

# Abstract

The native estrogenic steroid 17 $\beta$ -estradiol (  $E_2$  ) and its metabolites, estrone (  $E_1$  ) and estriol (  $E_3$  ), and the synthetic steroid 17 $\alpha$ -ethinyl estradiol (  $EE_2$  ) may distribute to water bodies and impact the eco-system with their estrogenic potency. Most studies focus on the removal efficiency of the sewage treatment plants regarding their emissions; however, there is limited information on the elimination of estrogenic chemicals during drinking water treatment processes.

This research investigated the removal rates of drinking water treatment units by spiking two levels ( 100 and 500 ng/L ) of the four estrogens into raw water. Four processes were simulated in the laboratory to evaluate the removal efficiencies : pre-chlorination, coagulation/sedimentation, rapid filtration, and post-chlorination. The study also reported the concentrations of the four estrogens in the raw water and treated water. Solid-phase extraction and LC/MS/MS with isotope-dilution techniques were utilized to analyze the four chemicals.

20–40% of  $E_1$ ,  $E_2$ ,  $EE_2$  and  $E_3$  were removed in the pre-chlorination unit; the coagulation/sedimentation procedure eliminated 17–52% of the chemicals, and  $E_2$  was the highest. The rapid filtration step took out over 95% of the compounds except for  $E_3$  ( 84 – 92 % ). The removal efficacy in post-chlorination process varied widely, which was 17–44%, and  $E_2$  was the lowest one. Obviously, the rapid filtration treatment is superior to the other processes in removing the chemicals (  $p < 0.0001$  ). The whole procedure got rid of over 88% of the chemicals excluding the  $E_3$  ( 64–85% ).

In terms of the influence of spiked levels, there is no significant difference

of E<sub>1</sub> and E<sub>3</sub> removal among the four processes, but it was significant for E<sub>2</sub> in the pre-chlorination and coagulation/sedimentation units (  $p < 0.05$  ). For E<sub>2</sub>, better efficiencies were observed at 500 ng/L in the pre-chlorination; however, the removal efficacy of coagulation/ sedimentation unit was higher at 100 ng/L. For EE<sub>2</sub>, there was only difference in the post-chlorination step (  $p = 0.002$  ). The elimination rates between these two spiked levels for E<sub>3</sub> in the rapid filtration treatment and post-chlorination units and almost reach statistical significance (  $p = 0.053$  and  $0.059$  ). Spiked levels did not influence the elimination performance through the whole procedure except for E<sub>3</sub> (  $p = 0.002$  ).

At 500 ng/L level, the removal efficacy of E<sub>3</sub> was much lower than that of E<sub>2</sub> in pre-chlorination (  $p = 0.031$  ), the removal percentage of E<sub>3</sub> was also notably lower than those of E<sub>1</sub>, E<sub>2</sub> and EE<sub>2</sub> in rapid filtration and through the complete process (  $p \leq 0.001$  ). There was no statistical difference among the removal rates of the four compounds in the coagulation/sedimentation and post-chlorination units. Regarding the 100 ng/L level, the removal efficiencies of the four units for the four estrogenic compounds varied. Nevertheless, the only difference in the removal efficacy for the four compounds was the coagulation/sedimentation, which E<sub>2</sub> was taken away much more than EE<sub>2</sub> (  $p = 0.028$  ).

The four steroid estrogens were detected from same raw waters. Among the detected samples, the average levels were 1.57–2.37 ng/L. On the other hand, none of the four compounds was detected in the treated drinking water.

*Key words* : removal efficiency ; solid-phase extraction ; LC/MS/MS ; pre-chlorination ; coagulation/sedimentation ; rapid filtration ; post-chlorination