Organic micropollutant removal from groundwater: comparison of pellet softening and nanofiltration

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ABSTRACT

This study investigated the fate of selected pharmaceuticals and estrogens and the characteristics of bulk organic matter during pellet softening and proposed a possible hybridization with nanofiltration (NF) treatment. A groundwater softening system called pellet softening was used to remove calcium ions from groundwater by crystallizing calcium carbonate on the surface of sand grains that were used as seeding material. This crystallization was confirmed by X-ray powder diffraction, and X-ray fluorescence and scanning electron micrographs were used to characterize the surface of the sand grains during pellet softening. The fluorescence excitation–emission matrix showed that humic-like substances were slightly removed and that specific UV absorbance values decreased after pellet softening. The humic fraction determined by liquid chromatography-organic carbon detection was slightly more attenuated than the fractions of biopolymers, building blocks, low molecular weight acids, and low molecular weight neutrals. Therefore, the aromatic content per unit of dissolved organic carbon was preferentially attenuated during pellet softening. The average removal efficiencies of the three estrogens and 12 selected pharmaceuticals during the softening process were 59 and 5.7%, respectively. However, there was a greater reduction of pharmaceuticals during NF.

Key words | estrogens, nanofiltration, pellet softening, pharmaceuticals, total hardness

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INTRODUCTION

The occurrence of organic micropollutants (OMPs) such as pharmaceuticals and estrogens, as well as their metabolites, and other personal care products has been detected in different water sources (Ternes *et al.* 1999, 2002; Heberer *et al.* 2002; Richardson 2003; Stackelberg *et al.* 2004; Kim *et al.* 2007; Benotti *et al.* 2009) with a wide range of concentrations from ng/L to µg/L (Heberer 2002; Mompelat *et al.* 2009). Many pharmaceuticals are not completely degraded in the human body (Dębska *et al.* 2004) and have broader effects when combined in an aquatic environment, even at low concentrations (Daughton & Ternes 1999). Jain *et al.* (2013) reported that some antiviral drugs are difficult to remove during conventional water treatment, and this can

result in intermediates, which are difficult to degrade. Therefore, it is important to monitor OMPs in aquatic environments and water treatment processes. Many studies have been conducted to investigate novel water treatment systems or develop new materials that can remove OMPs more effectively in water treatment processes (Maeng *et al.* 2015). Furthermore, most studies performed on the fate or removal of OMPs were conducted with surface water, where OMPs are often detected, and limited studies were carried out for groundwater and bank filtrate during water softening (calcium and magnesium removal). It is important to monitor OMPs in bank filtrate or groundwater treatment processes since groundwater and bank filtrate can be

contaminated by OMPs. Bank filtrate mostly flows from rivers to the aquifer, and the bank filtration systems are the hydraulic connections between the river and the aquifer.

Pellet softening by crystallizing calcium carbonate on the surface of sand grains in a fluidized bed reactor using lime, caustic soda, or soda ash has been used in the Netherlands as a key softening process to reduce the hardness of groundwater or bank filtrate, and its implementation as part of a centralized scheme was first verified at the Amsterdam Water Supply (Graveland *et al.* 1983). Pellet softening has received a great deal of attention worldwide (van Schagen *et al.* 2008b) and is now commonly used for groundwater softening in the Netherlands. In pellet softening, sand grains are used as the seeding material and commonly referred to as pellets, and calcium carbonate is crystallized on the surface of these sand grains through heterogeneous primary nucleation in a fluidized bed reactor (i.e., pellet reactor). Pellet softening is also considered in zero liquid discharge applications to recover more water and reduce concentrate in a reverse osmosis (RO) system (van Houwelingen *et al.* 2010).

In general, a pellet reactor comprises a cylindrical tank filled with the seeding material, usually sand grains (pellets) with a diameter of 0.15 to 0.4 mm, and the water is pumped upflow with constant water velocities of 60–100 m/h (Graveland *et al.* 1983; van Schagen *et al.* 2008a; Morgan *et al.* 2013). Withdrawing sand grains from the pellet reactor occurs after a period of softening or depends on groundwater characteristics. Surfaces of sand grains during pellet softening increase through the crystallization of calcium carbonate, and waste pellets are often reused for agricultural applications and steel industries (Van der Bruggen *et al.* 2009). Crystallization of calcium occurs once the pH is raised to approximately 9.0 by adding lime, caustic soda, or soda ash. Lime is used most often, since caustic soda and soda ash raise the sodium concentration in drinking water. The crystallization of calcium carbonate on the surface of sand grains leads to a gradual increase in their size, creating stratification with larger sand grains at lower levels of the reactor and smaller sand grains at upper levels. Larger sand grains are discharged through the bottom of the reactor, and fresh sand grains are introduced. Detailed information on the process and operation concepts are described in previous studies (van Dijk & Wilms 1991; Harms & Bruce Robinson 1992; van Schagen *et al.* 2008b).

Studies of advanced water treatment systems used to remove OMPs have found advanced oxidation processes (e.g., O_3/H_2O_2 and UV/H_2O_2) and high pressure membranes (e.g., nanofiltration (NF) and RO membranes) to be effective for certain contaminants of emerging concern (CEC) (Huber *et al.* 2003; Verliefde *et al.* 2009; Yangali-Quintanilla *et al.* 2010; Ramasundaram *et al.* 2013; Wang *et al.* 2015). However, questions still remain regarding the fate of OMPs in conventional groundwater or bank filtrate treatment processes. Central softening has been utilized in the Netherlands for more than 30 years, yet no literature is currently available on the removal of pharmaceuticals and estrogens. Conventional chemical softening processes are not designed for the removal of OMPs. However, it is important to determine the level of post-treatment required to compensate for limitations of the softening process for the removal of CECs and to investigate bulk organic matter characteristics in order to understand the effects of natural organic matter (NOM) on post-treatment steps for the removal of OMPs, since NOM is known as one of the prominent interfering substances and can form disinfection byproducts (DBPs). To the best of our knowledge, no study has investigated the removal of pharmaceuticals, the removal of estrogens, or NOM characteristics during pellet softening.

A pellet softening system is designed to remove calcium through the crystallization of calcium carbonate on the surface of pellets, not specifically for removing pharmaceuticals. Therefore, adequate hybridization with other advanced processes should be considered for drinking water treatment processes. The development of hybrid systems has enhanced the efficiency of OMP removal during water treatment (Sudhakaran *et al.* 2013). An integrated membrane system preceded by one or more non-membrane-based treatment processes (Schippers *et al.* 2004) can act as a multi-barrier system for removing both total hardness and OMPs.

NF is an effective treatment process to remove OMPs whose molecular weights range between 150 and 500 Da (Snyder *et al.* 2003), but the removal is dependent on the NF membrane properties, such as molecular weight cut-off (MWCO), pore size, surface charge, hydrophobicity–hydrophilicity, and surface roughness (Xu *et al.* 2005). Several

previous studies reported the performance of NF for the removal of pharmaceuticals (Radjenović et al. 2008; Omidvar et al. 2015) and investigated influential factors during operation, such as pH, ionic strength, transmembrane pressure, NOM (Zazouli et al. 2009), and fouling (Yangali-Quintanilla et al. 2009). Like other advanced water treatments, NF is not always effective for the removal of all OMPs. Therefore, it is important to investigate physicochemical properties of target contaminants when water utilities select proper water treatment for these compounds.

To overcome the limitations of pellet softening for the removal of OMPs, NF is a synergistic approach for hybridization, not only to attenuate OMPs but also total hardness and membrane foulants (e.g., calcium sulfate scaling) in the NF system. In this study, an NF system was considered as a potential hybridization of pellet softening to overcome the low removal of OMPs during pellet softening.

This study determined the behavior of 12 selected pharmaceuticals and three endocrine-disrupting compounds, including lipid regulators, stimulants, anticonvulsants, analgesics, non-steroidal anti-inflammatory drugs, and estrogens, during pellet softening. NF was also conducted, and its performance was compared to pellet softening. Further, this study investigated the NOM characteristics during pellet softening using advanced organic matter characterization tools, which to the authors' best knowledge, have not been previously reported.

MATERIALS AND METHODS

Experimental setup

A laboratory scale pellet reactor was used with a plexiglass column with an internal diameter of 15 mm, a height of 3,000 mm, and a nozzle at the bottom for the injection of sodium hydroxide (NaOH, 1.5 N). Sand grains were used as seeding material to fill the column to a height of 700 mm. A similar configuration was reported previously (Mahvi et al. 2005). Different upflow velocities of 50, 100, and 130 m/h were tested to determine the effect of water velocity on the removal of total hardness. Groundwater was used from a vertical well located at Sejong University (Seoul, Korea), and calcium chloride (CaCl$_2$; Sigma-Aldrich,

Kyunggido, Korea) was used to increase total hardness concentration in the groundwater (Table 1).

An NF membrane system was used to compare the removal performance of pharmaceuticals and estrogens. The NF system consisted of nine parallel membrane pressure vessels composing a spiral-wound polyamide membrane (NE4040-90; Woongjin Chemical Co. Ltd, Korea) with a total effective area of 71.1 m^2, and showed 90% rejection of sodium chloride (NaCl; molecular weight cut-off at approximately 200 Da).

Total hardness, alkalinity, and pH measurements

Total hardness was measured according to standard methods: the complexometric titration method with ethylenediaminetetraacetic acid (APHA 2012). The pH was measured using a pH meter (HI 8424; Hanna Instruments, USA).

Organic matter characteristics

A fluorescence excitation–emission matrix (EEM) was used to characterize the bulk organic matter characteristics with a fluorescence spectrophotometer (LS50B; PerkinElmer, USA). EEM spectra were obtained at scanned excitation wavelengths (ex) between 200 and 400 nm at 10-nm intervals and emission wavelengths (em) between 280 and 600 nm at 0.5-nm intervals. The water Raman data at 348 nm were regularly checked to confirm the stability of the lamp in the fluorescence spectrophotometer, and EEM fluorescence spectra were corrected using blank subtraction. The EEM depicted bulk organic matter characteristics with respect to four peaks, which were determined by fluorescence intensity at distinct ex and em wavelengths: tryptophan protein-like peaks, T1 (ex/em = 220–240 nm/ 330–360 nm), tryptophan protein-like peaks, T2 (ex/em =

Table 1 | Characteristics of influent used in this study

pH	Turbidity (NTU)	Alkalinity as CaCO$_3$ (mg/L)	Dissolved organic carbon (mg/L)	Total hardness as CaCO$_3$ (mg/L)
7.2–7.5	1.6 ± 0.5		4.5 ± 0.5	176 ± 11

270–280 nm/330–360 nm); humic-like peaks, A (ex/em = 230–260 nm/400–450 nm); and humic acid-like peaks, C (ex/em = 300–340 nm/400–450 nm). Liquid chromatography and organic carbon detection (LC-OCD; DOC-LABOR, Germany), with a detection limit for LC-OCD at <1–50 ppb, was used. A Gräntzel thin-film reactor was used in the LC-OCD system to oxidize dissolved organic matter, resulting in CO_2 production, which was detected by a gas analyzer (Ultramat 6; Siemens, Germany). LC-OCD was used to characterize bulk organic matter into five organic matter fractions (biopolymers, humic substances, building blocks, low molecular weight (MW) acids, and low MW neutrals), all of which were determined with respect to the organic carbon concentration (C mg/L). A detailed description of LC-OCD has been reported elsewhere (Huber et al. 2011). Specific UV absorbance (SUVA), the ratio between UV absorbance and dissolved organic carbon, was used to investigate changes in the aromaticity of organic matter during pellet softening.

Pharmaceuticals and estrogens

Twelve pharmaceuticals (gemfibrozil, bezafibrate, clofibric acid, caffeine, carbamazepine, ibuprofen, naproxen, phenacetine, acetaminophen, fenoprofen, ketoprofen, and pentoxifylline) and three estrogens (17α-ethinylestradiol or EE2, estrone or E1, and 17β-estradiol or E2) were spiked into groundwater at a concentration of 2 μg/L. The selected pharmaceuticals were pre-concentrated by performing online solid phase extraction with an EQUAN MAX™ system (Thermo Fisher Scientific, CA, USA), based on column switching techniques using a trap column and the analytical columns hypersil gold aQ (20 mm, 12 μm particle size) and hypersil gold (50 mm, 1.9 μm particle size; Thermo Fisher Scientific). The sample delivery system comprised a CTC PAL auto sampler manufactured by CTC Analytics (Zwingen, Switzerland) with six-port switching valves and a quaternary load pump. The measurement of mass spectrometry was performed on an Orbitrap Exactive model (Thermo Fisher Scientific), using ESI mode. The limit of quantification (LOQ) for the selected pharmaceuticals was <30 ng/L. EE2, E1, and E2 were determined by gas chromatography-mass spectrometry (GC-2010; Shimadzu, Japan) using an HP-5 type capillary column. C18 SPE

cartridges (HLB C18 cartridge 6 cc, 1 g; Oasis, USA) were used to enrich the estrogens. The LOQ for E2, E1, and EE2 was 30 ng/L. The procedure used for selected estrogens is described elsewhere (Liu et al. 2004).

Composition and surface characterization of pellets during pellet softening

Sand grains before and after pellet softening were characterized by X-ray fluorescence (XRF) (RIX2100; Rigaku, Japan) with an Rh source of 40 kV and 75 mA, X-ray powder diffraction (XRD; X-ray source: Cu source, 40 kV, 200 mA with Cu K_α radiation, λ = 1.5406 Å, Dmax2500, Rigaku, Japan), and scanning electron micrographs (JSM-6390; JEOL).

RESULTS AND DISCUSSION

Performance of pellet softening at different total hardness loadings and upflow velocities

A total hardness removal efficiency from 47 to 80% was observed when the pellet reactor was fed total hardness concentrations from 176 to 673 mg/L of calcium carbonate ($CaCO_3$) at a pH of 9; efficiency increased when the total hardness concentration increased (Table 2). The removal efficiency of total hardness can be enhanced by increasing the pH, but our aim was a total groundwater hardness between 90 and 110 mg/L of $CaCO_3$ after softening, so as to retain mineral nutrition in water. Upflow velocities of 50, 100, and 130 m/h were tested to investigate the effect of velocity on the removal of total hardness. Chen et al. (2000) reported good formation of calcium at a pH of 9 and an upflow velocity of 100 m/h. However, our study found no significant difference in total hardness removal at upflow velocities of 50, 100, and 130 m/h, and an upflow velocity over 130 m/h was not considered due to the fine particles discharging from the pellet reactor.

The crystallization of calcium on sand grains was confirmed by XRF analysis (Table 3). The chemical composition of sand grains before pellet softening was dominated by silicon dioxide (SiO_2) at 74.3%, followed by aluminum oxide (Al_2O_3) at 14.4%, and calcium oxide

Table 2 | Removal of total hardness by pellet softening at different total hardness and upflow velocities ($n = 4$)

Total hardness (mg/L as $CaCO_3$)				Total hardness (mg/L as $CaCO_3$)		
Influent	Effluent	Removal %	Upflow velocity (m/h)	Influent	Effluent	Removal %
176 ± 11	93 ± 31	47	50	510 ± 23	93 ± 20	82
284 ± 9	100 ± 27	65	100	510 ± 23	93 ± 18	82
522 ± 47	109 ± 53	79	130	510 ± 23	102 ± 34	80
673 ± 15	134 ± 75	80				

Table 3 | Chemical composition of sand (before and after softening) (wt.%) at total hardness 500 mg/L as $CaCO_3$

Components	Before pellet softening, %	After pellet softening, %
Na_2O	2.32	0.551
MgO	0.827	0.596
Al_2O_3	14.4	3.5
SiO_2	74.3	19.1
P_2O_5	0.056	0.026
SO_3	0.015	0.075
K_2O	5.03	1.27
CaO	1.27	73.3
TiO_2	0.178	0.122
Fe_2O_3	1.47	1.2
NiO	0.005	0.05
ZrO_2	0.004	0.015
SrO	0.017	0.068
PbO	0.003	0.005
ZnO	0.004	0.061
Rb_2O	0.011	0.010
MnO	0.023	0.043
CuO	0.001	0.015
Nb_2O_5	0.001	–
BaO	0.079	–

(CaO) at 1.27%, which is the typical composition of silica sand. The composition changed dramatically after softening to 19.1% SiO_2, 3.5% Al_2O_3, and 73.3% CaO, which indicated that calcium was successfully crystallized and dominated the surface of sand grains. Figure 1 shows scanning electron microscope images of sand grains before and after softening at an upflow velocity of 100 m/h, and the results obtained from XRD analysis that confirmed the crystallization of calcium are shown in Figure 2. XRD patterns

of sand grains showed that calcium peaks appeared only after softening. Results of XRD and XRF analyses confirmed the formation of $CaCO_3$ on the surface of sand grains through crystallization.

Changes in bulk organic matter characteristics

Advanced organic matter characterization tools such as EEM, LC-OCD, and SUVA were utilized to gain a better understanding of changes in bulk organic matter characteristics during groundwater softening via pellet softening. The characteristics of NOM are important to investigate in water treatment systems where the disinfection is carried out via chlorine. NOM with more aromatic organic matter tends to form higher level form DBPs than NOM with a low content of aromatic organic matter (US EPA 2006). Russell *et al.* (2009) reported that the removal of NOM was observed during water softening through adsorption onto or co-precipitation with calcium and magnesium. However, no previous study has reported the changes in bulk organic matter characteristics during water softening using EEM and LC-OCD. Based on the EEM results, there was a reduction of fluorescence intensity observed in the humic-like peaks (C and A peaks), and the tryptophan-like peaks (T) were unchanged after pellet softening (Figure 3). The groundwater was contaminated by the pond located near the groundwater well; high concentrations of dissolved organic carbon and a tryptophan-like peak in the groundwater were detected. The dissolved organic carbon concentration commonly detected in the groundwater was between 0.5 and 1.0 mg/L; however, the groundwater was contaminated because the pond was contaminated by food waste during the time of this study. Baker *et al.* (2004) reported that wastewater or treated wastewater showed the
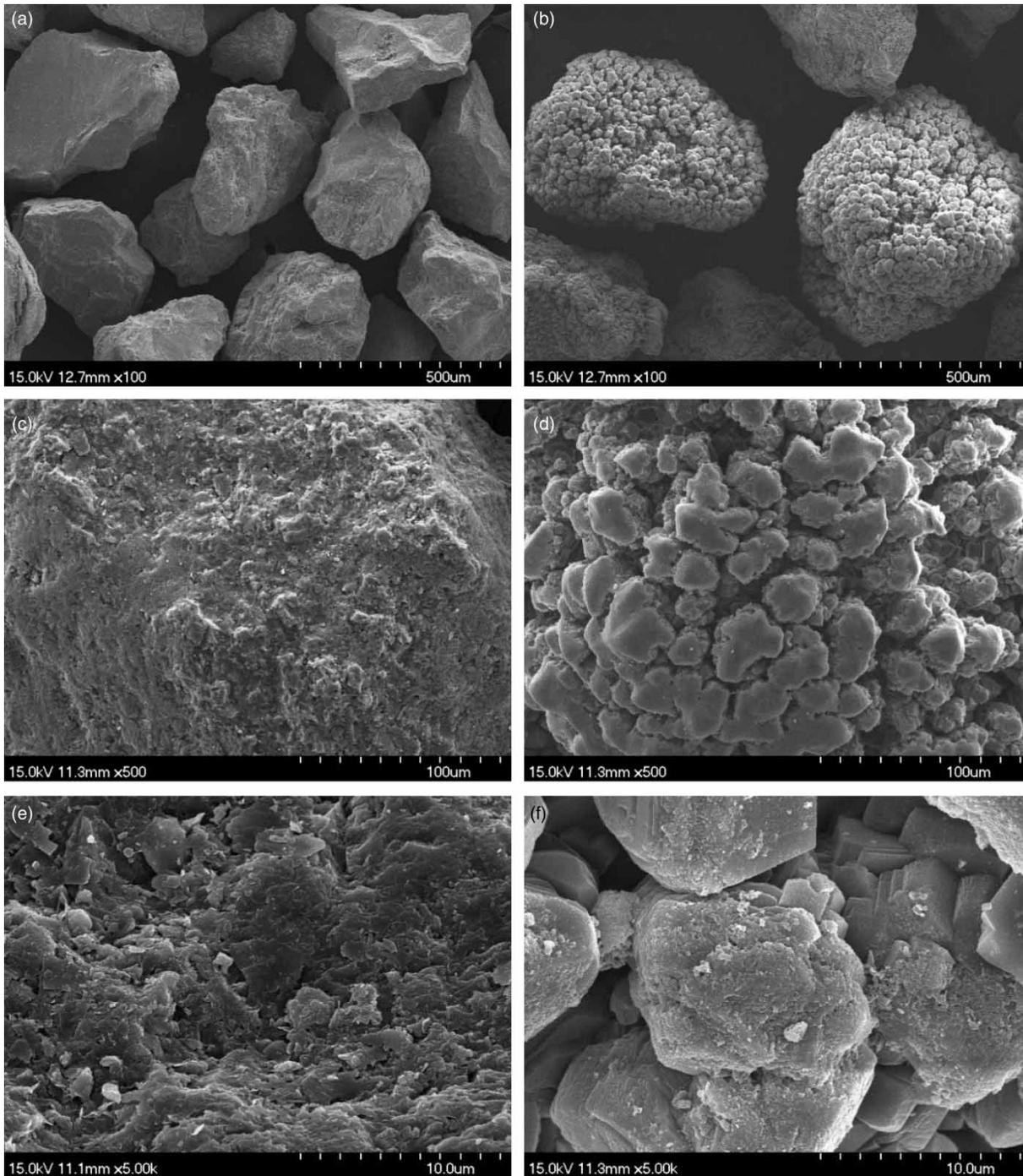
Figure 1 | Scanning electron microscope images showing pellet at different scale bars 500, 100, and 10 μm; before softening (a, c, and e) and after softening (b, d, and f) (total hardness 673 mg/L as $CaCO_3$ at pH 9 and upflow velocity 100 m/h).

highest tryptophan-like fluorescence intensity compared to waters that were less impacted by wastewater, and tryptophan-like peaks can be used as an indicator of organic pollution, along with other traditional water quality parameters, such as dissolved oxygen, pH, and turbidity (Khamis & Stevens 2013). Previous studies reported the
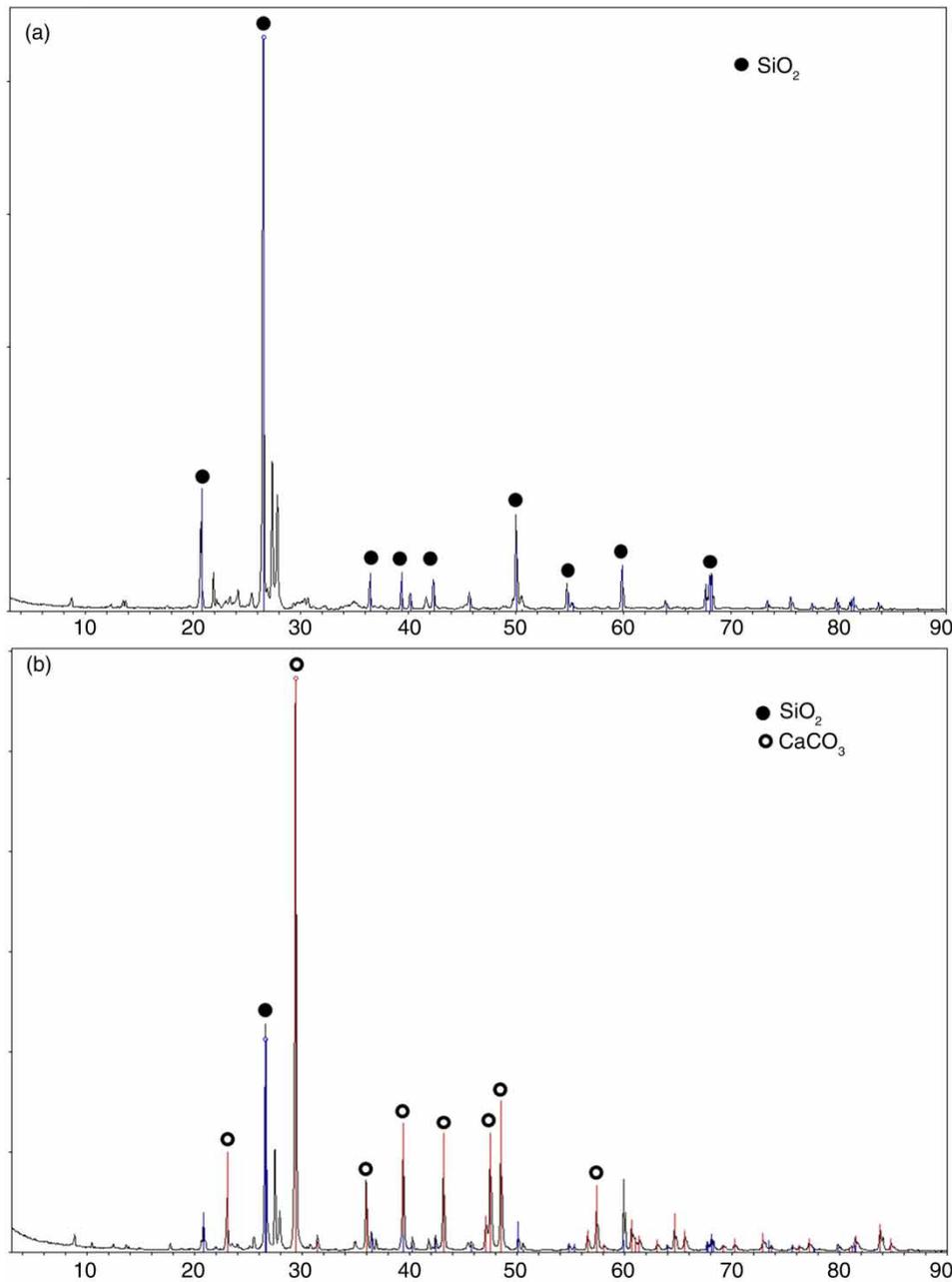
Figure 2 │ X-ray diffraction patterns of pellet before (a) and after (b) pellet softening (total hardness 673 mg/L as $CaCO_3$ at pH 9 and upflow velocity 100 m/h).

preferential removal of aromatic organic matter during chemical softening (Liao & Randtke 1986; Thompson et al. 1997; Roalson et al. 2003). We also confirmed by EEM that humic-like substances (C and A), which represent aromatic organic matter characteristics, were preferentially attenuated during pellet softening. At a higher pH, humic acid in humic-like substances becomes more soluble, and more

negative charges are generated in the acidic functional groups of humic substances (Uyguner-Demirel & Bekbolet 2011). Negative charges of humic substances could adsorb onto a positively charged calcium carbonate that crystallized on the surface of sand grains during pellet softening. However, tryptophan-like substances were not effectively attenuated because of the high pKa value of α-amino
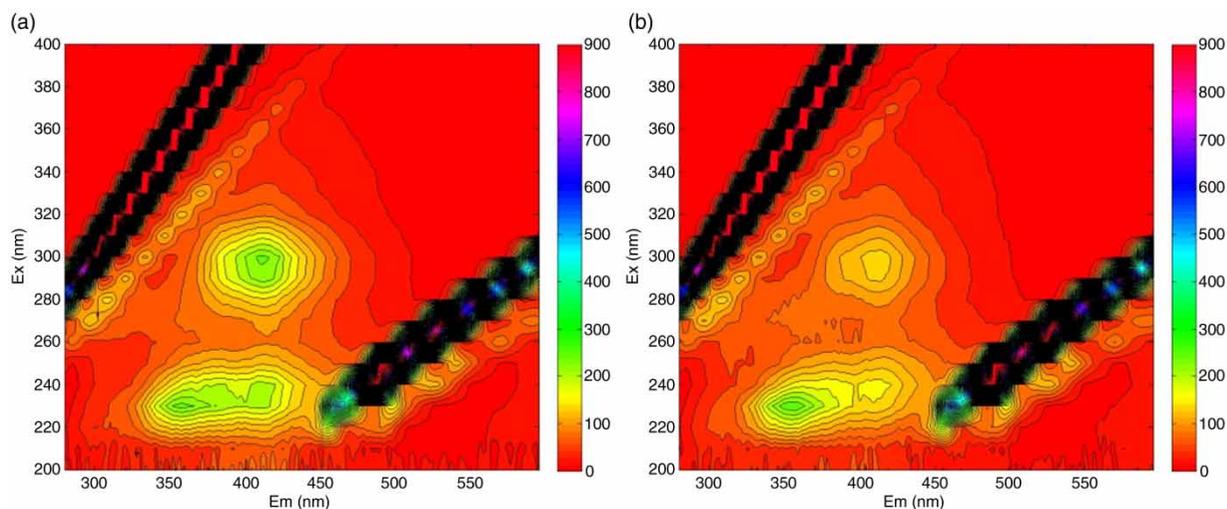
Figure 3 │ Fluorescence EEM spectra of dissolved organic matter in groundwater before (a) and after (b) pellet softening.

group (9.4), indicating less negative charge compared to that of humic-like substances.

LC-OCD analysis grouped bulk organic matter into five different organic matter fractions (biopolymers, humics, building blocks, low MW acids, and low MW neutrals) before and after pellet softening (Figure 4). The humic fraction determined by LC-OCD (humics 800–1,000 Da) was reduced slightly greater than the other four fractions, and low MW acids in very low concentrations were not attenuated. As expected, biopolymers, which were also detected

as tryptophan-like substances in EEM, were not changed. SUVA values decreased from 5.7 to 3.4, 4.1, and 3.9 when initial total hardness concentrations were 673, 284, and 522 mg/L, respectively. As such, more positively charged metal ions (e.g., calcium ions) are available for binding negatively charged aromatic organic matter. Based on advanced organic matter characterization tools, a slightly higher removal was observed for humic-like substances during pellet softening.

Fate of pharmaceuticals and endocrine disrupting compounds

The selected pharmaceuticals were grouped into four categories according to usage in order to determine similarities in removal during pellet softening (lipid regulator, stimulants, analgesic, and nonsteroidal anti-inflammatory drugs). The 12 selected pharmaceuticals exhibited very low removal patterns and showed no similarities by group. Furthermore, there was no significant change in the removal of pharmaceuticals when the total hardness increased from 284 to 673 mg/L. Neither the degree of total hardness removal nor the initial total hardness concentration during pellet softening had any effect on the removal of the selected pharmaceuticals via crystallization or co-precipitation. The concentration of the selected pharmaceuticals was lower than the concentration of NOM
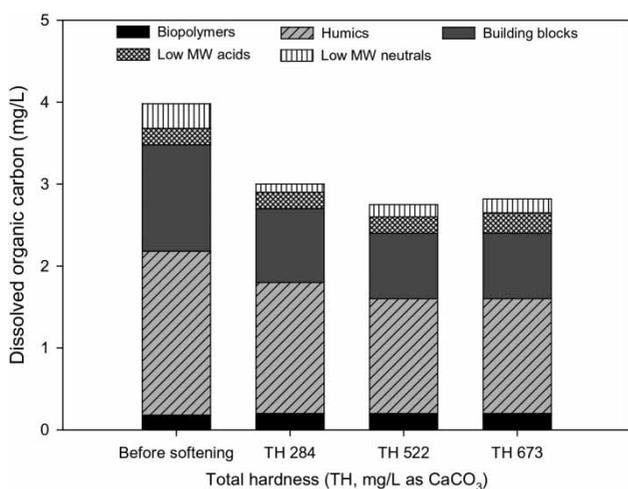

Figure 4 │ Bulk organic matter fractions (biopolymers, humics, building blocks, low MW acids, and low MW neutrals) determined by LC-OCD at different total hardness concentrations during pellet softening (284, 522, and 673 mg/L as CaCO₃).

in the groundwater, and most of the pharmaceuticals were of the hydrophilic and ionic species during pellet softening (pH of 9). The average removal efficiencies of the four different groups of pharmaceuticals during pellet softening were 4.4, 5.8, and 6.8% for total hardness concentrations of 284, 522, and 673 mg/L, respectively, indicating that pellet softening is ineffective for removing the selected pharmaceuticals. Previous studies reported similar results, in which chemical lime softening was ineffective (<25%) for the removal of pharmaceutical and personal care compounds (Westerhoff et al. 2005), and coagulation and lime softening processes were ineffective for the removal of antibiotics (Adams et al. 2002). This study found that pellet softening showed a similar performance to a conventional chemical softening process, and the calcium that crystallized on the surface of the sand grains had no influence on the removal of the selected pharmaceuticals. Many of the selected pharmaceuticals were not effectively removed (<7%) during pellet softening, but the removal efficiency of pharmaceuticals by NF (NaCl 90% and a MWCO of ~200 Da) was significantly higher (Figure 5). For example, bezafibrate (MW: 361) was significantly rejected (>95%), which is at least five times higher than the rate of removal by pellet softening; also, the NF removal efficiencies of gemfibrozil (MW: 250), fenoprofen (MW: 242), ibuprofen (MW: 206), and carbamazepine (MW: 236) were 82, 80, 77, and 67%, respectively. NF rejected compounds with MWs greater than 300, primarily by steric hindrance, and did not completely reject compounds with a MW between 200 Da and 250 Da. Rejection of ionic compounds such as gemfibrozil (MW: 250), fenoprofen (MW: 242), and ibuprofen (MW: 206) was slightly higher than rejection of a neutral compound (carbamazepine, MW: 236), which may be attributed to electrostatic interactions (repulsion) between the charge of anionic pharmaceuticals and the negative charge of the NF membrane surface. The hybridization of pellet softening with NF may be a good multi-barrier approach for improving the performance of pellet softening and NF in drinking water treatment systems. In this study, the hardness removal by pellet softening was only 80% at the optimum conditions; therefore, about 20% of the calcium after softening can complex with anionic pharmaceuticals. Thus, the removal of anionic compounds that are not effectively rejected by NF can be improved by complexing with the remaining calcium, since NF is effective in the removal of divalent ions such as calcium and magnesium. However, it is important to consider the pretreatment process for organic matter when pellet softening is hybridized with NF. Pellet softening is not effective for the removal of organic matter; therefore, the dissolved organic carbon concentration like that used in this study would lead to serious organic fouling on the surface of the NF membrane.

For estrogens, the removal efficiencies of E1, E2, and EE2 at a total hardness of 522 mg/L of $CaCO_3$ and an upflow velocity of 100 m/h were 59 ± 12, 60 ± 21, and $57 \pm 11\%$, respectively (Figure 6). The higher attenuation of estrogens
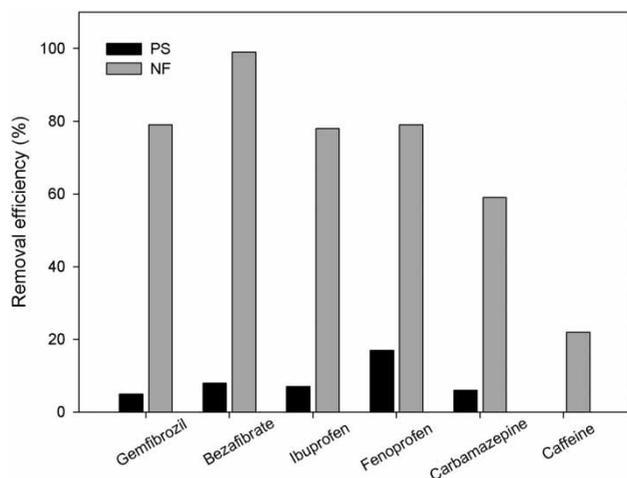

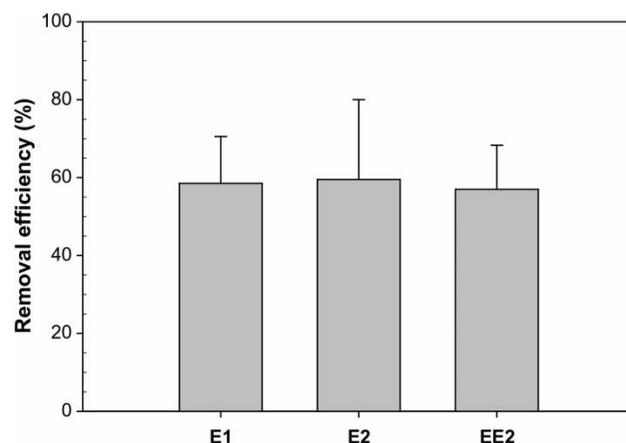Figure 5 | Pharmaceutical removal by pellet softening or NF.

Figure 6 | Removal of selected estrogens (17α-ethinylestradiol (E1), estrone (E2), and 17β-estradiol (EE2)) by pellet softening (total hardness of 522 mg/L as $CaCO_3$, flow velocity: 100 m/h).

may be due to hydrophobic characteristics (log K_{ow} E1: 3.43, E2: 3.94, and EE2: 4.15) via adsorption onto sand grains. Estrogens with a log K_{ow} between 3.43 and 4.15 are preferred for adsorption onto solids, and previous studies reported that adsorption was the dominant mechanism of estrogen removal (17β-estradiol, estriol, and testosterone) during soil passage (Mansell *et al.* 2004; Mansell & Drewes 2004; Maeng *et al.* 2013). Westerhoff *et al.* (2005) reported that neutral hydrophobic compounds, based on log K_{ow} in 22 different endocrine-disrupting compounds and pharmaceutical personal care products, showed a relatively higher removal efficiency compared to compounds with low log K_{ow} values during lime softening, resulting from their sorption onto small particles and precipitated solids. However, bezafibrate, with a log K_{ow} of 4.25 and hydrophobic characteristics similar to estrogens, showed a low reduction during pellet softening. Bezafibrate becomes an ionic compound (pK_a: 3.6) during pellet softening at a pH of 9, and the low reduction may be due to the electrostatic interaction between the negatively charged surface of sand grains and the anion in bezafibrate. Moreover, the occurrence of interactions between NOM in groundwater and the spiked estrogens should not be neglected since dissolved organic matter molecular composition and concentration affect the interactions of pharmaceuticals and personal care products in water (Hernandez-Ruiz *et al.* 2012).

Some reduction was observed in the selected estrogens during pellet softening. However, the activity of estrogens needs to be investigated to confirm complete removal because transformation products can retain estrogenic activity. Hammes *et al.* (2011) detected the bacterial colonization of pellets in a full-scale plant (Leiduin, The Netherlands) for the first time, and characterized the biomass on calcite pellets using adenosine triphosphate and denaturing gradient gel electrophoresis analysis. Further study is necessary to investigate any possible degradation of adsorbed estrogens onto sand grains and the desorption capacity of estrogens.

CONCLUSION

The removal of total hardness via crystallization with selected pharmaceuticals and estrogens during pellet softening was investigated, and the main conclusions are as follows:

- The removal efficiencies of total hardness were 47, 65, 79, and 80% for groundwater with an initial total hardness of 176, 284, 522, and 673 mg/L of $CaCO_3$ at a pH of 9, respectively. The chemical compositions determined by XRD and XRF confirmed that the crystallization of calcium successfully occurred on the surface of sand grains.

- EEM showed that humic-like substances were preferentially removed during pellet softening, and tryptophan protein-like peaks were unchanged. The humic fraction determined by LC-OCD was slightly more attenuated than the fractions of biopolymers, building blocks, low MW acids, and low MW neutrals. SUVA values decreased, indicating that a lower concentration of aromatic organic matter remained after pellet softening. The negatively charged aromatic organic matter could adsorb onto the positively charged calcium carbonate that crystallized on the surface of sand grains during pellet softening.

- In general, most of the 12 selected pharmaceuticals were not effectively attenuated during pellet softening, but a relatively higher amount of estrogens were removed compared to pharmaceuticals. It is expected that the hydrophobic characteristics of neutral compounds such as E1, E2, and EE2 led to higher removal during pellet softening and were considered to be important factors.

- The removal efficiencies of bezafibrate, gemfibrozil, fenoprofen, ibuprofen, and carbamazepine by NF were 99, 82, 80, 77, and 67%, respectively, and were significantly higher than removal efficiencies by pellet softening. The rejection of ionic compounds such as gemfibrozil, fenoprofen, and ibuprofen was slightly higher than the rejection of a neutral compound (carbamazepine), which may be attributed to the electrostatic interactions between the negative charge of anionic pharmaceuticals and negative charge of the NF membrane surface.

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