DIVISION OF ENVIRONMENTAL CHEMISTRY

238th ACS National Meeting
Washington, DC
August 16-20, 2009

THURSDAY MORNING

Emerging Contaminants, Pharmaceuticals and Personal Care Products, and Organohalogens in Wastewater and Municipal Biosolids

R. U. Halden, *Organizer*
A. Sapkota, *Organizer, Presiding*

8:30 —214. Assessment of estrogenicity and estrogenicity drivers in a WWTP mixing zone. **S. A. Pagsuyoin**, R. J. Classon, W. Hedgepeth, W -S. Lung, L. M. Colosi

8:50 —215. Removing steroids from contaminated waters using radical reactions. **S. P. Mezyk**, E. Abud, K. L. Swancutt, D. D. Dionysiou

9:10 —216. Nitrosamine and chloropicrin formation from strong base anion-exchange resins. **J. M. Kemper III**

9:30 —217. Removing contaminant *beta*-lactam antibiotics from waters using radical reactions. **M. K. Dail**, S. P. Mezyk, J. R. Peller

9:50 —218. Dispersability behavior of diagnostic gold nanoparticles in the presence of humic substances. **V. L. Pallem**, H. A. Stretz, M. J. M. Wells

10:10 — Intermission.

10:30 —219. Oxidative transformation of lincosamide antibiotics by manganese oxide. **W -R. Chen**, Y. Ding, C. T. Johnston, B. J. Teppen, S. A. Boyd, H. Li

10:50 —220. Radical chemistry of mixed aliphatic-aromatic nitrosamines in water. **E. Abud**, S. P. Mezyk, K. L. Swancutt, T. Foust, J. J. Kiddle

11:10 —221. Sonochemical degradation of pharmaceuticals and personal care products using continuous and pulsed ultrasound in aqueous solution. **R. Xiao**, L. Weavers

11:30 —222. Sulfate radical remediation of contaminant antibiotics in water. **K. Rickman**, S. P. Mezyk

11:50 —223. Transformation of tetracycline antibiotics promoted by aluminum oxide surfaces. **W -R. Chen**, C -H. Huang

12:10 —224. Absolute kinetics and efficiencies of oxidizing and reducing radical reactions with sulfa antibiotics in water. **T. Neubauer**, S. P. Mezyk, J. R. Peller

ABSTRACTS

ENVR 214

Assessment of estrogenicity and estrogenicity drivers in a WWTP mixing zone

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The persistence and toxicity effects of endocrine-disrupting chemicals (EDCs), including environmental estrogens, have not been well-characterized in wastewater treatment plant (WWTP) mixing zones. This study incorporates liquid chromatography-tandem mass spectrometry (LC/MS-MS) measurements of several key estrogenic compounds (*e.g.*, estradiol, estrone, etc.) into a surface water model for low-flow mixing zone conditions. This model will ultimately be used to back-calculate the attenuation rate of estrogens in rivers receiving effluent from small and medium-sized municipal WWTPs. Estrogenicity measurements, as determined using a fluorescent enzyme-linked receptor assay (ELRA), are also reported as means to evaluate the formation of estrogenicity "hot spots" within the mixing zone of the medium-sized municipal WWTP. Finally, composite estrogenicity measurements are compared with individual estrogen concentrations to identify key estrogenicity drivers and important interactions between multiple contaminants in municipal effluent. Keywords: estrogenic activity, receptor assay, LC/MS-MS.

ENVR 215

Removing steroids from contaminated waters using radical reactions

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Of the many classes of chemicals that have been identified as pharmaceutical contaminants in water, one of the most important is the steroids. Steroids are particularly significant, as they can have biochemical effects even at extremely low levels. Unfortunately, their quantitative removal is very difficult due to the presence of much higher levels of other species such as dissolved organic matter and carbonate. Therefore, radical-based treatment processes continue to gain interest as the

technology of choice. These technologies, collectively called advanced oxidation/reduction processes (AO/RPs) generate oxidizing and/or reducing radicals in the water, which react with, and destroy, these chemicals. In support of the application of these technologies, we report here on our direct rate constant measurements for the reactions of the oxidizing hydroxyl (·OH) and sulfate ($SO_4^{-\cdot}$) radicals, as well as reducing hydrated electrons (e_{aq}^-) and hydrogen atoms (H·), with estrogenic steroids in waters.

ENVR 216

Nitrosamine and chloropicrin formation from strong base anion-exchange resins

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Strong base anion-exchange resins represent an important option for water utilities and homeowners to address growing concerns with nitrate, arsenate, and perchlorate contamination of source waters. For three common varieties of commercial anion-exchange resins, we evaluated the importance of releases of nitrosamines, dimethylnitramine, and chloropicrin when the resins were subjected to typical column flow conditions with and without free chlorine or chloramine application upstream or downstream of the columns. In the absence of disinfectants, resins usually released 2-10 ng/L nitrosamines, with excursions of up to 20 ng/L following regeneration. However, the lack of significant nitrosamine release in a full-scale anion-exchange treatment system after multiple regeneration cycles indicates that releases may eventually subside. With free chlorine or chloramine application upstream, nitrosamine concentrations were more significant, at 20-400 ng/L depending on resin type.

ENVR 217

Removing contaminant *beta*-lactam antibiotics from waters using radical reactions

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Beta-lactam antibiotics are some of the most prevalent pharmaceutical contaminants currently being found in aquatic environments. Their presence, even at trace levels, will contribute to the production of antibiotic-resistant bacterial strains. Therefore, the active removal of all antibiotic activity may be necessary under some water use, or reuse, applications. The radical-based advanced oxidation processes (AOPs) are being investigated for their suitability for this chemical elimination in different quality waters. However, a full understanding of the kinetics and mechanisms of all the radical

reactions involved under the conditions of use is necessary to ensure that AOP treatment occurs efficiently and quantitatively. Therefore, in this study, we report on kinetic measurements and radical degradation efficiencies involving both the oxidation and reduction of a large library of ß-lactams in aqueous solution over the anticipated plant-scale range of temperatures.

ENVR 218

Dispersability behavior of diagnostic gold nanoparticles in the presence of humic substances

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The fate and transport of diagnostic gold nanoparticles in surface waters would significantly depend on their interactions with humic substances, which are ubiquitously found in natural aquatic systems. The current study employs UV-visible absorbance and fluorescence spectroscopy to investigate the interactions of commercial humic acid (HA) with gold nanoparticles having core size of 5 nm; and coated with two different surfactants beta-D-glucose and citrate. The humic substances are fluorescent in nature, providing an interesting tool to characterize the interactions between these natural polyelectrolytes and model water soluble gold nanoparticles due to photo-physical changes. Quenching of fluorescence intensity was observed with ß-D-glucose coated gold nanoparticles whereas an enhancement effect was noticed with the citrate coated particles when mixed with humic acid having concentrations of 2 and 8 ppm. Examining the quenching/enhancement of fluorescence provides insight into the structural changes taking place at the gold nanoparticle and humic acid interface. The quenching behavior suggested ligand exchange due to intimate contact between the HA and ß-D-glucose coated gold nanoparticles, whereas the enhancement effect with citrate particles would indicate over-coating leading to increased transfer distances for fluorescent resonance energy transfer.

ENVR 219

Oxidative transformation of lincosamide antibiotics by manganese oxide

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Lincosamides are among the frequently detected antibacterial agents in wastewater treatment plant effluents and surface runoff from agricultural practice, posing potential ecological and health risks. Lincosamide antibacterials cannot degrade easily, hence are persistent in the environment. This study reveals that MnO_2 serves as a powerful oxidant to oxidize lincosamides. The reaction occurs mainly *via* opening the pyranose ring along with multiple oxygenation and dehydrogenation steps, leading to a variety of degradation products. The transformation products were identified by LC/MS/MS. The reaction pathways involve the cleavage of the C-O bond in the pyranose ring and formation of new carbonyl group, which was further confirmed by FTIR analysis. The reactions were affected by aqueous conditions and composition (*e.g.*, pH, presence of dissolved organic matter, and inorganic species), suggesting that environmental factors play an important role in the attenuation of lincosamide reactions in the soil-water environment.

ENVR 220

Radical chemistry of mixed aliphatic-aromatic nitrosamines in water

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Nitrosamines (R,R'N-NO) are a diverse group of carcinogenic chemicals that are ubiquitous in the environment. While considerable research has been reported on the low molecular weight aliphatic nitrosamines, there is much less information available for the aromatic-containing species. The mixed aliphatic/aromatic nitrosamines are representative of the alkaloids formed in tobacco smoke. In this work, we have synthesized a library of model mixed aromatic-aliphatic containing nitrosamines, with phenyl/benzyl/pyridyl moieties and linear chains containing 1-4 carbon atoms. The oxidation and reduction of these chemicals in water, utilizing the advanced oxidation process radicals (hydroxyl radical, ·OH; hydrated electron, e_{aq}^-, hydrogen atom H·) was then conducted using electron pulse radiolysis techniques. The measured reaction rate constants, radical degradation efficiencies, and reaction pathways for these three radicals were determined, and compared to data previously reported for the aliphatic nitrosamines.

ENVR 221

Sonochemical degradation of pharmaceuticals and personal care products using continuous and pulsed ultrasound in aqueous solution

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Pharmaceuticals and personal care products (PPCPs) is one large and important class of emerging organic contaminants. In this study, the degradation of two PPCPs (ibuprofen and ciprofloxacin), and two other environmentally relevant compounds (daidzein and *p*-nitrophenol, *p*-NP) by continuous and pulsed ultrasound were investigated. The pseudo first-order degradation rate constants, k (s^{-1}), were determined under an initial concentration of 10 micromole/L, power density of 45 W/L, and pH of 4. A comparison of rate constants between continuous and pulsed ultrasound revealed that the efficiency of pulsed ultrasound was either faster or slower than continuous mode degradation and compound dependent. To explore the reason for compound dependent increases or decreases in pulsed ultrasound degradation efficiency, a bulk solution OH radical trapping agent, KI, was added and sono-irradiated together with each compound to examine the portion of degradation that occurred in the bulk phase. Results indicated that the percentage of degradation of compounds in bulk phase is strongly associated with the octanol-water partition coefficient (K_{OW}) of the compound.

ENVR 222

Sulfate radical remediation of contaminant antibiotics in water

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The removal of trace amounts of pharmaceuticals such as antibiotics from waters is one of the biggest problems currently facing water utilities. The use of advanced oxidation processes (AOPs), which utilize the generation of radicals to non-selectively destroy such chemical contaminants in waters, is therefore being considered. Typically AOPs generate oxidizing hydroxyl radicals, but another approach is the use of sulfate radical-based AOPs. Sulfate radicals are also highly oxidizing species that could be used to remediate contaminated waters. In this study, we have determined the absolute rate constants for sulfate radical reaction with a large library of antibiotics in waters, utilizing the hydrated electron reduction of persulfate ($S_2O_8^{2-}$) by electron pulse radiolysis. Preliminary measurements for the efficiency of these reactions have also been determined through steady-state radiolysis and HPLC techniques.

ENVR 223

Transformation of tetracycline antibiotics promoted by aluminum oxide surfaces

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Tetracycline antibiotics (TCs) including tetracycline (TTC), oxytetracycline (OTC) and chlorotetracycline (CTC) adsorbed strongly to aluminum oxide (Al_2O_3), and the surface interaction promoted structural transformation of the TCs – a phenomenon not recognized previously. For example, at [TC]=0.04 mM, [Al_2O_3]=0.17 g/L, pH=5, and T=22°C, rapid adsorption of TCs to Al_2O_3 occurred in the first three hours, followed by steady decrease of TCs in which the kinetics could be fitted by a first-order decay model, and product formation. Evaluation of the effect of initial TC concentration, initial Al_2O_3 concentration and pH showed that the transformation rate of TCs was strongly related to adsorption - higher adsorption, faster transformation rate. Experiments conducted under oxygen-free conditions yielded the same results as those in the presence of oxygen, indicating that redox reaction was not involved. Product evaluation indicated that Al_2O_3 transformed TTC to its anhydrotetracycline (AHTTC) and two other unidentified products, transformed CTC to iso-CTC and keto-CTC, and transformed OTC to an unidentified isomerized product. Al oxide surfaces, owing to their strong Lewis acidity, facilitated the above acid-catalyzed dehydration and isomerization of TCs. The formation of AHTTC is of concern because of its higher cytotoxicity than TTC.

ENVR 224

Absolute kinetics and efficiencies of oxidizing and reducing radical reactions with sulfa antibiotics in water

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Absolute rate constants and reaction efficiencies are of fundamental importance for the implementation and optimization of advanced oxidation process (AOP) treatment of contaminant drugs in waters intended for reuse. In this work, we have measured these parameters for hydroxyl radical and hydrated electron reaction with a library of sulfa antibiotics in water using a combination of electron pulse radiolysis/absorption spectroscopy and steady-state radiolysis/HPLC measurements. The consistent radical reaction rate constant of ~8.5 x 10^8 M^{-1} s^{-1} for hydroxyl radical oxidation in water implies

a common initial reaction mechanism, believed to be addition of this radical to the sulfanilic acid moiety in these drugs. Concomitant consistent degradation efficiencies of ~45% were also determined for these chemicals. In contrast, the reduction of these contaminants by hydrated electron reaction had widely varying rate constants and efficiencies suggesting that reduction occurs predominately at the heterocyclic ring for each of the sulfa drugs.