

# Adsorption of 17 $\beta$ -estradiol by Activated Carbons Preloaded with NOM

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## 1. Introduction

17 $\beta$ -estradiol (E2) and estrone (E1) are found responsible for a major proportion of endocrine disrupting effects identified in aquatic environmental systems (Routledge et al. 1998; Chistianshen et al. 2002). Because of their small molecules, they can hardly be removed by conventional water purification systems. Activated carbon (AC) adsorption, is one of the best available technologies for advanced treatment of small organic molecules, and its application is increasing, however, due to the presence of natural organic matter (NOM) in drinking natural water sources the adsorption capacity for small organic molecules are decreased, which is caused probably by competition for adsorption site, when the carbon pores are large enough to admit both the small molecules and NOM, or by blockage of NOM for small molecules to enter micro-pores. The competition effect of NOM on E1 and E2 has been observed by a few researchers, however, the mechanisms involved has not yet been clarified.

The objective of this study was to investigate the adsorption capacity of E2 using three ACs having different pore distributions and being preloaded by NOM from a natural river water source.

## 2. Materials and Methods

### 2.1 Stock solution of 17 $\beta$ -estradiol (E2)

The stock solution of E2 (about 1033  $\mu\text{g/L}$ ) was prepared by dissolving a weighted amount of E2 (Wako Pure Chemical Co., Osaka, Japan) in Milli-Q water. The preparation was made by adding 0.02g of E2 powders to a glass water container filled with about 0.5L of Milli-Q water. After stirring for 24 hours in the temperature controlled room at about 20  $^{\circ}\text{C}$ , the suspension was filtered to remove the E2 fraction not dissolved using a pre-washed 0.2  $\mu\text{m}$  PTFE membrane. The filtered solution was then stored in a dark refrigerator at 5  $^{\circ}\text{C}$  as the stock solution.

### 2.2 NOM-containing river water

Nagara River water (NRW) was used as the NOM source. The water was pretreated by subsequently filtering through 0.45 $\mu\text{m}$  and 0.2 $\mu\text{m}$  membrane filters to remove suspended solids and microorganisms.

### 2.3 Activated carbons

Filtrisorb 400 (Calgon Co., USA), a well-used granular activated carbon (F400) and two kinds of microporous activated carbon fibers with narrow and broad pore size distribution, designated as ACF15 and

ACF25 (Nippon Kynol, Japan) respectively were utilized as the adsorbents. The average pore size of both ACF15 and ACF25 is smaller than 20nm. For F400 15% of the surface area is structured in pores having widths greater than 20nm. The specific surface area of F400, ACF15 and ACF25 is 1075, 1300 and 2000  $\text{m}^2/\text{g}$ , respectively. The pretreatment method of these activated carbons is documented elsewhere (Pelekani et al., 1998).

## 2.4 Adsorption experiment

Preloading of activated carbons with NOM was achieved by allowing adsorption of NOM to reach equilibration after shaking the reactor that contained 0.008g of AC and 0.8L of NOM-containing water for 7 days at 20  $^{\circ}\text{C}$ . The mixed solution after adsorption was allocated into 100ml glass bottles and variable volumes of E2 stock solution were added to yield E2 initial concentrations ranging from 10~500 $\mu\text{g/L}$  for followed experiments for E2 adsorption. The bottles were sealed with Teflon-lined caps, placed on a shaker for stirring at 20  $^{\circ}\text{C}$  for 7 days. After that, the solution was filtered to separate AC particles. NOM was quantified using the index of UV-adsorbance at 260nm (UV260). E2 was analyzed following the internal standard method with an Agilent 1100 series LC/MSD system (HP1100MSD).

## 3. Result and Discussion

### 3.1 Adsorption capacity of NOM

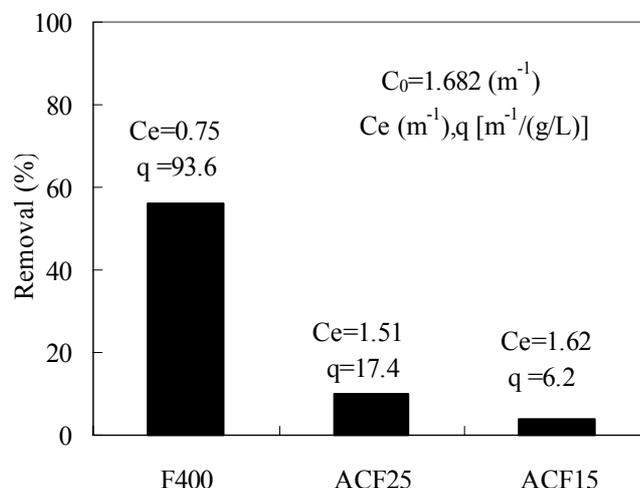


Fig 1. The removal of the NOM assessed by UV260

The NOM concentration in Nagara River water assessed by UV260 was  $1.68 \text{ m}^{-1}$ . After adsorption with F400, ACF15 and ACF25, the remaining concentrations become 0.75, 1.62 and  $1.51 \text{ m}^{-1}$ , which corresponded to NOM removals of 56%, 4% and 10%, respectively, as shown in Fig.1. The equilibrium adsorption capacity against these three liquid phase concentrations were 93.6, 6.2, 17.4 [ $\text{m}^{-1}/(\text{g/L})$ ] respectively, with the magnitude following the order of  $\text{F400} > \text{ACF25} > \text{ACF15}$ . F400 has 15% of surface area in pores above 20nm, which is much higher than ACF15 and ACF25. This might be responsible for the observed higher adsorption capacity of NOM with the coal-based F400. Broader pore size distribution of ACF25 than ACF15 is likely the reason that led to the result that the removal of ACF25 was about 2.5 times higher than ACF15.

### 3.2 Adsorption capacity of 17 $\beta$ -estradiol

E2 adsorption by preloaded activated carbons with NOM was conducted in the initial E2 concentration ( $C_{0E2}$ ) range from  $10 \mu\text{g/L}$  to  $500 \mu\text{g/L}$ . E2 equilibrium concentration ( $C_{eE2}$ ) was analyzed after adsorption reached equilibrium. The remaining of E2, given as the ratio of  $C_{eE2}$  to  $C_{0E2}$ , was showed in Fig.2. For F400 and ACF25, the remaining E2 in most reactors was below the detection limit, indicating nearly complete adsorption removal of E2. E2 was detected only for the reactors with initial E2 concentrations of  $500 \mu\text{g/L}$  for F400, and  $300 \mu\text{g/L}$  and  $500 \mu\text{g/L}$  for ACF25. For ACF15, however,

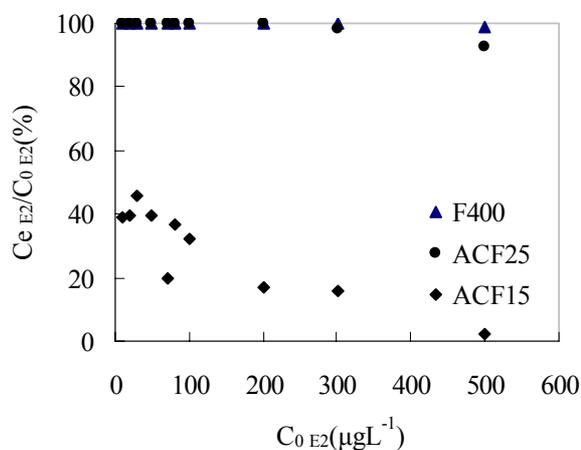


Fig 2. Ratio of E2's  $C_e$  to  $C_0$  in percentage at the whole range of E2 initial concentrations

the remaining of E2 was confirmed at the whole initial concentration range.

Equilibrium adsorbent phase concentration for E2 ( $q_{E2}$ ) was calculated by the following mass balance equation:

$$q_{E2} = (C_{0E2} - C_{eE2}) / C_{AC}$$

Values of  $q_{E2}$  when the E2 initial concentration is  $500 \mu\text{g/L}$  for F400, ACF25 and ACF15 are 44.9, 42.0 and  $1.15 \text{ mg g}^{-1}$ , respectively. The difference between ACF25 and ACF15 is much bigger than that between ACF25 and F400. It showed that the effect of pore size distribution difference between ACF25 and ACF15 was quite bigger

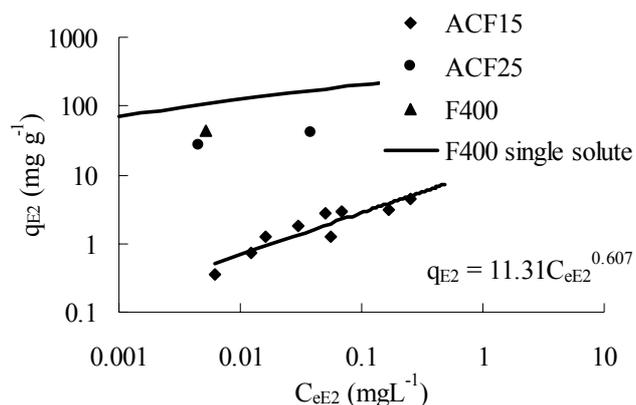


Fig 3 Relationship between  $q_{E2}$  and  $C_{eE2}$  for F400 and ACF25, adsorption isotherms for ACF15 and F400 single solute.

than that between ACF25 and F400, when the E2 initial concentration is  $500 \mu\text{g/L}$ . Because no E2 was detected at most initial concentration range for F400 and ACF25, adsorption isotherm only for ACF15 was obtained. Adsorption isotherm for E2 single solute with F400 was obtained by previously experiment showed in Fig.3. Apparently,  $q_{E2}$  with the preloaded F400 is lower than that of the fresh F400 at the same equilibrium concentration. It can be explained that the pore blockage with NOM did affect the adsorption capacity for E2 adversely. Because of the lack of adsorption isotherm for preloaded ACF25 and F400, the effect of pore blockage can not be quantified.

### 4. Conclusion

Preloaded activated carbon adsorption experiment was conducted to observe the adsorption behavior between NOM and E2. The results indicated that the adsorption capacity of fresh ACs for NOM followed the order of  $\text{F400} > \text{ACF25} > \text{ACF15}$ ; the adsorption capacity of preloaded ACs for E2 followed the order of:  $\text{F400} > \text{ACF25} > \text{ACF15}$ . Preloading with NOM caused reduction in the adsorption capacity of E2.

### References

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