自來水淨水程序對酸性藥物處理效能評估

Acidic pharmaceutical removal in drinking water treatment process

中文摘要

近年來，國內外逐漸開始重視藥物與其他 PPCPs (pharmaceutical and personal care products) 污染飲用水(drinking water)的問題，許多研究者嘗試以不同處理方法(water treatment processe)對於各種人類常用藥物之去除效果做探討。本研究評估以自來水工程(Engineering of Drinking water treatment)中之混凝沉澱(coagulation)、加氯消毒(chlorination disinfection)、前加氯消毒（pre-chlorination）等方法去除水中四種常用之酸性消炎止痛藥(Diclofenac、Ibuprofen、Naproxen、Ketoprofen)之去除效果，並探討濁度(NTU)及濁水中加鈣離子(Ca2+)對於四種藥物之去除效果之影響。本研究中藥物殘餘濃度(residuals concentration)皆以高效能液相層析儀(HPLC)作偵測，並以核磁共振儀(NMR)觀察加氯消毒副產物(chlorination disinfection by-products)。

研究結果發現在酸性條件下混凝沉澱對於此四種酸性藥物均有去除效果，其中以 FeCl3 爲混凝劑之去除效果略優於 AlCl3。加氯消毒只對 Diclofenac 及 Naproxen 有效，對 Ibuprofen 與 Ketoprofen 則無效，其去除藥物效果會隨著加氯量增加、pH 值降低而上升。在前加氯實驗中，Diclofenac 進行前加氯實驗效果較單一使用混凝沉澱或加氯消毒之去除方法均更爲有效；而 Naproxen 之前加氯去除效果與加氯去除效果類似；因此 Naproxen 在前加氯中主要是受到加氯消毒的影響而 Diclofenac 則同時會受到加氯消毒及混凝沉澱兩種機制作用。在加氯消毒無效而混凝沉澱有效的 Ketoprofen 及 Ibuprofen 的實驗中發現，前加氯的效果在 pH 值 6~7 間去除效果優於單一進行混凝沉澱或加氯消毒，這表示氫氧化鐵 Fe(OH)3 可能可成爲加氯氧化酸性藥物的反應中的催化劑（catalytic agent）。此外，以濁水進行混凝沉澱杯瓶試驗（Jat ters）後發現，在要有效去除濁度的先決條件下，混凝劑 FeCl3 無法有效去除水中酸性藥物，在濁水中加入鈣離子也同樣無效。因此，建議未來可在醫院廢水或藥廠廢水排放前先設計前置處理水中藥物，以防止自來水廠在濁水的情況下無法去除此類藥物。

以 HPLC 及 NMR 針對加氯消毒進行副產物分析，發現 Diclofenac 及 Naproxen 於加氯消毒過程中的確會形成消毒副產物，且反應時間越久則副產物結構越複雜，Naproxen 主要被氯取代的位置爲苯環兩側周邊的官能基，而 Diclofenac 則主要爲結構式中兩個苯環間的 NH 基，所產生之消毒副產物是否具有對環境及人體健康更高毒性爲未來重要的研究方向。

英文摘要

In recent years, the contamination of PPCPs (Pharmaceutical and personal care products) in drinking water has become an important issue internationally. Many

researchers have used different water treatment processes to remove residual drugs in drinking water. This research evaluated the outcomes of using coagulations, chlorination disinfection and pre-chlorination in the drinking water treatment on removing the four commonly used NSAIDs drugs (Ibuprofen, Diclofenac, Naproxen and Ketoprofen) in water. Also, this study discussed the relationship of turbidity and the effectiveness of adding Ca^{2+} in raw water on removing the four NSAIDs. The residual concentrations of drugs in this research were measured by HPLC and the chlorination disinfection by-products were observed with NMR.

The results show that under the acidic condition, coagulations helped removing the four NSAIDs drugs better than the basic condition, and the performance of $FeCl_3$ was slightly better than the $AlCl_3$. Chlorination disinfection only can remove Diclofenac and Naproxen but no use for Ibuprofen and Ketoprofen; and the performance of drug removal improved as the chlorination dosage increased and with pH decreased. Pre-chlorination was more effective in removing Diclofenac than the other two methods, and it has about the same performance on eliminating Naproxen as chlorination disinfection; therefore Naproxen is mainly affected by chlorination disinfection and Diclofenac is mainly affected by both coagulation and chlorination. In the experiment of eliminating ketoprofen and Ibuprofen, pre-chlorination had better outcomes than only use coagulations or chlorination disinfection when the pH value was between 6 to 7. Therefore, $Fe(OH)_3$ may be the catalytic agent of acidic medicine being oxidation by free chlorine. Also, after conducting Jar test with mixing coagulations in muddy water, it was found that under the condition that turbidity must be effectively removed; $FeCl_3$ has no use for eliminating the acidic drugs in water even if Ca^{2+} was added. Therefore, it is strongly recommend that hospitals or pharmaceutical factory should design a treatment process before discharging waste water to prevent the situation where the targeted medicine can not be removed.

After analyzing the by-product of chlorination disinfection with HPLC and NMR, the results show that disinfected by-products were produced in the process of chlorination disinfection of Diclofenac and Naproxen, and the by-products chemical structure will become more complex if the response time is longer. Chlorine may attack Naproxen chemical structure at the site around aromatic functional groups, and Diclofenac may be attacked at the NH functional group between the two aromatic functional groups. Whether the disinfected by-products are harmful to human health and environment can be a very important research direction in the future studies.