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REMOVAL OF ANTIBIOTICS FROM SURFACE AND DISTILLED WATERIN CONVENTIONAL WATER TREATMENT PROCESSES

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Abstract: Conventional drinking water treatment processes were evaluated under typical water treatment plant conditions to determine their effectiveness in the removal of seven common antibiotics: carbadox, sulfachlorpyridazine, sulfadimethoxine, sulfamerazine, sul- famethazine, sulfathiazole, and trimethoprim. Experiments were conducted using synthetic solutions prepared by spiking both distilled/ deionized water and Missouri River water with the studied compounds. Sorption on Calgon WPH powdered activated carbon, reverse osmosis, and oxidation with chlorine and ozone under typical plant conditions were all shown to be effective in removing the studied antibiotics. Conversely, coagulation/flocculation/sedimentation with alum and iron salts, excess lime/soda ash softening, ultraviolet irra- diation at disinfection dosages, and ion exchange were all relatively ineffective methods of antibiotic removal. This study shows that the studied antibiotics could be effectively removed using processes already in use in many water treatment plants. Additional work is needed on by-product formation and the removal of other classes of antibiotics.

CE Database keywords: Abatement and removal; Water treatment; Chlorination; Ozonization; Disinfection; Potable water.

Introduction

Recent studies have determined that a variety of antibiotics are present in surface and groundwater throughout the United States, as well as in many other countries (Halling-Sorenson et al. 1998; Daughton and Ternes 1999; Kolpin et al. 1999; Meyer et al. 1999; Meyer et al. 2000a,b; Potera 2000). This occurs, in part, from the discharge or disposal of antibiotics from medical, municipal, and agricultural sources (Halling-Sorenson et al. 1998; Daughton and Ternes 1999). These finding have raised concern regarding poten-tial human health effects caused by low levels of antibiotics in drinking waters (Daughton and Ternes 1999). In a recent literature review of studies on pharmaceutical compounds in the environ- ment, however, virtually no studies were found on potential health effects of chronic low-level exposure to pharmaceuticals.

Similarly, virtually no studies on the removal of pharmaceuti- cals via conventional drinking water treatment processes have been reported. On the other hand, a variety of research addressing methods for treatment of wastewaters containing antibiotics and other pharmaceuticals has been conducted. Generally, biological treatment processes have been shown to be ineffective in the re- moval of antibiotics. For example, Ingerslev and Halling- Sorensen (2000) found that 12 different sulfonamides were not readily biodegradable in activated sludge. Kummerer et al. (1997) investigated treatment of hospital and pharmaceutical wastewater at several wastewater treatment

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plants in Germany. This research showed that many pharmaceuticals could not be biodegraded during conventional biological treatment, nor could they be adsorbed by sewage sludge.

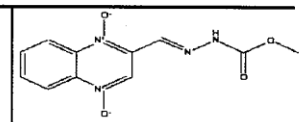
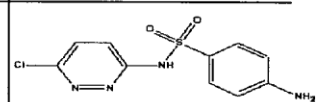
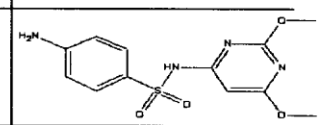
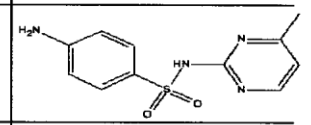
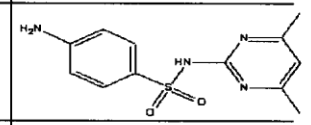
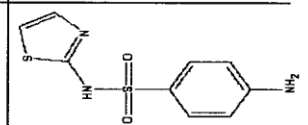
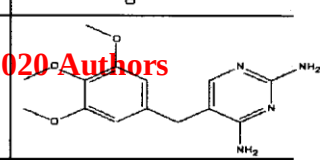
Some combined chemical/biological treatment processes ap- pear to be more effective. Garcia et al. (1995) used aerobic diges- tion integrated with activated carbon filtration and reverse osmo- sis (RO) to reduce biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total dissolved solids (TDS) in phar- maceutical wastewater by approximately 80%. Most of the published studies, however, investigated the removal of pharmaceu- ticals other than antibiotics.

Oxidative treatment has also been shown to be a viable option for the treatment of pharmaceutical process water. Rey et al. (1999) used ozone to inactivate wastewater from pharmaceutical manufacturers of cytostatic drugs. The results showed that more than 90% removal of the compounds was achieved after 45 min. In addition, none of the solutions of oxidized cytostatics gave positive results for the Ames test, indicating that the by-products were not mutagenic. Hofl et al. (1997) used three advanced oxi- dation processes [H_2O_2/ultraviolet (UV), O_3 /UV, and H_2O_2 / Fe^{2+}] for the removal of adsorbable organic halogen (AOX) and COD of pharmaceutical wastewater. The results showed that under test conditions the Fenton method (i.e., Fe^{2+}/H_2O_2) needed the shortest reaction time, and was the most appropriate for the degradation of large amounts of COD (>500 mg/L). There was no significant difference between H_2O_2 /UV and O_3 /UV pro-cesses while ozone alone caused the slowest degradation.

Belter et al. (1973) patented an ion exchange process that used a weak-base anion exchange resin to absorb streptomycin, which could subsequently be eluted with a dilute acid solution. In a later study, Belter (1983) again used ion exchange to remove and re- cover the antibiotics from pharmaceutical water.

Table 1. Chemical Structure and Selected Properties of Study Compounds

The purpose of the current research was to determine the ef- fectiveness of conventional water

Compound, Abbrev., and [CAS #]	Molecular Formula and Weight	pKa	log K_{ow}	Solubility (mg/L)	Analysis Wavelength (nm)	Structure
Carbadox (CARB) [6804-07-5]	$C_{11}H_{10}N_4O_4$ MWT = 262.224	?	?	?	240	
Sulfachloropyridazine SCPD [80-32-0]	$C_{10}H_9ClN_4O_2S$ MWT = 284.719	5.49[§]	?	?	275	
Sulfadimethoxine (SDMX) [122-11-2]	$C_{12}H_{14}N_4O_4S$ MWT = 310.327	5.9 (25 °C)[*]	1.63[‡]	3.43(10^2)[‡]	275	
Sulfamerazine (SMRZ) [127-79-7]	$C_{11}H_{12}N_4O_2S$ MWT=264.301	7[†]	0.14[‡]	2.02(10^2) (25 °C)[‡]	275	
Sulfamethazine (SMZN) [57-68-1]	$C_{12}H_{14}N_4O_2S$ MWT=278.328	7.65[§]	0.28[‡]	4.3(10^2) [‡]	275	
Sulfathiazole (STZL) [72-14-0]	$C_9H_9N_3O_2S_2$ MWT= 255.309	7.1 (25 °C)*	-0.43 (pH 7.5)[δ]	?	275	
Trimethoprim (TRMP) [738-70-5]	$C_{14}H_{18}N_4O_3$ MWT=290.321	7.1 (20 °C)[‡]	0.91[‡]	4.00(10^2) (25 °C)[‡]	230	

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treatment processes in the re- moval of common antibiotics under conditions typical of drinking water treatment plant operations. Specifically, this research exam- ined coagulation, lime softening, powdered activated carbon (PAC) sorption, chlorination, ozonation, ion exchange, ultraviolet photolysis, and reverse osmosis processes.

Materials and Methods

All water treatment chemicals were at least reagent grade and were obtained from Fisher Scientific. Seven antibiotics were in- vestigated in this research: carbadox (CARB), sulfachlorpy- ridazine (SCPD), sulfadimethoxine (SDMX), sulfamerazine (SMRZ), sulfamethazine (SMZN), sulfathiazole (STZL), and tri- methoprim (TRMP) (Table 1). All of these compounds, except

CARB and TRMP, belong to the sulfonamide class of antibiotics. The studied compounds were obtained from the USGS for use in this study. The powdered activated carbon used in this study was Calgon WPH Pulv.

Sample Preparation

Samples were prepared from two standard mixes: Mix F (CARB, SMRZ, SMZN, and SDMX) and Mix G (STZL, SCPD, and
TRMP). These two mixes were selected to allow chromatographic
separation during analysis via reverse-phase high-pressure liquid chromatography (HPLC). Stock solutions of Mixes F and G were prepared with concentrations of 20 mg/L of each antibiotic. Samples were prepared for various treatments by spiking either distilled/deionized (DD) water or Missouri River water (MRW) with the stock solution to an initial concentration of 50 µg/L of each compound. Solutions in DD water were buffered with phos-

phate, while MRW was used as collected. Prior to spiking, MRW was always analyzed for the compounds considered in the study and found to contain none above the detection limit.

The MRW was collected directly from the Missouri River near Jefferson City, Mo. MRW was used unfiltered for lime softening and metal salt coagulation, but prefiltered through a 0.45-µm fil- ter for PAC adsorption, chlorination, ozonation, UV oxidation, ion exchange, and reverse osmosis. Distilled/deionized water was used to examine each process in the absence of turbidity and competition from natural organic matter (NOM).

Analytical Methods

After processing via a specific treatment method, samples were concentrated using solid-phase extraction (SPE) and analyzed using reverse-phase HPLC with ultraviolet detection. The SPE utilized Oasis 6-mL MCX cartridges (Waters No. 186000256) and a 12-position vacuum manifold (Supelco Corp.). In the extraction, the cartridges were prepared by rinsing with 2-mL DD water, 2 mL methanol, 2-mL methanol–ammonium hydroxide (MAH) so- lution, and 2-mL sulfuric acid solution. The MAH solution con- sisted of 95% methanol and 5% ammonium hydroxide [volume-to-volume ratio (v/v)]. The sulfuric acid solution was prepared by adjusting the pH of DD water to 3 using sulfuric acid. Next, 500 mL of sample (or standard) was extracted through the cartridge, followed by a rinse with 3 mL of DD water. The pharmaceuticals were then eluted from the cartridge into a 10-mL test tube with 3 mL of methanol followed by 3 mL of MAH solution. The eluant was spiked with 1,000 µL of a solution of 25-mg/L *t*-buthylazine (TBUT) in methanol as the

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internal standard. The sample wasthen evaporated at 55°C under nitrogen sparge to approximately 20 µL. Finally, 300 µL of 20-mM phosphate buffer solution (pH 6) was added to the sample, followed by transfer to a HPLC vial for analysis.

Reverse-phase HPLC analysis of the study compounds was conducted using a Waters HPLC system [600E controller, 717 autosampler, 996 UV-VIS detector, and Millenium 2010 software(ver. 2.0)] with detection at 275 nm. The method used a Nova-Pak C18 (3.9×150 mm^2) column with a binary gradient from 95% solution A (90/10 ammonium acetate/acetonitrile) to 100% solu- tion B (50/50 ammonium acetate/acetonitrile) over a 15-min ramp. The retention times for antibiotics in Mix F were 5.2, 6.1, 8.0, and 16.2 min for CARB, SMRZ, SMZN, and SDMX, respec- tively; for Mix G they were 5.5, 7.7, and 13.4 min for STZL, SCPD, and TRMP, respectively. The internal standard (TBUT) had a retention time of 22 min. All samples were extracted and analyzed in duplicate providing an average coefficient of varia- tion for duplicate samples of 10%.

Aqueous ozone concentrations were measured using the indigo method (Hach Method 8311). Chlorine was measured using the DPD method (Hach Method 8167) (Hach 1997).

Experimental Design

In these experiments, eight common water treatment processes were evaluated for effectiveness in removing the studied com- pounds. These processes are described below.

Metal Salt Coagulation

Aluminum sulfate [alum; $Al_2(SO_4)_3$ $14H_2O$] and ferric sulfate[$Fe_2(SO_4)_3$ $4H_2O$] were studied as coagulants. Only MRW was examined in the coagulation experiments because DD water has no turbidity. The experiments were conducted in a six-gang stirrer (Phipps & Bird PB700) at a pH of 6.8. Coagulant dosages were 0,20, 40, 64, and 107 mg/L of $Al_2(SO_4)_3$ $14H_2O$, and 0, 25, 42, 85, 127, and 169 mg/L of $Fe_2(SO_4)_3$ $4H_2O$. Optimum sweep flocconditions for alum coagulation have been shown to be at a pH of 7 to 8 with an alum dosage of from 30 to 40 mg/L of $Al_2(SO_4)_3$ $14H_2O$ (Amirtharajah and Mills 1982).

After chemical addition, the samples were mixed at 100 revo- lutions per minute (rpm) for 1 min, flocculated at 30 rpm for 20 min, and then allowed to settle for 3 h. Samples were then care- fully removed and filtered through a 0.45-µm glass fiber filter (Whatman 934-AH) prior to SPE and HPLC analysis.

Lime Softening

In the lime softening experiment, the total, calcium, and magne-sium hardness of the MRW used was determined to be 268, 173,and 95 mg/L as $CaCO_3$, respectively. The alkalinity of the MRW was 77 mg/L as $CaCO_3$. Excess lime/soda ash softening was usedto remove both the calcium and magnesium hardness. Lime andsoda ash dosages were 232 and 191 mg/L as $CaCO_3$, respectively. The softening method involved diluting the Mix F or G stock solution into 2 L of MRW to create a solution at a concentrationof 50 µg/L of each antibiotic. Next, lime and soda ash were addedand the pH was adjusted to 11.3±0.25 using a concentrated so-dium hydroxide solution. The solutions were mixed/flocculated/settled in an identical manner as for the coagulation describedabove. Similarly, sample processing and analysis was conducted as described for the coagulation experiments.

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Powdered Activated Carbon Sorption

The PAC sorption experiments were conducted in a six-gang stir- rer with both MRW and DD water. After placing the appropriate solution into five separate beakers, PAC was added at dosages of 0, 5, 10, 20, and 50 mg/L. The solutions were mixed for 4 h prior to sampling. Shorter contact times, however, are often used in water treatment plants depending on the point of application and the hydraulic design of the plant [American Water Works Asso- ciation (AWWA) 1990]. Samples were taken, filtered, and ana- lyzed in the same manner as described for coagulation. While this contact time might not allow equilibrium to be achieved, it is representative of typical PAC contact times used in water treat- ment plants.

Chlorination

The chlorination experiments were conducted by placing 2 L of filtered MRW or DD water (buffered with 20 mM phosphate) with a pH of 7.5 into beakers on a six-gang stirrer. After spiking with Mix F or Mix G, chlorine was then added to the solution in the form of hypochlorite (OCl^-) solution. Oxidation of the study compounds by free chlorine was conducted at a chlorine concen- tration of 1.0±0.2 mg/L as Cl_2 . Because the pK for the $HOCl/OCl^-$ system is 7.6 at 20°C (White 1999), the concentra- tions of hypochlorous acid (HOCl) and hypochlorite (OCl^-) were approximately equal. Aliquots were collected for 30 min at 5-min intervals and immediately quenched using a slight excess of so- dium sulfite. The SPE and HPLC analysis was then conducted on unfiltered samples.

Ozonation

The ozonation experiments were conducted in a 6-L Pyrex reactor containing 4.5 L of solution consisting of Mix F or G in DD water or Missouri River water buffered to pH 7.5. Ozone was produced at a concentration of 2% [weight-to-weight ratio (w/w)] using an OZAT-0 (Ozononia) ozone generator. The gas-phase ozone con-centration was determined using a PCI ozone monitor (Model HC-12) and corresponds to an ozone saturation concentration (C_{sat}) of 7.1 mg/L (H=0.00187 atm L mg^{-1}; Pontius 1990). In these experiments, the ozone contact with the stock solution was initiated by placing a fine-bubble diffuser into the solution. Vola- tilization losses were shown to be negligible in air-sparge experi- ments. The ozone concentration was then tracked with time using the indigo method for both DD water and MRW systems. Samples were removed periodically for SPE and analysis of phar- maceuticals. The sample beakers contained a slight excess of so- dium thiosulfate solution to allow rapid quenching of residual ozone.

Ultraviolet Photolysis

Ultraviolet photolysis was carried out in a 3.6-L Pyrex photore- actor. A low-pressure mercury vapor lamp (Pen Ray Model 90- 0004-01) (254 nm) was situated in a 5-cm-diameter optical quartz sleeve along the midline of the reactor. The dose rate of the lamp was 5.4 mW/cm^2 at 1.9 cm radius (UVP Inc., Upland, Calif., personal communication, 2001). Refrigerated water passed through tubes along the outside of the reactor to maintain a tem- perature of 20±1°C.

Both filtered MRW and DD water buffered to pH 7.5 with 20 mM phosphate solution were examined. After insertion of the lamp into the reactor, samples were taken at reaction times of 0 to 30 min at 5-min intervals. The SPE and HPLC analysis was then conducted on unfiltered samples.

Ion Exchange

Ion exchange on both strong-acid cation (SAC) and strong-base anion (SBA) resins was examined. The SAC and SBA resins used were Dowex 50W-50×4×400 (11113-61-4, Sigma) and Dowex 1×4-400 (60267-37-0, Sigma), respectively. In these experi- ments, 5-mL glass columns were packed with 0.66 g (3 mL) of weighed dry resin and constituted with DD water overnight be- fore introducing samples. In these column studies, both filtered MRW and DD water spiked with

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antibiotics were passed through the columns at a rate of 1.2 mL/min at a loading rate of 3 gpm/ft^2 (gallons per minute per square foot) using a four-channel peristal- tic pump. The MRW and the buffered DD water influent solutionswere at pH 7.6 and 7.3, respectively. The effluent was collected in500-mL samples followed by SPE and HPLC analysis.

Reverse Osmosis

Removal of antibiotics from filtered MRW and DD water via low-pressure reverse osmosis was examined using a BarnsteadRO system (Model D2716) that utilized a cellulose acetate mem- brane (D2731). The MRW was prefiltered prior to spiking and RO treatment with a 0.45-µm glass fiber filter. The feed rate was 1.9 L/min. The effluent was then analyzed for the antibiotics via SPE and HPLC. Additionally, the total dissolved solids of the feed, product, and waste streams was also analyzed using a Corning CD-55 TDS sensor.

Results and Discussion

The MRW used in this study was collected immediately prior to particular experiments. Specific values and confidence intervals are presented in Table 2. Although not measured directly, a cation/ anion balance indicates water high in sulfate and/or chloride. The pH_{sat} for calcium carbonate based on mean values of alkalinity, calcium hardness, TDS, and temperature was calculated to be 7.8,

Table 2. Chemical and Physical Parameters of Missouri River Waterused in Study

Item	Value (95% confidence interval)
Temperature (°C)	21 (±1.5)
pH	7.7 (±0.32)
Alkalinity (mg/L as $CaCO_3$)	77 (±6.6)
Total hardness (mg/L as $CaCO_3$)	268 (±12.7)
Calcium hardness (mg/L as $CaCO_3$)	173 (±1.8)
Magnesium hardness (mg/L as $CaCO_3$)	96 (±3.7)
Turbidity (NTU)	21 (±4.3)
DOC (mg/L) (0.45-µm filter paper)	10.7 (±6.4)
TDS(mg/L)	482 (±89.8)

indicating that the calcium carbonate system was in equilibrium within the variation observed in the data (Table 2) (U.S. Filter 1996).

Metal Salt Coagulation

Coagulation is the process by which chemicals are added to water to cause destabilization of colloidal particles, allowing aggrega- tion through flocculation, followed by sedimentation. Concurrent removal of soluble species can occur through adsorption of the species on the destabilized colloids followed by concomitant re- moval of the colloids and the adsorbed species.

In this work, however, no significant removal (α=0.05) of anyof the antibiotics considered was achieved with alum or ferric saltcoagulation. Using either coagulant, turbidity was reduced from

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an initial 22 NTU to less than 3 NTU for all coagulant dosages. This work suggests that the studied antibiotics are not likely to be effectively removed via the coagulation process with alum or iron salts. It is interesting to consider, however, that in natural systems, the antibiotics would be in contact with natural colloidal matter (e.g., clays) for extended periods, providing the opportunity for potential sorption of antibiotics on colloidal matter to occur. If adsorbed on colloids, the antibiotics could be co-removed in a coagulation/flocculation/sedimentation process. Additional study is required to test this possibility.

Excess Lime–Soda Ash Softening

The excess lime/soda ash softening process involved precipitation of calcium and magnesium as $CaCO_3$ and $Mg(OH)_2$, respec- tively. During these precipitation processes, large surface areas are generated in solution due to the (initially) exceedingly small diameter of precipitate particles; the large surface areas provide the opportunity for coprecipitation processes to occur (Letterman 1999). Because this study employed excess lime softening in which both $CaCO_3$ and $Mg(OH)_2$ flocs were formed, the pharma- ceuticals were presented with the opportunity to coprecipitate with two different types of solid.

In this work, however, no significant removal (α=0.05) of any of the antibiotics studied was achieved during the softening pro- cess. Thus, lime softening is not a viable means of removing the studied compounds in drinking water treatment plants.

Powdered Activated Carbon Sorption

Calgon WPH Pulv PAC is commonly used in drinking water treatment plants for the removal of a wide range of synthetic organic chemicals, taste and odor compounds, and NOM. In these

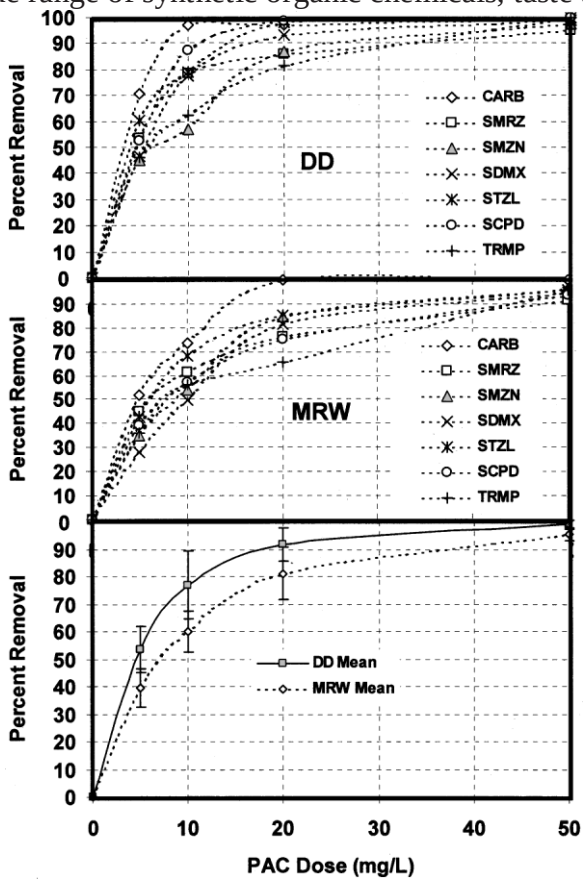

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Fig. 1. Percent removal of study compounds for powdered activated carbon (Calgon WPH Pulv) in distilled/deionized (DD) water (top) and Missouri River water (MRW) (middle). Average removal (bot- tom) for DD and MRW showing overlapping 95% confidence intervals.

experiments, contact times of 4 h were employed to simulate actual processing in water treatment plants better than running the experiments to equilibrium at each dosage.

In DD water, the percent removal of each of the antibiotics ranged from 57 to 97% and 81 to 98% for PAC dosages of 10 and 20 mg/L, respectively (Fig. 1, top). In MRW, the percent removal of each of the antibiotics ranged from 49 to 73% and 65 to 100% for PAC dosages of 10 and 20 mg/L, respectively (Fig. 1, middle). With a PAC dosage of 50 mg/L in both DD water and MRW, the percent removal was greater than 90% for all compounds (Fig. 1). There was no statistical difference between the average removal of the studied antibiotics from DD versus MRW based on over- lapping 95% confidence intervals (Fig. 1, bottom)

The results show that PAC sorption provides a viable means with which to treat these pharmaceuticals at common PAC dos- ages. However, PAC is typically used for only a portion of the year at many treatment plants; therefore, expanded usage would increase operating costs correspondingly.

Chlorination

Chlorination experiments were conducted at a chlorine concentra- tion of 1 mg/L as Cl_2 in both DD water and MRW. From the results of these experiments, reaction times required for 50 and 90% removal ($t_{0.50}$ and $t_{0.90}$, respectively) were determined for

Table 3. Times to 50 and 90% Removal ($t_{0.5}$ and $t_{0.9}$, Respectively) of Studied Antibiotics for Reaction with Free Chlorine at 1.0 mg/L as Cl_2

	$t_{0.5}$ (min)		$t_{0.9}$ (min)	
Compound	DD	MRW	DD	MRW
CARB	0.8	3.4	4	35.5
SCPD	2.1	3.6	12.8	27.9
SDMX	2.0	2.9	9.1	10.1
SMRZ	1.8	3	9.1	15.9
SMZN	2.0	2.9	9.6	9.7
STZL	0.6	2.8	3	8
TRMP	2.8	4.3	23.2	40.5

ranged from 2.8 min for STZL to 4.3 min for TRMP. Ninety percent removal of the studied compounds in MRW required from 8 min for STZL to 35.5 and 40.5 min for CARB and TRMP, respectively (Table 3). In DD water, removal times were shorter than in MRW. The reason for the slower reaction rates in MRW compared with DD water suggests that NOM may complex or otherwise interact with the studied compounds in a manner that reduces reactivity.

CT (concentration time) values for free chlorination to achieve a 99.9% reduction in *Giardia lamblia* range from 56 mg min/L at 20°C (pH 7) to 312 mg min/L at 5°C (pH 9) (Let- terman

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1999). These values correspond to a contact time of from 6 to 31 min at 1 mg/L for the 0.5-log removal often required for the chlorine disinfection stage in a typical surface water treatment plant. Thus, at these contact times with chlorine, removal of the studied antibiotics is expected to range from at least 50 to greater than 90%.

Chemical oxidation of organic compounds using free chlorine as the oxidant can often lead to chlorinated by-products. In fact, HPLC/UV chromatograms from this study show that oxidation by-products are being formed from chlorination. While examina- tion of the by-products was beyond the scope of this study, the possible formation of chlorinated by-products (and their relative
toxicity) should be investigated in further research.

Ozonation

Ozonation reactions with the studied antibiotics were rapid; re- movals of greater than 95% were achieved for each compound within 1.3 min in MRW and utilized 0.006 mM (0.3 mg/L) of absorbed ozone (Fig. 2). (Reactions were even faster in DD water

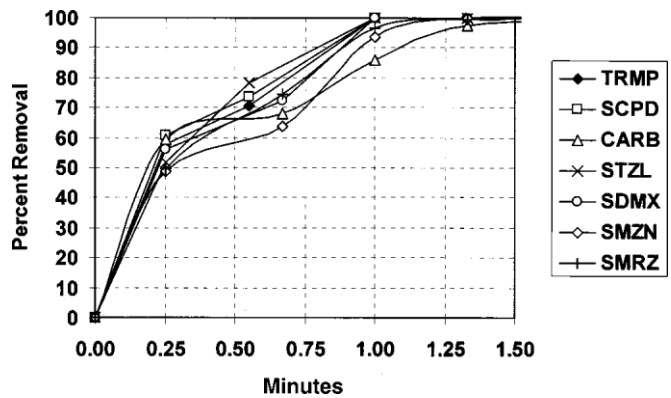
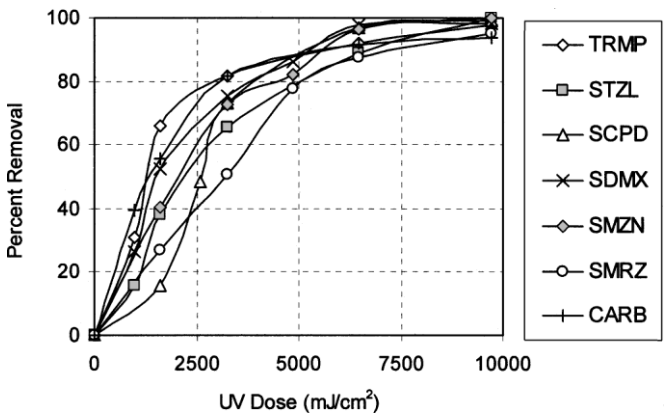


Fig. 2. Percent removal of study compounds versus ozonation time
the studied compounds (Table 3). In MRW, half-lives ($t_{0.50}$)



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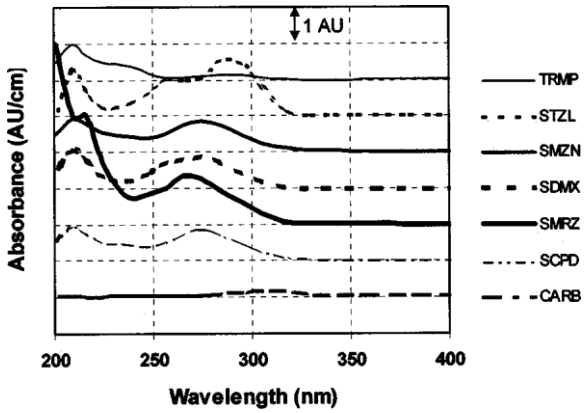

Fig. 3. Percent removal of study compounds versus ultraviolet dose (254 nm) in distilled/deionized water

systems.) The bulk ozone concentration in the MRW within this time period was always measured to be less than 0.05 mg/L by the indigo method, indicating rapid ozone consumption in the liquid phase. Thus, even with very low bulk ozone concentrations (below levels typically employed in water treatment plants), ozone was found to be highly effective at achieving pharmaceu- tical oxidation to levels below detection limits.

No additional absorbance peaks on the HPLC/UV chromato- grams were observed after ozonation of the pharmaceuticals. As- suming that some oxidation by-products were formed, this lack of additional peaks on the HPLC/UV chromatograms would suggest one of two possibilities: either the by-products do not absorb in the ultraviolet spectrum due to ozonation of absorption bands, or the retention times of the by-products are much shorter than those of the parent compounds. Shorter by-product retention times could be caused by increased hydrophilicity resulting from the formation of additional acidic or related functional groups. Deter-mination of the nature and concentrations of the resulting oxida- tion by-products was beyond the scope of this study and warrants additional research.

Ultraviolet Photolysis

Analysis of the ultraviolet photolysis results requires comparison with UV dosages commonly utilized in disinfecting water. Typical ultraviolet dosages for water disinfection are on the order of 30

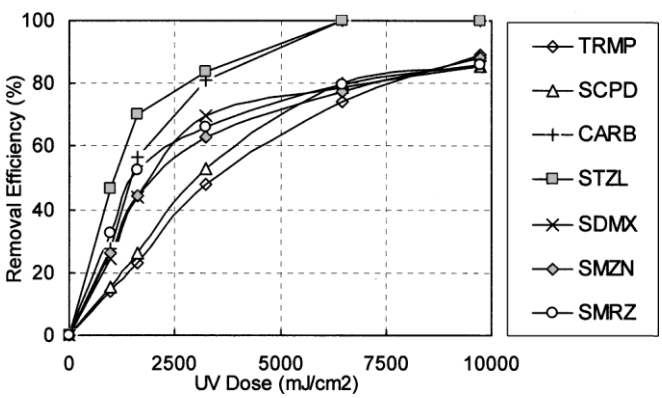

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Fig. 4. Percent removal of study compounds versus ultraviolet dose (254 nm) in Missouri River water

Fig. 5. UV spectra for study compounds at concentration of 32 mg/L (except for sulfathiazole (STZL) and sulfamerazine (SMRZ) which were each at 16 mg/L). Absorbance of each compound was less than
0.1 absorbance units (AU) at 400 nm. Note that initial concentration of pharmaceuticals in UV photolysis (and all other) experiments was 50 µg/L or almost three orders of magnitude lower than for these scans.

$mJ•cm^{-2}$ ($mW•s•cm^{-2}$) (T. Masters, Aquionics Inc., Erlanger, Ky., personal communication, 2001).

Even with UV dosages of 3,000 mJ/cm^2, each of the antibiot- ics examined was removed from both DD water and MRW only between 50 and 80% (Figs. 3 and 4, respectively). These dosages are on the order of 100 times greater than the aforementioned typical disinfection dosage. Although reactor configuration has a significant effect on absorbed UV dosage, it is apparent that UV radiation at 254 nm at typical dosages used for disinfection is not effective at removal of the study antibiotics.

This relative inefficiency results in part from the lack of suf- ficiently strong ultraviolet absorption of the studied compounds (at 254 nm). Ultraviolet/visible spectrophotometric analysis was performed on the studied compounds at concentrations approxi- mately three orders of magnitude greater than the 50 µg/L used in the UV-photolysis experiments (see Fig. 5). The calculated UV absorbance of the pharmaceuticals studied would be on the order of 0.00001 to 0.00005 cm^{-1} at 254 nm based on these data. This absorbance may be compared with the absorbance of filtered Mis-souri River water (Fig. 6), which ranges from 0.90 to 0.07 cm^{-1} at 200 and 300 nm, respectively, and is 0.11 cm^{-1} at 254 nm. Therefore, the pharmaceuticals are not competitive with NOM for UV radiation. Furthermore, it should be noted that the pharma-

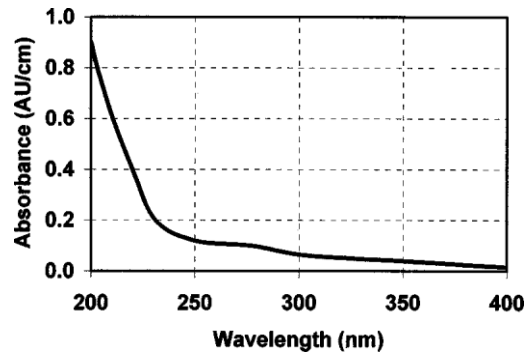

Fig. 6. Ultraviolet absorbance spectrum of Missouri River water used in study

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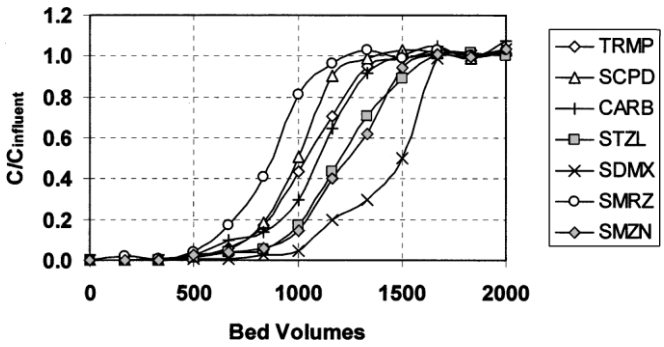

Fig. 7. Ion exchange breakthrough curve for study compounds in distilled/deionized water on Dowex 1×4-400 strong-base anion exchange resin

Table 4. Ion Exchange Capacities for Studied Antibiotics in Distilled/Deionized (DD) Water and Missouri River Water (MRW) on Dowex 1×4-400 Strong-Base Anion Exchange Resin

Compound	Capacity in DD water		Capacity in MRW		% difference
	(mg/g)	(mol/mL)	(mg/g)	(mol/mL)	
TRMP	0.23	3.7E-06	0.18	2.9E-06	21
SCPD	0.25	4.0E-06	0.16	2.6E-06	34
CARB	0.25	3.8E-06	0.16	2.7E-06	36
STZL	0.28	4.9E-06	0.12	2.1E-06	57
SDMX	0.32	4.7E-06	0.13	2.0E-06	58
SMZN	0.28	4.7E-06	0.12	2.0E-06	58
SMRZ	0.21	3.7E-06	0.10	1.8E-06	51

ceuticals considered were chosen in part for their ability to absorb in the UV spectrum to facilitate HPLC/UV analysis.

These results show that UV photolysis alone (at 254 nm) is not a viable means of removing the studied compounds from drinking water at typical dosages used for disinfection at water treatment plants.

Ion Exchange

Ion exchange using a strong-acid cation exchange resin resulted in immediate breakthrough for all studied compounds in both DD water and MRW at pH 7.3 and 7.6, respectively (data not shown). At significantly lower pH levels (uncommon in water treatment plants), it is possible that greater capacities might have been achieved due to increased positive character of the pharmaceuti- cals, related to the protonation of amine groups.

Anion exchange experiments employing a strong-base anion exchange resin were only slightly more effective. Breakthrough curves for these experiments with DD water and MRW are pre- sented in Figs. 7 and 8, respectively. In DD water, there was little immediate breakthrough from the column (Fig. 7). However, only fairly low capacities of 3.7×10^{-6} to 4.9×10^{-6} mol/mL resin (0.21–0.32 mg compound/g resin) were achieved.

Even lower ion exchange capacities were achieved in MRW (Fig. 8). The percent reduction in capacity between DD water and MRW ranged from 21 to 58% (Table 4).

Overall, the primary reason for the low exchange capacities may be related to the insufficient ionized functional groups on the pharmaceuticals. The pK_as for the studied compounds (excluding

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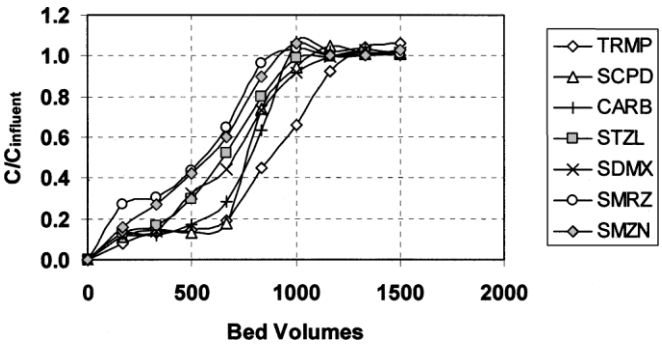

Fig. 8. Ion exchange breakthrough curve for study compounds in Missouri River water on Dowex 1×4-400 strong-base anion ex- change resin

CARB) ranged from 5.5 to 7.65 (Table 1). (The pK_a for CARB was not found in the literature.) The small amount of anion ex- change capacity observed may be due to weak interactions be- tween the partially negative functional groups on the pharmaceu- ticals and the cationic functional groups on the SBA resin. The functional groups gain their localized negative charge in part from unpaired electrons on oxygen (and nitrogen) species or due to aromatic moieties.

The reduced capacity observed in the MRW experiments is suspected to result from competition for exchange sites with the NOM present in solution. The NOM is expected to contain sig- nificant humic substances, which are rich in carboxylate and phe- nolic groups in the dissociated, anionic form at the experimental pH (Thurman 1985). These experiments suggest that ion ex- change is not a viable means of controlling the concentrations of these pharmaceuticals in drinking water.

Reverse Osmosis

Reverse osmosis was examined using a low-pressure reverse- osmosis system with a cellulose acetate membrane. In these ex- periments, a total dissolved solids rejection of 86% was achieved. The rejection rate for the antibiotics averaged 90.2% (s=0.09) from DD water and 90.3% (s=0.15) from MRW. With the rejec- tion rates observed, 99 and 99.9% rejection could be achieved with two and three RO units in series, respectively. Reverse os- mosis is not usually economical (and hence is not common) in most municipal drinking water plants. Although available only in selected treatment plants, RO is a viable means of removing these pharmaceuticals from drinking water.

Conclusions

Common drinking water treatment processes were examined under typical plant conditions with respect to their ability to re- move seven antibiotics from distilled/deionized and Missouri River water. Powdered activated carbon effectively removed the antibiotics at typical plant dosages. However, a residuals issue could exist in that the antibiotics are simply transferred from the water to the PAC, which would typically end up in backwash solids from rapid sand filters. Based on the results for PAC, one would expect that similar granular activated carbons (GACs) would also be highly effective at removing the study antibiotics. Granular activated carbon is typically utilized in postfiltration contactors or in GAC-capped filters (AWWA 1990), and can often be even more effective that PAC. Additional research is required on the use of GAC to treat antibiotics.

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Oxidation of the antibiotics with both ozone and chlorine at typical doses was effective at removal of the studied antibiotics. The chlorination and ozonation by-products and pathways, as well as the pharmacological properties of these by-products, were not determined in this study. Oxidation with combined chlorine species or with chlorine dioxide was not examined, but also war- rants further study.

Reverse osmosis was effective at removal of the studied com- pounds with rejection levels of greater than 90%. A concentrated reject stream, however, would still require additional attention.

Little antibiotic removal resulted from coagulation/ flocculation/sedimentation with alum or ferric salt, excess lime/ soda ash softening, ultraviolet radiation, or ion exchange. Overall, the results of this study suggest that control of the studied antibi- otics can be achieved at surface water treatment plants with com- mon treatment steps, i.e., carbon sorption and oxidation with ozone or chlorine species. Further work is needed on the removal of other antibiotics and pharmaceuticals in conventional drinking water treatment plants.

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