### Chemosphere 93 (2013) 2562-2567

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

# Removal potential of anti-estrogenic activity in secondary effluents by coagulation



<sup>a</sup> Environmental Simulation and Pollution Control State Key Joint Laboratory, State Environmental Protection Key Laboratory of Microorganism Application and Risk Control (MARC), School of Environment, Tsinghua University, Beijing 100084, PR China <sup>b</sup> Shenzhen Laboratory of Microorganism Application and Risk Control, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, PR China

# HIGHLIGHTS

- DOM fractions <3000 Da in HOA and HON of secondary effluents were two key anti-estrogenic fractions.
- The anti-estrogenic activity of secondary effluents was limitedly removed by coagulation.

ARTICLE INFO

Accepted 20 September 2013

Available online 20 October 2013

Received in revised form 17 August 2013

Article history

Keywords:

Coagulation

Fractionation

Received 1 March 2013

Anti-estrogenic activity

Dissolved organic matter

Size exclusion chromatography

Secondary effluent

• The two key anti-estrogenic fractions were refractory during coagulation.

# GRAPHICAL ABSTRACT



#### ABSTRACT

Anti-estrogenic activity in wastewater is gaining increased attention because of its endocrine-disrupting function. In this study, the level and removal efficiency by coagulation of anti-estrogenic activity in secondary effluents of domestic wastewater treatment plants were studied. Anti-estrogenic activity was detected in secondary effluent samples at a tamoxifen (TAM) equivalent concentration level of 0.38- $0.94 \text{ mg-TAM L}^{-1}$ . Dissolved organic matters (DOM) with the molecular weight (MW) less than 3000 Da in hydrophobic acids (HOA) and hydrophobic neutrals (HON) fractions of the secondary effluent were the key fractions related to anti-estrogenic activity. Coagulation with FeCl<sub>3</sub> and polyaluminium chloride (PAC) can remove the anti-estrogenic activity of the secondary effluents, but the removal efficiency was limited. The removal efficiency using FeCl<sub>3</sub> coagulant was higher than that induced by PAC. Dissolved organic carbon was continuously removed with increased coagulant dose  $(0-120 \text{ mg L}^{-1} \text{ FeCl}_3)$ or  $0-60 \text{ mg L}^{-1}$  PAC). However, the removal of anti-estrogenic activity was not enhanced further when the coagulant concentration was beyond a critical value ( $30 \text{ mg L}^{-1} \text{ FeCl}_3$  or  $10 \text{ mg L}^{-1} \text{ PAC}$ ). The highest removal of anti-estrogenic activity was about 36% by FeCl<sub>3</sub> and 20% by PAC. Size exclusion chromatography results indicated difficulty in removing DOM with MW less than 3000 Da in the secondary effluent during coagulation even at a high coagulant concentration, which led to low removal efficiency of anti-estrogenic activity.

© 2013 Elsevier Ltd. All rights reserved.

# 1. Introduction

Wastewater reuse is an important method of dealing with the global water crisis. Nevertheless, conventional treatment processes in wastewater treatment plants (WWTPs) fail to remove all synthesized and natural organic chemicals in effluents. Endocrine-disrupting chemicals (EDCs) are widely detected in WWTP effluents.





Chemosphere

霐

<sup>\*</sup> Corresponding author at: Environmental Simulation and Pollution Control State Key Joint Laboratory, State Environmental Protection Key Laboratory of Microorganism Application and Risk Control (MARC), School of Environment, Tsinghua University, Beijing 100084, PR China. Tel.: +86 10 6279 4005; fax: +86 10 6279 7265

E-mail address: hyhu@tsinghua.edu.cn (H.-Y. Hu).

<sup>0045-6535/\$ -</sup> see front matter © 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.chemosphere.2013.09.073

EDCs are exogenous agents that interfere with the synthesis, secretion, transport, binding, action, or elimination of natural bodily hormones that are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior (USEPA, 1997). EDCs are also considered to be potentially harmful to wildlife (Colborn et al., 1993).

Today, anti-estrogenic activity, a typical endocrine-disrupting effect, is frequently detected in surface water, municipal, and industrial wastewater. Improper contact and intake of chemicals or medicines with anti-estrogenic activity reportedly disrupt the function of the endocrine system of organisms, leading to masculine characteristics in females (Hodgson, 2004). Therefore, the presence of anti-estrogenic compounds in the environment adds to the potential ecological risk.

Since the 1990s, chemicals with anti-estrogenic activity have been reported in surface water and wastewater. Some natural phytochemicals and wood extracts found in pulp mill effluent exhibit anti-estrogenic activity (Collins et al., 1997; Orrego et al., 2010). Synthetic chemicals and treatment by-products from industrial and municipal wastewater, such as some polynuclear aromatic hydrocarbons (Tran et al., 1996) and some plasticizers (Okubo et al., 2003), also show anti-estrogenic activity and are discharged into aquatic environments. In research report, surface water has been affected by secondary effluents with anti-estrogenic activity (Vega-López et al., 2007).

Researchers are also attempting to monitor and control antiestrogenic activity in wastewater and reclaimed water. Conroy et al. (2007) found that after storage, the anti-estrogenic activity dramatically increases. Moreover, Stalter et al. (2011) concluded that anti-estrogenic activity is undetectable in the influent but appears in the effluent of a secondary clarifier possibly because of the effective removal of estrogen agonists during conventional activated sludge treatment.

In recent years, researchers have also begun to evaluate the effects of tertiary treatment on anti-estrogenic activity in reclaimed water. Wu et al. (2009) found that chlorination increases the anti-estrogenic activity of secondary effluents. Stalter et al. (2011) found that ozonation and activated carbon do not decrease the anti-estrogenic activity of secondary effluents, but even increase the anti-estrogenic activity after ozonation.

In wastewater reclamation plants, coagulation combined with filtration is widely used as an effective method of removing organic colloids. Coagulants such as FeCl<sub>3</sub>, PAC, polyaluminium silicate sulfate, and aluminum sulfate demonstrate high efficiency in removing SS and turbidity in reclaimed water, which helps reduce membrane fouling for the post-filtration process (Abdessemed et al., 2000; Haberkamp et al., 2007; Baek and Chang, 2009). FeCl<sub>3</sub> can also reportedly form stronger and heavier flocs over a broader pH range and is less sensitive than alum in case of poor filtrate quality caused by overdosing (Stephenson and Duff, 1996). Arnaldos and Pagilla (2010) suggested that alum can remove dissolved organic nitrogen and dissolved non-reactive phosphorus.

However, the effects of coagulation on the anti-estrogenic activity in secondary effluents or reclaimed water are still hardly known.

This study aimed to assess the effects of coagulation on antiestrogenic activity in secondary effluents, and identify the key fractions related to anti-estrogenic activity in secondary effluents.

### 2. Materials and methods

# 2.1. Sampling

Secondary effluent samples were collected from two municipal WWTPs (WWTP-Q and WWTP-G) in Beijing, China. The anaerobic–

anoxic-oxic process is used in WWTP-Q, and the oxic-anoxicanaerobic process is used in WWTP-G. Samples were kept at 3– 6 °C on ice, and immediately transported to the laboratory for water quality measurement, preparation, and coagulation experiments within 24 h.

# 2.2. Water quality analysis

Water samples before and after coagulation were passed through 0.45  $\mu$ m glass filters before water quality analysis. The pH was measured with a Mettler Toledo Fe20 analyzer. The concentration of dissolved organic carbon (DOC) in water samples was measured with a Shimadzu TOC-5000A analyzer. UV absorbance was measured with a Shimadzu UV-2401PC UV-VIS recording spectrophotometer. Measurements were performed in triplicate.

#### 2.3. Coagulation experiments

Coagulation experiments were performed on a coagulation instrument in laboratory. One liter of secondary effluent sample was used for coagulation, and the coagulants FeCl<sub>3</sub> and PAC were used at the dosages of  $0-120 \text{ mg L}^{-1}$  for FeCl<sub>3</sub> and  $0-60 \text{ mg L}^{-1}$  for PAC. In addition, the maximum coagulant concentrations were beyond the actual condition by about 100%, so as to obtain convincing and significant results.

Coagulants were added to the sample after 30 s of rapid stirring  $(200 \text{ rmin}^{-1})$ . Stirring  $(150 \text{ rmin}^{-1})$  was continued for 2 min, and the samples were left undisturbed for 30 min to enable precipitation. The pH monitoring during coagulation revealed that it was about 7.6 before coagulation and insignificantly varied thereafter.

#### 2.4. Fractionation by resin adsorption

According to the original protocol of Leenheer (1981) and a modified one introduced by Zhang et al. (2009), nonionic macroporous resin Supelite XAD-8 (20–60 mesh), cation-exchange resin Dowex Marathon MSC (H) (20–50 mesh), and anion-exchange resin Duolite A-7 (free base) were selected, purified and conditioned. Then they were respectively packed into glass columns (0.25 L) for fractionation. After preparing the resins, 1 L of water sample filtrate was fractionated into six fractions as in the procedure shown in Supplemental Fig. 1 (Zhang et al., 2009). Thereafter, all six fractions were diluted to the original sample volume (1 L) with ultrapure water.

### 2.5. Size exclusion chromatography

Size exclusion chromatography (SEC) was used for the molecular weight (MW) analysis of the fractions on a Shimadzu LC-20 high-performance liquid chromatography system combined with a Shimadzu SPD-M20A UV detector and two connected columns (a TSK-GEL G3000PWXL column followed by a TSK-GEL G2500PWXL column).

The columns were kept at 40 °C, and the mobile phase was composed of MILLI-Q ultrapure water buffered with phosphate (0.0024 M NaH<sub>2</sub>PO<sub>4</sub> and 0.0016 M Na<sub>2</sub>HPO<sub>4</sub>) and 0.025 M sodium sulfate. For each measurement, 100  $\mu$ l of the fractions was injected and UVA signals were monitored during the following 60 min. The MW standards used were polyethylene glycol (330, 700, 1050, 5250, 10225, and 30000 Da) and acetone. After calibration, the retention time in the SEC chromatogram was converted to the MW, and the baseline was adjusted to a zero line. Download English Version:

# https://daneshyari.com/en/article/6309661

Download Persian Version:

https://daneshyari.com/article/6309661

Daneshyari.com