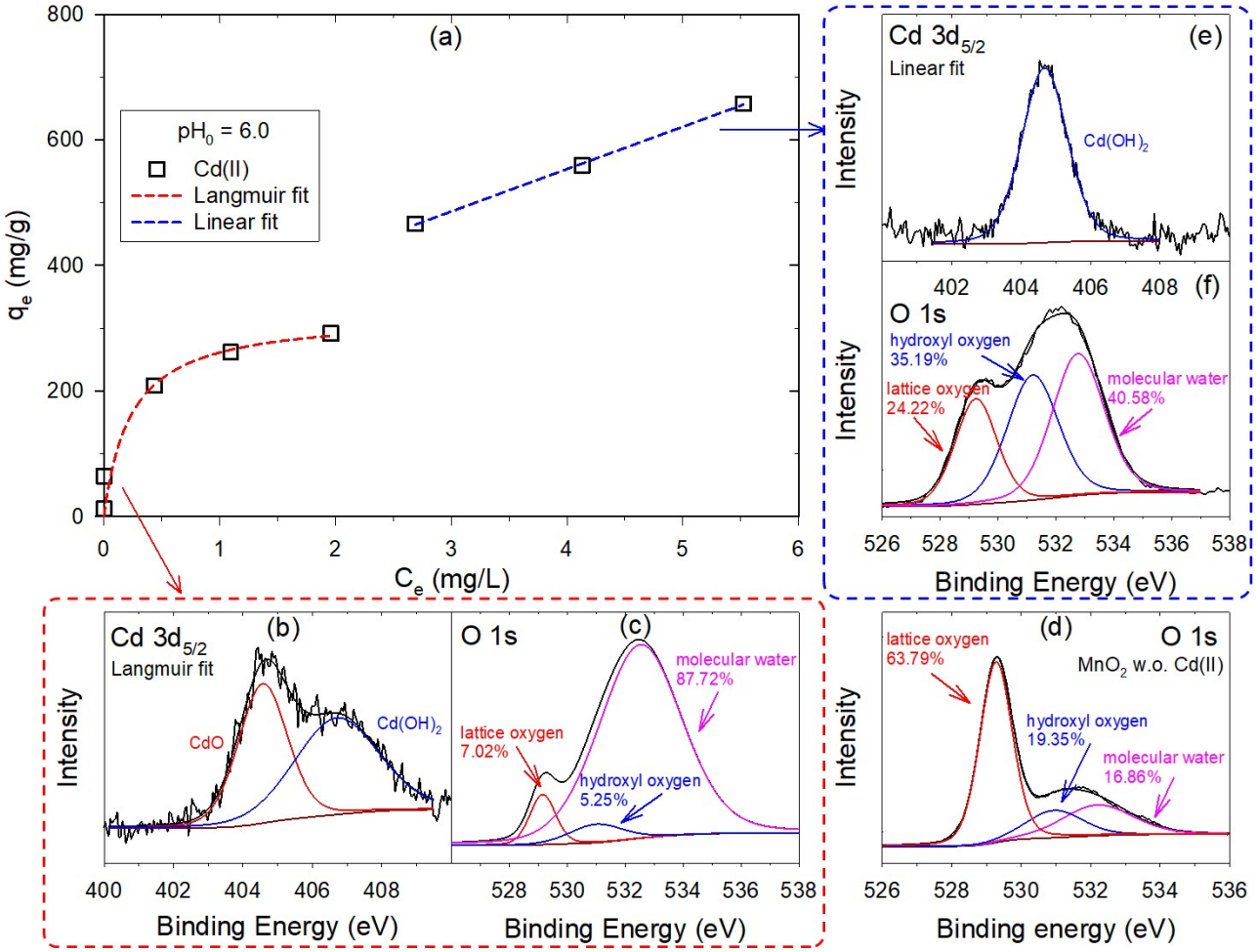

Figure S7. (a) Adsorption isotherm of Cd(II) onto MnO_2. Conditions: pH_0 = 6.0, $[MnO_2]_0$ = 100 μM, $[Cd(II)]_0$ = 1 - 100 μM. XPS spectra of (b) Cd $3d_{5/2}$, (c) O 1s of MnO_2 adsorbed Cd(II) matching Langmuir fit curves. Conditions: pH_0 = 6.0, $[MnO_2]_0$ = 100 μM, $[Cd(II)]_0$ = 2 μM. (d) O 1s spectra of MnO_2 generated in UV/permanganate process without Cd(II). Conditions: pH_0 = 6.0, $[MnO_2]_0$ = 100 μM. XPS spectra of (e) Cd $3d_{5/2}$, (f) O 1s of MnO_2 adsorbed Cd(II) matching linear fit curves. Conditions: pH_0 = 6.0, $[MnO_2]_0$ = 100 μM, $[Cd(II)]_0$ = 100 μM.

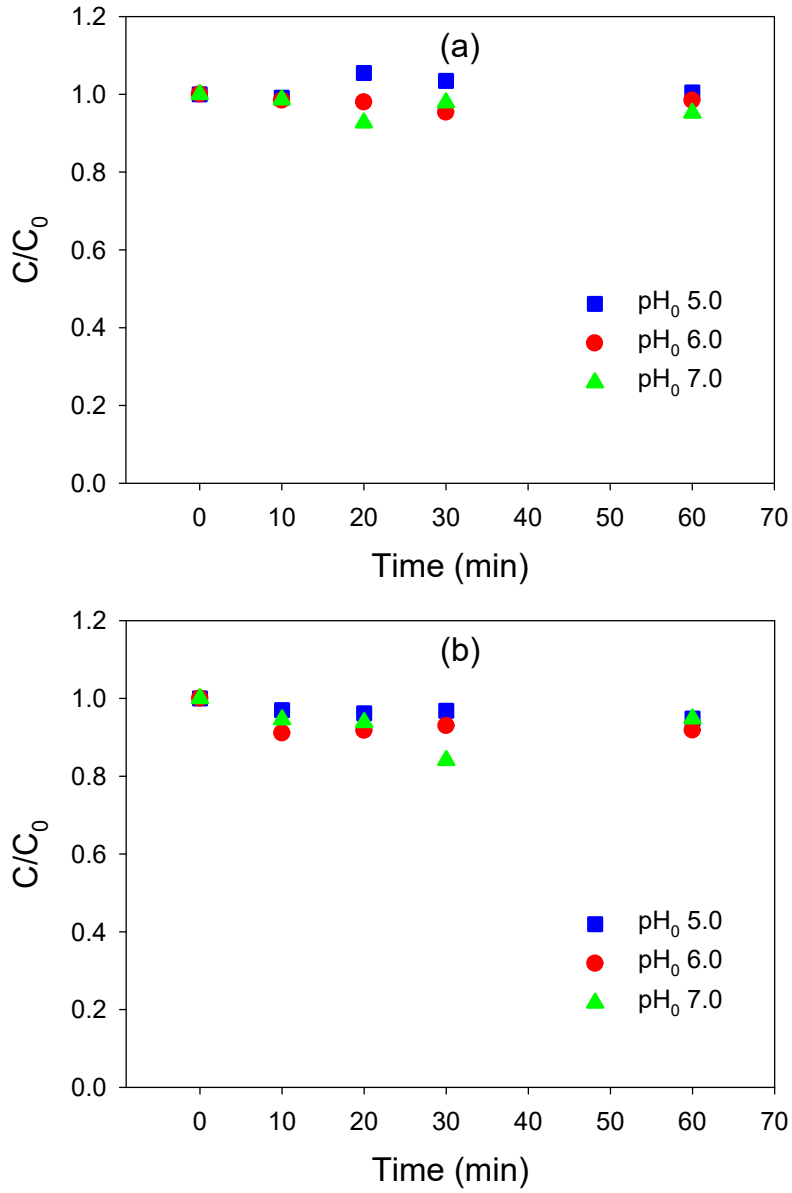

Figure S8. Removal rate of Cd(II) by the (a) UV irradiation and (b) permanganate at pH_0 5.0 - 7.0. Conditions: $[KMnO_4]_0$ = 100 μM, $[Cd(II)]_0$ = 20 μM.

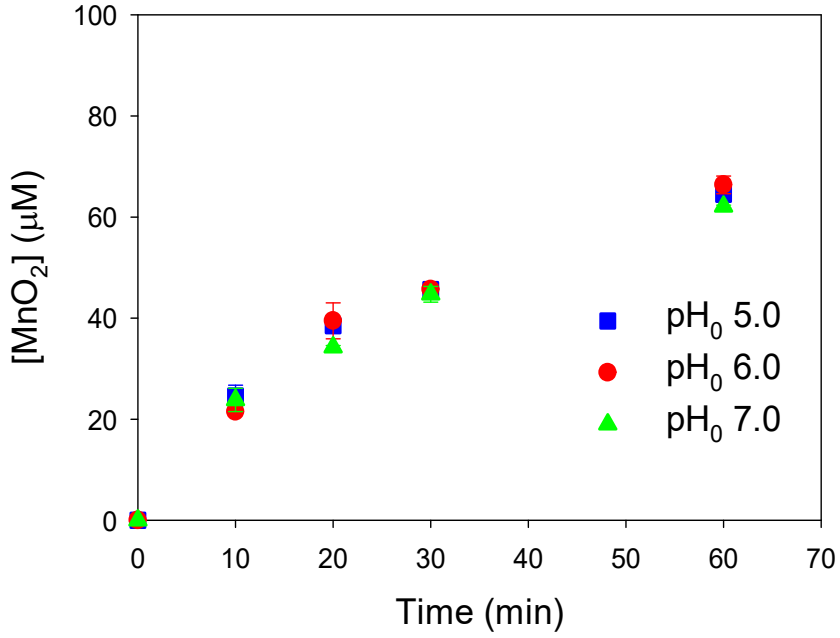

Figure S9. Effect of pH_0 on MnO_2 generation in the UV/permanganate process during Cd(II) removal.

Conditions: pH_0 = 5.0 - 7.0, $[KMnO_4]_0$ = 100 μM, $[Cd(II)]_0$ = 20 μM.

Figure S10. pH variation during Cd(II) removal by the (a) UV/permanganate process, (b) UV irradiation and (c) permanganate at pH_0 5.0 - 7.0. Conditions: $[KMnO_4]_0$ = 100 μM, $[Cd(II)]_0$ = 20 μM.

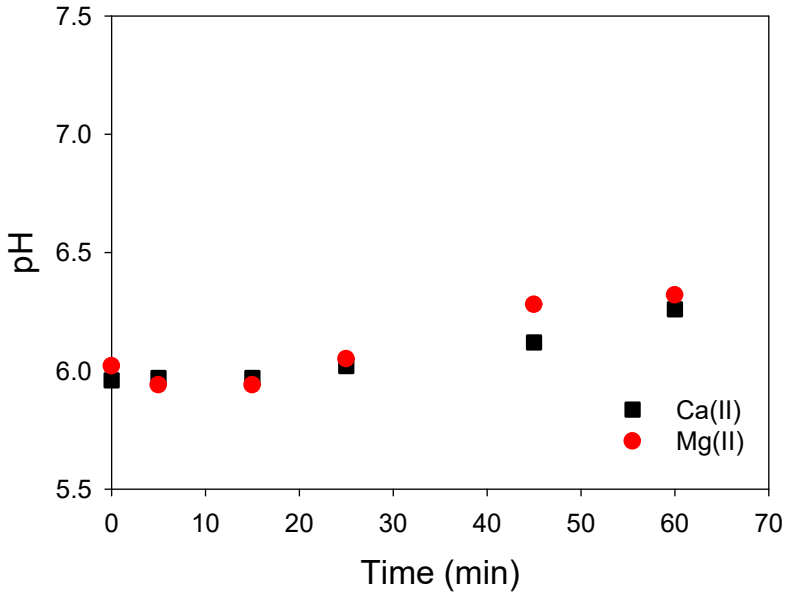

Figure S11. pH variation during Cd(II) removal by the UV/permanganate process in the presence of cations. Conditions: $[KMnO_4]_0$ = 100 μM, $[Cd(II)]_0$ = 20 μM, $[Ca(II)]_0$ = $[Mg(II)]_0$ = 1 mM, pH_0 = 6.0.

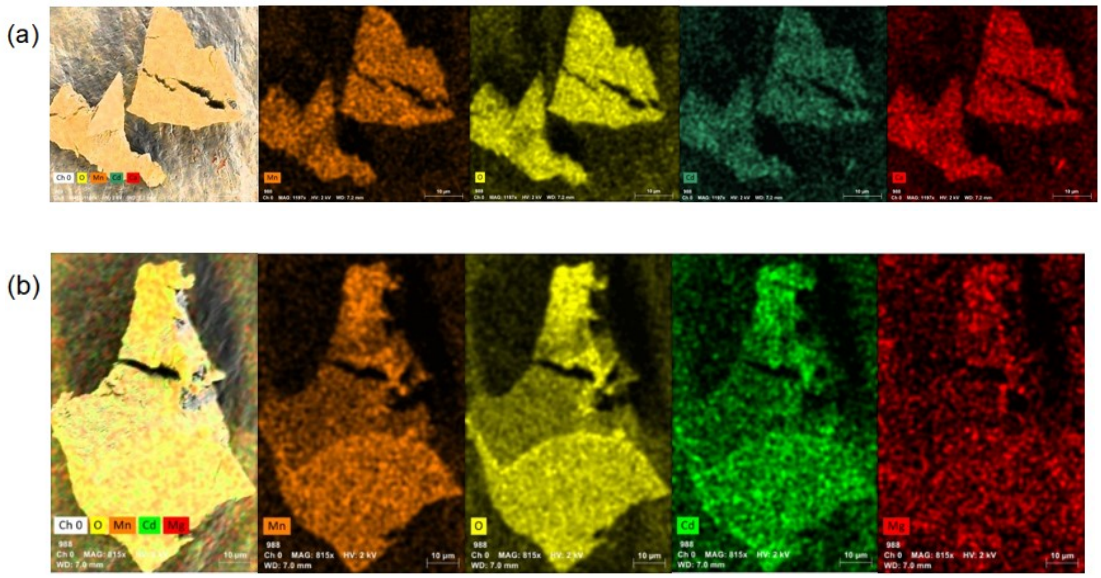

Figure S12. SEM-EDS of MnO_2 generated from UV/permanganate process during Cd(II) removal in the presence of (a) Ca(II) and (b) Mg(II). Conditions: $[KMnO_4]_0$ = 100 μM, $[Cd(II)]_0$ = 20 μM, $[Ca(II)]_0 = [Mg(II)]_0$ = 1 mM.

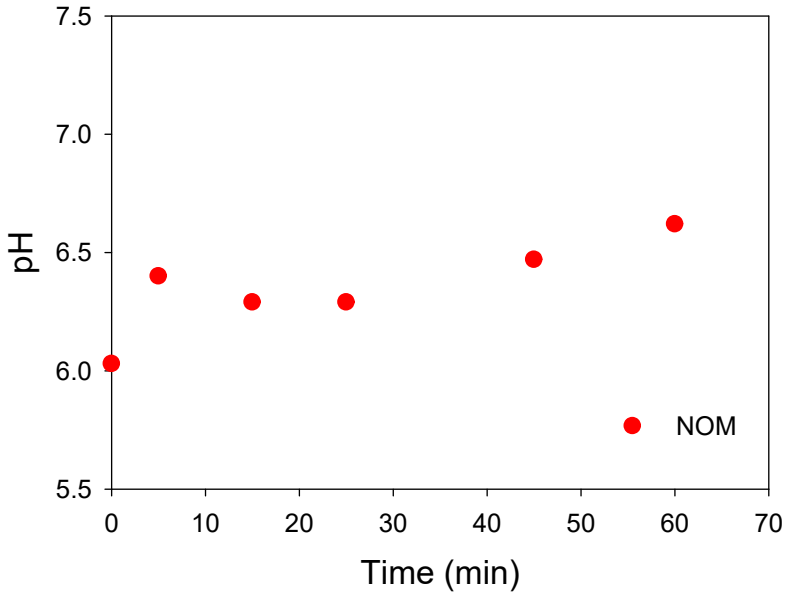

Figure S13. pH variation during Cd(II) removal by the UV/permanganate process in the presence of NOM. Conditions: $[KMnO_4]_0$ = 100 μM, $[Cd(II)]_0$ = 20 μM, $[NOM]_0$ = 3 mg/L.

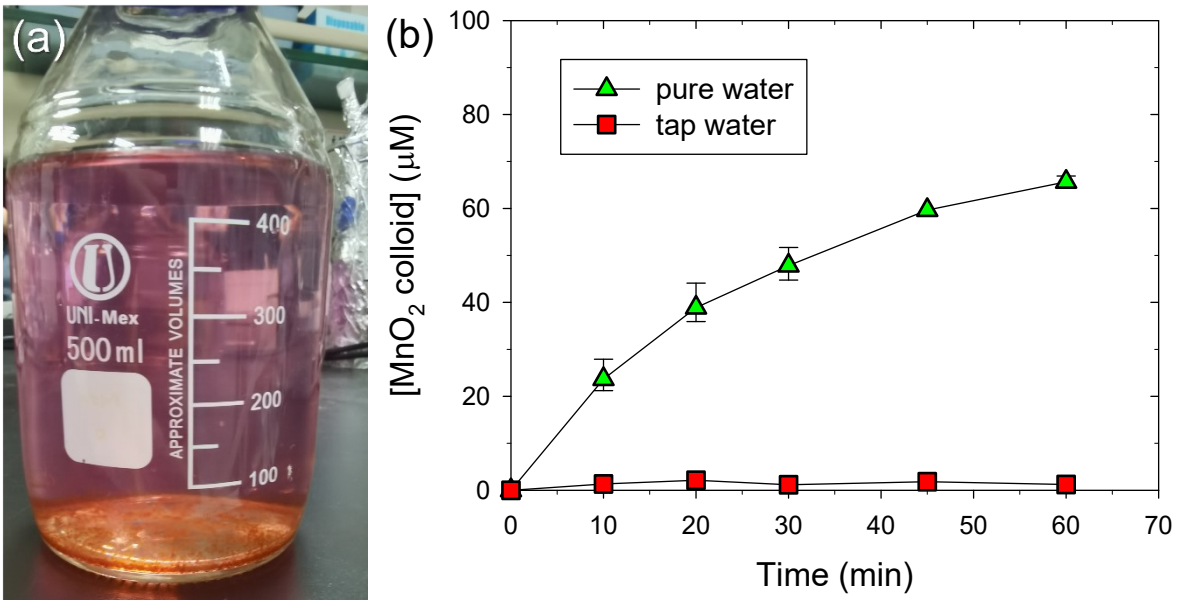

Figure S14. (a) The final testing solution of Cd(II) removal by the UV/$KMnO_4$ process in tap water for 1 h. (b) The time-dependent concentration of colloidal MnO_2 during Cd(II) removal by UV/$KMnO_4$ in tap water. Conditions: $[KMnO_4]_0$ = 100 μM, $[Cd(II)]_0$ = 20 μM, pH_0 = 6.0.