Molecular basis for actinide/lanthanide separations

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The organic molecules CyMe₄-BTBP and CyMe₄-BTPhen, are potential SANEX/GANEX extractants due to their high selectivity for minor actinides over lanthanides.¹ This selectivity opens the possibility of a partitioning and transmutation strategy for managing spent nuclear fuel. Our work with Ln(III) (Ln = Pr, Eu, Tb), U (IV/VI) and Th(IV) has provided significant information about metal speciation with these extractants in both the solid [Fig. 1] and solution states [Fig. 2] through the use of single crystal XRD, EXAFS, electronic absorption (IR/Raman) and NMR spectroscopies. Selected parts of this work will be presented to demonstrate how the application of multiple characterisation techniques can provide information about metal speciation under extraction conditions. Further work is planned to investigate the speciation of transuranics with these extractants.
Investigating the kinetics of the hydroxyl radical reaction with lanthanide complexed-DTPA

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As geological waste disposal of high-level radioactive waste has considerable negative impact on the environment the recycling of nuclear fuels through solvent extraction processes to extract the remaining actinides is one of the most important strategies required for viable nuclear power in the future. The aim of this study was to establish the radiolytic stability of the extraction ligand DTPA (diethylenetriaminepentaacetic acid) under TALSPEAK acidic pH conditions was first investigated through its reaction rate constant with the hydroxyl radical. Specific rate constants were obtained over a range of pH conditions using thiocyanate competition kinetics. Based on literature pKₐ values and rate constant measurements at multiple pH's, rate constants for the species DTPA-H₅, DTPA-H₄⁻ and DTPA-H₃²⁻ of 2.69 x 10⁹, 3.40 x 10⁹ and 3.26 x 10⁸ M⁻¹ s⁻¹ have been determined. This approach was then used to elucidate the same kinetic parameters for Eu³⁺, Lu³⁺ and Gd³⁺ lanthanide metal-complexes.
Radiation-induced radical degradation kinetics of separations ligands

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The full development and implementation of solvent extraction-based nuclear waste reprocessing separations requires an understanding of the radiation-induced ligand degradation occurring. Radiation effects on solvent extraction formulations may result in decreased ligand concentration, lower metal distribution ratios, reduced separation factors through the generation of undesired complexing products, and impaired solvent performance due to films, precipitates, and increased viscosity. Recently, we have undertaken a systematic investigation into the kinetics of some of the important radicals (hydroxyl, $\cdot$OH, and nitrate, NO$_3$\textsuperscript{$\cdot$}) with extraction ligands (e.g. TBP, DTPA) and modifier/buffers (e.g. Cs-7SB, lactic acid). These measured rate constants are also compared to distribution ratio values for solvent systems irradiated by both gamma and alpha irradiation.

I&EC 4

Kinetics of the ALSEP process studied by microfluidic solvent extraction

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Separation of the minor actinides (Am, Cm) from the lanthanides at an industrial scale remains a significant technical challenge for closing a nuclear fuel cycle. One bottleneck in the design of next-generation solvent extraction-based nuclear fuel reprocessing schemes is a lack of interfacial mass transfer rate constants obtained under well-controlled conditions for lanthanides and actinides; such rate constants are a prerequisite for mechanistic understanding of the extraction chemistries involved and are of great assistance in the design of new processes. In addition, rate constants obtained under conditions of known interfacial area have immediate, practical utility in models required for the scaling-up of laboratory-scale demonstrations to industrial-scale solutions. Existing experimental techniques for determining these rate constants suffer from two key drawbacks: either slow mixing or unknown interfacial area. The volume of waste produced by traditional methods is an additional, practical concern in experiments involving radioactive elements, both from disposal cost and experimenter safety standpoints. We utilize a plug-based microfluidic system that uses flowing plugs (droplets) in microfluidic channels to determine absolute interfacial mass transfer rate constants under conditions of both rapid mixing and controlled interfacial area. Experiments were performed to determine the rate constants of the ALSEP process, which separates the fission products from used nuclear fuel in one combined process.
following co-extraction of U, Np, and Pu. The utility of these rate constants for mechanistic insight and process design will be discussed.

I&EC 5

Experimental-theoretical approach to understanding Am-DTPA complexation under TALSPEAK conditions

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One of the most significant challenges affecting the development of a closed nuclear fuel cycle is the separation of minor actinides from lanthanide contaminants in spent nuclear fuel. While several methods have been explored, the TALSPEAK process remains one of the most promising although, the fundamental chemistry behind the separation is still not fully understood. The vast quantity of data available for TALSPEAK provides an excellent platform for studying the basic fundamental factors that dictate the chemical separations process. In this contribution, we will describe our efforts evaluating the specific interactions of Am³⁺ with DTPA for the pH range 2.5 - 4.5 through a combination of Raman spectroscopy and hybrid density functional theory (DFT) to understand the metal-ligand interactions. Since the Am³⁺ - DTPA complexes can exist at various degrees of protonation, the experimental data allows for determination of the ratios of those complexes at their respective degrees of protonation across the pH range investigated. The DFT results will tie experimental trends in preferred protonation sites to Am-DTPA orbital interactions. Also, we will describe how the electronic structure and bonding associated with DTPA leads to selectivity of minor actinide species.

I&EC 6

Two-phase calorimetric measurements of the enthalpy of extraction of f-elements using solvating phase transfer reagents

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Liquid/liquid extraction continues to be the preferred method for processing spent nuclear fuel into manageable components. Before implementing such processes, it is important to build thermodynamic models to describe these extraction systems. Traditionally, thermodynamic parameters (ΔH, and ΔS) for biphasic reactions have been determined indirectly using the van `t Hoff method after ΔG values are determined. Though this method is sound, direct measurement of the thermodynamic parameters can provide more accurate results simultaneously allowing comparison of media effects. Recent work has shown direct measurement of the enthalpies of extraction for biphasic reactions is possible using two-phase calorimetry. In this presentation, the
calorimetrically determined heat of extraction of f-elements by the solvating extractant TBP will be reported on. The results obtained will be compared with van 't Hoff measurements for the same extractant and the merits of applying heats of extraction obtained via calorimetry will also be discussed.

I&EC 7

Complexation of purified Cyanex301 with Ln(III) and An(III)

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The complexation of purified Cyanex301, bis(2, 4, 4-trimethylpentyl)dithiophosphinic acid, with trivalent lanthanides (Nd, Sm, Tb) and curium was studied with spectroscopic methods. The complex species were identified and the formation constants were determined by spectroscopic titrations.

I&EC 8

Evaluation of the hydrolytic stability of dithiophosphinic acids

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Electrospray ionization mass spectrometry (ESI-MS), direct insertion probe mass spectrometry (DIP-MS) and NMR spectroscopy were used to evaluate the stability of nine dithiophosphinic acid derivatives (R₂PS₂H) as toluene solutions in contact with 1 M HNO₃. Prior to contact with acid, the positive ion mass spectra contained ions corresponding to the intact ligands (principally [(R₂PS₂H)H]⁺ and [(R₂PS₂H)Na]⁺), and a disulfide couple that is formed by oxidative dimerization of the ligands. The latter is indicated principally by ions having the structural formula [(R₂PS₂)₂H]⁺ and [(R₂PS₂)₂Na]⁺, and previous studies have provided strong evidence that these species contain a disulfide linkage. The time-dependent intensities of the ions derived from the intact ligands upon contact with 1 M nitric acid showed that the dicyclohexyl, bis(2-norbornyl) and diphenyl derivatives were largely stable, to contact times beyond 1000 min. In contrast, the bis(o-trifluoromethylphenyl) [o,o] and di-t-butyl derivatives were highly reactive, and had disappeared within 250 min. Four other derivatives, bis(o-tolyl), 2,4,4-trimethylpentyl, and both o-(trifluoromethyl)-m-(trifluoromethyl) [o,m], and bis(m-trifluoromethylphenyl) [m,m], displayed intermediate behavior, reacting more slowly, but displaying tendencies suggesting disappearance of the intact ligands within 500 – 1000 min. Phosphorus-31 NMR studies of the acid contacted dithiophosphinic acid (DPAH) solutions showed little evidence of degradation of the cyclohexyl, norbornyl, or phenyl
DPAH derivatives following two weeks contact with 1 M nitric acid. The $^{31}$P NMR spectra of the remaining DPAH derivatives indicated complete degradation after two weeks contact with nitric acid.

I&EC 9

Algal oils to "drop-in" replacements for petroleum transportation fuels

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The goal for this program is to develop and demonstrate the technical and economic feasibility of producing high quality transportation fuels from a non-food feedstock. How focus has been on genetically modifying a marine microalga (Dunaliella spp.) for high lipid content and most beneficial fatty acid chain length. A multi-step, catalytic process is being optimized to produce high quality hydrocarbon biofuels from lipid-rich biomass that are nearly identical to their petroleum-derived counterpart. Key advantages of the proposed biofuels process are its feedstock flexibility, output flexibility/control and very limited hydrogen requirement (this is not a hydrogenation process). Technical challenges include genetic modification of Dunaliella spp. to overproduce fatty acids, lipid extraction using low energy separation processes to remove unwanted compounds from lipids/FFAs, efficient hydrogenation into FFAs, optimization of the thermo-catalytic decarboxylation process, hydroisomerization and dehydrocyclization as necessary, and quantification of the fuel properties.

I&EC 10

Hydrothermal process for making hydrocarbons from wet algal biomass

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Algal biomass is attractive for renewable liquid fuels, but much water accompanies this aquatic biomass feedstock. The energy requirements for drying algae are very high, which militates against a large-scale fuel production process employing this step. Thus, there is a need for processes that convert wet algal biomass directly and therefore operate in the aqueous phase. Our lab has been developing one such process, which uses hydrothermal liquefaction to produce a crude bio-oil from wet algae paste and then
hydrothermal catalytic upgrading of the biocrude to make a largely hydrocarbon product in high yield. This presentation will provide new results from our lab on the liquefaction pathways and kinetics and on the roles and effectiveness of different upgrading catalysts for removing heteroatoms from and reducing the viscosity of the biocrude. We will present information about how the fate of different atoms (C, H, N, S, P) in the algal biomass depends on the liquefaction and upgrading conditions used in the processing steps.

I&EC 11

Progress towards elucidating biocatalysts in the synthesis of n-alkenes in plants and algae

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Plants and some algae have the ability to synthesize hydrocarbons. Of particular interest are n-alkenes, since they are chemically similar to gasoline and diesel fuels. However, the metabolic pathways, the enzyme biocatalysts, and the genes that encode these biocatalysts are unknown. We will report on our progress on uncovering in plants and algae which metabolic conversion pathways yield simple hydrocarbons and the genes and enzymes involved.

I&EC 12

Dissecting the metabolic network associated with hydrocarbon synthesis using maize silks as a model system
Biological sources of non-isoprenoid hydrocarbons are near ideal drop-in replacements for current petroleum-derived fuels. Maize silks are an excellent model system for the fine-scale elucidation of the currently undefined metabolic network responsible for hydrocarbon production. The silk cuticle is particularly abundant in hydrocarbons of 19-35 carbon atoms. In addition, these complex arrays of hydrocarbons differ among maize genotypes and during silk development, suggesting complex genetic interactions in the regulation of this metabolic network. To dissect this network, we have taken advantage of the differences in hydrocarbon profiles between two inbred maize lines, B73 and Mo17, to probe a B73xMo17 genetic mapping population of 660 lines. We have identified genomic regions (quantitative trait loci) that regulate total hydrocarbon accumulation and regions that affect final abundance of individual constituents. Combined with transcriptomic analyses from two stages of silk development, these approaches are providing candidate genes involved in the synthesis of hydrocarbons.

I&EC 13

Insights from model compound studies into hydrothermal production of hydrocarbons from algae

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Experiments with wet algal biomass are very useful for understanding how the yields and compositions of different product fractions (e.g., crude bio-oil, aqueous phase products, gaseous products, solid products) vary with hydrothermal processing conditions. Such data can be used to develop phenomenological kinetics models that have utility for process design and optimization. Such data provide little insight into the details about the chemistry that occurs, however. To elucidate some of these details, we have completed several studies with simpler organic molecules that mimic the structural features and functional groups present in microalgae and/or crude algal bio-oil from hydrothermal liquefaction. This presentation will provide results from experimental and modeling studies related to the hydrothermal reactions of phytol, ethyl oleate, phenylalanine, and a model phospholipid under typical liquefaction conditions. We will also present results from the hydrothermal catalytic reactions of benzofuran that lead to removal of the oxygen atom and production of a hydrocarbon product stream.

I&EC 14
Molecular-scale speciation studies in solvent extraction: Lessons from TALSPEAK

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Having accumulated more than 65,000 tons of irradiated nuclear fuel during sixty years of operating light water power reactors in the U.S., the task of managing the byproducts of fission represents a significant challenge. Stopping work on the geologic repository has spurred new consideration of other processing options, including developing reagents and processes for waste volume reduction. Given the complexity of irradiated fuel residues, it is reasonable to expect that the interactions between fuel components and separations reagents will be potentially complex. In a recent investigation of the TALSPEAK process for trivalent lanthanide actinide separations, a variety of complementary analytical methods have been applied to provide a detailed characterization of molecular scale insights into the process. In this presentation, selected results from these investigations will be discussed as a general approach to developing new processing schemes. Work supported by the U.S. Department of Energy, Office of Nuclear Energy, FCR&D Sigma Team for Minor Actinide Separations.

I&EC 15

Building thermodynamic models of solution mixtures to support predictive modeling of liquid-liquid distribution systems

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Accurate characterization of liquid-liquid distribution equilibria often relies on proper consideration of non-ideal solution chemistry in aqueous electrolyte and non-aqueous solute mixtures. Quantitative description of chemical interactions in complex liquid phases may be realized through the process of thermodynamic parameterization of theoretically represented mixtures. The construction of such thermodynamic models allows for numerical representation of non-ideal solute behavior in aqueous and organic phase components of a liquid-liquid distribution. Here we describe a process of building such thermodynamic model for aqueous buffer: Eu³⁺ / H⁺ / Na⁺ / NO₃⁻ / H₂Mal / HMal⁻ / H₂O, where Mal describes malonate, based on Pitzer ion-interaction theory. Predictive description of the equilibrium set guiding the liquid-liquid distribution of Eu(III) between aqueous malonate solutions and mixtures of bis(2-ethylhexyl)phosphoric acid, HDEHP,
in $n$-dodecane, as afforded by a computational package SXFIT, will be illustrated. The program is an iterative fitting procedure, which allows the identification of an equilibrium model for the distribution of a solute in a liquid-liquid system. We will discuss the alterations to SXFIT calculations based on continuous improvements in the accuracy of the thermodynamic model for aqueous malonate mixtures.

I&EC 16

**Determining organic phase activity coefficients of di-(2-ethylhexyl) phosphoric acid by vapor pressure osmometry**

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We present the current progress towards obtaining the organic phase activity coefficients of the extractant di-(2-ethylhexyl) phosphoric acid (HDEHP) using the technique of vapor pressure osmometry. In conjunction with accurate concentration data, characterization of the activity coefficient for each component is necessary to calculate the equilibrium constants for solvent extraction processes, and correctly model the system over a broad range of concentrations. Examining the extractant HDEHP is motivated by its role in advanced nuclear fuel reprocessing steps, where robust models are sought after, in addition to its place as an industrial extractant. To this end, vapor pressure osmometry data for HDEHP in $n$-dodecane and common solvents at multiple temperatures is analyzed, yielding correlations for the HDEHP dimer activity coefficient. Additionally, osmometry data for HDEHP complexed with metal ions is presented and discussed.

I&EC 17

**Modeling solvent extraction systems using the programs SXLSQI and SXFIT**

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SXLSQI and SXFIT are two modeling programs permitting a thorough interpretation of thermodynamic data. SXFIT is the latest in a series of programs designed to model solvent extraction systems of increasing complexity, with complete freedom to define the constituents from which the composition of each phase is to be specified in the data and from which all species of a model for a system are assumed to be formed. Activity coefficients in the nonaqueous and aqueous phases, water activity, apparent molar volumes of aqueous species, and solution density needed for the conversion of concentration from the molarity to the molality scale are all taken into account by the program. Over the years, the stoichiometry and speciations involved in many systems
have been elucidated. For example, the cesium extraction efficiency of the CSSX process chosen by the USDOE for cesium removal from high-level waste stored at the Savannah River Site can be predicted correctly for varying feed composition. Cesium and strontium extracted using cobalt dicarbollide and polyethylene glycol can also be modeled accurately. And lately, these thermodynamic modeling programs are being used to model europium extraction using TALSPEAK-like conditions, therefore increasing the understanding of the behavior in this complex system. Other examples will also be presented.

I&EC 18

Trivalent lanthanides in the nuclear fuel cycle: Thermodynamic extraction modeling

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Development of the predictive modeling capabilities of solvent extraction processes requires a fundamental quantitative understanding of non-ideality effects and speciation in relevant aqueous and organic solutions. In spent nuclear fuel reprocessing trivalent lanthanides are present at significant concentration levels among the nuclear fission products, and the separation of the trivalent actinides is desirable but difficult step in closing the nuclear fuel cycle. Despite extensive research over several decades, the mechanism and speciation of the TALSPEAK (The Trivalent Actinide-Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes) process is still not fully understood. Our research is aimed at investigating liquid-liquid distribution behavior of the lanthanide ions and their effect on the speciation of the organic extractant bis(2-ethylhexyl) phosphoric acid (HDEHP) under varying conditions. Advancement of the aqueous and non-aqueous solution models can improve our knowledge and prediction of the trivalent metal ion extraction mechanism.

I&EC 19

Thermodynamic signatures of aggregate formation in solvent extraction systems

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In solvent extraction systems for treatment of spent nuclear material aggregation phenomena, such as third phase formation, can interfere with the efficiencies of the processes. The predictability of these phenomena in the organic phase have been challenging due to the lack of a fundamental understanding of the mechanism that drives these aggregate formations. Of fundamental importance are the thermodynamics
of the formation of such aggregates in non-aqueous solvents. We present here some recent studies aimed at probing the thermodynamics of typical aggregates characteristic of those observed in treatment of nuclear fuel.

I&EC 20

Study on the kinetics of membrane extraction of spent nuclear fuel elements

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Separating the useful from radiotoxic elements in spent nuclear fuel is important for future closed nuclear fuel cycles. Solvent Extraction (SX) is one of the most common methods and has advantages of fast kinetics and high efficiencies. However, SX may not be practical when using aggressive chemicals and certain reagent in the system. In this work, we have investigated the possibility of using supported liquid membranes (SLM) to overcome some of the problems of SX for metal ions extraction from aggressive oxidizing media. Neodymium (III) ions and oxidized cerium (IV) ions were transported through a membrane which was pre-impregnated in bis(2-ethylhexyl)phosphate and tributyl phosphate, respectively. Additionally, we show that separation of americium and curium is feasible by using oxidized cerium (IV) and lanthanum (III) as a surrogate. The results show no significant membrane degradation after more than 30 hours of contact with the oxidizing media. The effects of aqueous phase acidity on extraction kinetics are discussed.

I&EC 21

Nonconstant pattern mass-transfer-zone method for design and optimization of molybdenum-99 separation process using a titania support

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The increasing availability of high-surface-area metal oxide sorbents and their superior chemical and radiolytic stability offer new opportunities in the area of radiochemical separations. Utilization of inorganic sorbents for efficient process design is often challenging due to rate-limiting adsorption kinetics. The slow adsorption kinetics, relative to mass transfer rates, stem from restricted diffusion through pores due to small size of the pathway and irregular pore structure. In this study, a non-constant pattern mass-transfer-zone (NCP-MTZ) method was applied to the design and optimization of 99Mo separation on titania support. 99Mo, parent of 99mTc, is the most commonly used radioisotope in nuclear medicine. Nearly all of the 99Mo is produced in research and test reactors by irradiation of highly enriched uranium (HEU) targets. Under the Global Threat Reduction Initiative, GTRI, Argonne is developing processing options for the current producers to allow production of 99Mo from low enriched uranium (LEU) targets.
The goal is to deliver a product solution that is of the same or higher Mo purity than the current solution and is of equal or better compatibility with current purification process. The results of this work indicate that the NCP-MTZ method is a highly efficient approach to column design for a system with slow adsorption/desorption kinetics relative to mass transfer rates, and is highly attractive for conditions encompassing low solute-concentration/high capacity system that are often encountered under nuclear or environmental conditions.

I&EC 22

Fungal processes for direct bioconversion of cellulose to hydrocarbons

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Very little research has examined the potential role of fungi in renewable fuel production. Ascochyta sarcoides (NRRL 50072) is an endophytic fungus that can utilize cellulose as its sole carbon source and excretes "myco-diesel", a mixture of straight chained and branched medium chain-length hydrocarbons of C5-C10 chain length, in the range of gasoline fuel, including heptane, 2-pentene, octane, 1-methyl-cyclohexene, 3,5-octadiene, and cyclodecene (Griffin et al. 2010). Experimental results have verified hydrocarbon compound production under different growth conditions. Biomass yields have improved from 0.05 g/L to 4.8 g/L. The pH tolerance of A. sarcoides is acidic, and optimal temperature is 16-23°C. Volatiles are released throughout its growth cycle but are low in concentration. Studies are in progress to determine optimum conditions for volatile production on cellulose. Future research will focus on combining knowledge of genetics with metabolic modeling to determine how A. sarcoides and other fungi produce these fuel compounds.

I&EC 23

Conversion of biomass to fuels in autothermal, short contact time reactors

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The production of fuels from biomass may be accomplished by its conversion to small fragments, the selective removal of oxygen from carbohydrates, and the conversion of small intermediates into larger hydrocarbons via carbon-carbon bond formation reactions. We will discuss the operation of reactors that combine upstream metal-based exothermic volatilization of biomass with zeolite-based deoxygenation and C-C bond
formation in millisecond contact times thereby avoiding solid carbonaceous by-products. The related development of inorganic molecular catalysts required for facile heat and mass transfer and mathematical models to describe process chemistry will also be presented.

I&EC 24

Lignin deconstruction for the production of liquid fuels and chemicals

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Most of the interest in lignocellulosic biomass has focused on the conversion of the cellulosic fraction to ethanol via fermentation. Regardless of the technical maturity of these processes, they remain fundamentally inefficient with respect to the potential of the initial biomass feedstocks. As a result, the structurally rich chemical nature of the lignin fraction is essentially used for a purpose far below its potential. The utilization of lignin as a source of alternative fuels and feedstock chemicals provides a potentially sustainable alternative to benzene, toluene, and xylene-based compounds derived from petroleum. Thus our efforts have focused on unlocking through a combined strategy of: (1) manipulation of lignin production in lignocellulosic feedstock plants, (2) the development of thermochemical strategies for lignin specific solubilization, and (3) the subsequent catalytic upgrading of the liberated lignin sub-components to viable fuel and feedstock chemicals. In this presentation new developments and remaining challenges will be discussed.

I&EC 25

Pyrolysis-GC/MS characterization of biomass

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Pyrolysis-GC/MS (Py-GC/MS) is an analytical technique that can provide compositional and structure information about the holocellulose and lignin components in biomass. Samples are rapidly pyrolyzed, and the resulting pyrolysates are transferred to a GC column for analysis. Pyrolysates produced are characteristic of the biomass source and provide insight into the range of products that can be expected when biomass feedstocks are subjected to fast thermal depolymerization processes. Our current studies are focused on the characterization of lignin in energy crops such as
switchgrass and high lignin feedstocks such as walnut shells and peach pits. Py-GC/MS analysis of wild type and mutated arabidopsis has also been utilized in order to understand the changes in lignin composition and structure induced during genetic mutations. To this end, we have developed a method for the determination of syringyl:guaiacyl (S:G) ratios in lignin based on Py-GC/MS calibration using mixtures of sinapyl and coniferyl alcohols.

I&EC 26

Synthesis and development of polymer-supported reagents as ion-selective complexants

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The selective binding of metal ions to polymer-supported reagents is important for many applications, including environmental remediation, wastewater treatment, and catalysis. An overview will be presented of our research with an emphasis on the latest accomplishments, including a new series of phosphates and phosphonates bound to crosslinked polymer beads.

I&EC 27

Polymers in electronics: The coupling of molecular and process parameters for high imate performance

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Since the invention of the point contact transistor over 50 years ago, semiconductor technologies have become a ubiquitous mainstay of our Society. Continued advancements in these technologies rely heavily on materials research spanning many areas including polymer and organic materials which play significant roles as sacrificial, passive and active layers in electronic and photonic devices. The research outlined in this talk will identify fundamental materials parameters that will allow for the definition of materials architectures leading to sub-nanometer scale dimensional control of features for future semiconductor fabrication technologies. To enable advanced applications, this control must be extended into the micro- and macro-scales. Molecular structure and the processing associated with incorporation of materials into devices both play an active role in ultimate performance. The relationships between these parameters will be explored.

I&EC 28
High performance carbonate-based sorbents for the capture of CO₂

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The release of carbon dioxide from fuel combustion into the atmosphere is one of the leading causes of global warming. The existing technologies for the capture of CO₂ suffer from various economical drawbacks and new technologies are desired. According to a report by US Energy Information Administration (EIA), the amount of CO₂ released in 1980 was 18,500 million metric tons and it increased to 29,195 million metric tons in 2006¹. Concerns have prompted countries to meet at the 17th Conference of the Parties (COP 17) to the UN Framework Convention on Climate Change (UNFCCC) in December 2011 to once again discuss a method to reduce the emission of global warming gases into the atmosphere.

Amine-based sorbents are commercially utilized, but they have numerous disadvantages, including steam loss due to solvent regeneration, solvent loss due to vaporization, sensitivity to SOₓ and O₂, and high capital and operating costs. In the present investigation, modified and unmodified sodium-based sorbents were tested for the CO₂ capture in a fixed-bed reactor under simulated flue gas conditions. The performance of the sorbents was tested at various carbonation temperatures and water concentrations. A very high performance has been achieved for the modified sorbents compared to unmodified sorbents (7.69 mol of CO₂/kg of Na₂CO₃). The sorbent was also demonstrated to retain its high capacity for multiple cycles.

I&EC 29

Fun with titanates

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Sodium titanates are remarkably effective ion-exchange materials for the decontamination of radioactive and industrial wastewaters. For example, monosodium titanate (MST) is used at the Savannah River Site to remove Sr-90 and transuranics from high-level waste solutions that feature sodium and hydroxide concentrations in excess of 5.0 M and 1.3 M, respectively. Sodium titanates are also effective for the removal of hazardous metals such as chromium, lead and cadmium from neutral and weakly acidic solutions. These materials have also been shown to be effective for the delivery of biologically relevant metals to living cells under physiological conditions. MST is produced by a sol-gel process as spherically shaped particles of about 1 - 20 microns in size. Very recently we have synthesized sodium titanates that feature nanosize particles. This paper will follow the development of materials beginning with
the decontamination of nuclear wastes and concluding with materials for medical and catalytic applications.

I&EC 30

What's a nice girl like me doing in a career like this?

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On completing graduate school, I anticipated the long, stable scholarly career my professors revered. Now, forty years later, having worked in every sector of the chemical enterprise – academe, industry, not-for-profit, government contractors and small business – I reflect with bemusement on the actual path of my long, fascinating and rewarding career. Unpredictable opportunities, personal preferences and choices made possible: solving environmental, defense, health-related and nuclear problems; serving in positions including bench chemist, college professor, principal investigator, program manager, technical manager, business unit director, business development manager, systems engineer and consultant; working for organizations such as Hewlett-Packard, Rockwell International, Lockheed-Martin/Sandia National Laboratories, Midwest Research Institute, California State University-Fresno, Business Results Inc. and others. This talk will reflect on how this all happened – the struggles, rewards, constants (most notably ACS), turning points and lessons learned.

I&EC 31

Associates of Applied Science to ACS Fellow

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The ACS Fellows program was started “to recognize members of ACS for outstanding achievements in and contributions to Science, the Profession, and the Society.” What gets a person with an Associates of Applied Science in Chemistry to the honor of ACS Fellow?

The journey from applied chemical technology professional to ACS Fellow was a journey of 46 years with service to my university, my profession and my professions society. It’s easy to enumerate the contributions; it’s much harder to define those characteristics that got us to this pinnacle in our career.

I&EC 32

Mentoring, one way this ACS Fellow gives back to her profession

Mary K Moore, mkmoore@eastman.com. Eastman Chemical Company, United States
Being in the Inaugural Class of ACS Fellows was quite an honor. Mentoring and giving back to my profession has been just the way I am. We all have mentors that have influenced us personally and professionally. Mentoring is a two-way street, many mentors will say that the learn more than the people the mentor. I will share some stores of mentors and the people that have influenced their careers.

I&EC 33

STEM education reform: Evidence and private empiricism

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Science, technology, engineering and mathematics (STEM) education reform is a national priority. Whether for preparation of future scientists and engineers, K-12 teachers, or the need for a scientifically literate population who are able to make informed choices at the ballot box, most would agree that improvements are needed. Over the years a great deal of time, effort and resources have been devoted to improvements in STEM education, arguably with little success. However, many of these reform efforts were designed and implemented by individuals or groups who, while enthusiastic and engaged, often were not aware of prior research or work in this area. Additionally many reform efforts have been hampered by lack of appropriate tools to assess them. Over the past fifteen years or so, research on learning, teaching and assessment has emerged that has provided us with a foundation on which to build and assess STEM reform efforts. This presentation will present some of that research, and some recommendations about how we can move forward to a successful implementation of STEM reform.

I&EC 34

How does a catalyst evolve? Literal and figurative perspectives

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Since H. S. Taylor's definition of active centers, understanding of the nature of active sites in petroleum cracking catalysts has undergone many revisions. I've been associated with some of the major players over the past half-century and more, and I've made some small contributions myself. This historical evolution is described from the perspective of my participation.

From a few random nanoscale defect sites to organized nanostructures with numerous designed defects, cracking catalysts have matured to become major contributors to our economy and lifestyle. Starting with Eugene Houdry's treated clays, then progressing to synthetic "amorphous" aluminosilicates, cracking catalysts took a giant step forward with
crystalline zeolites and continued to evolve thereafter. Some of the steps involved in how we got from there to here will be reviewed, and some of the technical contributions – many published, some not – will be described.

Finally, my own evolution as a figurative catalyst will be briefly described, as I emulated Eugene Houdy (on a much less grand level) in exercising environmental concerns, leading to promotion of sound science advocacy for environmental protection in work with Clearwater, Inc., my local Environmental Review Board, and Pace University's graduate program in environmental science.

I&EC 35

Lessons in life and leadership from an inaugural ACS Fellow: From analytical bench chemist to ACS President and still going strong

Catherine T. Hunt, CatherineHunt@dow.com. The Dow Chemical Company, United States

It gives me great pleasure to participate in the inaugural ACS Fellows' Symposium, a Presidential symposium, hosted by I&EC. This is a very special opportunity to share my experiences and insights from analytical bench chemist to ACS President and Beyond!

Come prepared to engage with colleagues and friends in the kickoff of the inaugural ACS Fellows program!

I&EC 36

Renewable energy and climate change

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The Intergovernmental Panel on Climate Change issued the Special Report on Renewable Energy Sources and Climate Change Mitigation (SRREN) at http://srren.ipcc-wg3.de/ (May 2011 electronic version; printed form ISBN 978-1-107-60710-1, 2012). More than 130 scientists contributed to the report.* The SRREN assessed existing literature on the future potential of renewable energy for the mitigation of climate change within a portfolio of mitigation options including energy conservation and efficiency, fossil fuel switching, RE, nuclear and carbon capture and storage (CCS). It covers the six most important renewable energy technologies – bioenergy, direct solar, geothermal, hydropower, ocean and wind, as well as their integration into present and future energy systems. It also takes into consideration the environmental and social consequences associated with these technologies, the cost and strategies to overcome technical as well as non-technical obstacles to their application and diffusion.
The Webster’s dictionary defines "Invention" as "discovery, finding" meaning, "to produce (as something useful) for the first time through the use of imagination or of ingenious thinking and experiment." This is distinctly different from the definition of "Innovation" as "the introduction of something new". Others have also described innovation as, "the first commercial use of new technology/invention". Hence, though the pursuit of new knowledge/science (and hence invention) is commendable and a necessary first step, yet the successful development/commercialization of new technology or the original invention (and hence innovation) is crucial to industry for value creation. Such innovation usually requires several additional inventions on the way to successful commercialization. Requirements and skill sets at the individual and the organizational levels are very different for the path to "Invention" and "Innovation". Personal reflections of such requirements will be presented from author’s experiences over 40 years of conducting and leading industrial research and development projects. Enablers and barriers to "Invention" and "Innovation" will be highlighted. Three examples of such "Inventions" and "Innovation" in ethylene epoxidation catalysis will be covered that have provided several hundreds of million dollars worth of cumulative benefits over the past three decades and provided added capacity equivalent to a world scale unit. Two other examples of "Invention" will be presented that have the potential of becoming Innovations and create value in the future. These are in the areas of three-way automotive emissions control and in the production of ethylene from methane by selective oxidative coupling of methane.

Adventures with surfactants and red bugs

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Discussion will include an overview of surfactant uses and presentation of a wide variety of surfactant related projects over the author's career.
Melanie J. Lesko, leskom@tamug.edu. Department of Marine Sciences, Texas A&M University at Galveston, Galveston, Texas 77553, United States

Over a 30+ year career I have focused on service to my community and to ACS. Most of my career has been at Texas A&M University at Galveston (TAMUG), a branch campus of TAMU, located on a small island adjacent to Galveston Island. It is a full 4 year university but all of its degree programs are marine oriented. I have strived to make chemistry more interesting and accessible to the marine biology and oceanography students. In fact I facilitate TAMUG’s ability to offer an ACS accredited chemistry minor by virtue of a cooperative arrangement with the chemistry department at our main campus in College Station. In this talk I will talk about engaging non-chemistry students, revisit the highs and lows of my service, some forays into research with undergraduates and peers, and the role of ACS in the career of a chemist on a campus with no chemistry department.

I&EC 40

Development of a continuous plug flow reactor and control system for the production of cyclopropyl amine

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Cyclopropylamine is becoming an increasingly important moiety in pharmaceutical formulations used as anti-viral agents and antibiotics for the treatment of drug resistant bacterial strains. As a consequence, market demand has become large enough to support a continuous process. Eastman Chemical Company has developed a continuous process using a plug flow reactor to convert cyclopropyl amide to cyclopropyl amine via the Hofmann rearrangement utilizing sodium hypochlorite and caustic. While the Hoffmann Rearrangement represents a reasonably old “name reaction”, there were unique problems associated with the production of cyclopropyl amine. In this presentation, we will be discussing the steps required for the transformation of the batch process for the conversion of cyclopropylamide to cyclopropylamine to a continuous process, the unique problems encountered in the process, and the roles played by various chemical and chemical engineering disciplines as they interacted to overcome problems and worked together to develop the process.

I&EC 41

Actinides in science and technology: 21st century challenges

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More than one hundred years after the discovery of radioactivity and seventy years after the report of the first man-made transuranium elements (neptunium), actinide science
remains a “hot” topic (pun intended). Continuing research on the synthesis of new elements has conclusively established that the actinides are indeed a 5f series with fourteen members. In addition to their interesting chemistry, similar to that of both their 5d and 4f progenitors, actinides possess nuclear properties that are unique in the periodic table. Actinides alone enable energy production based on nuclear fission. Most of the actinides from thorium through americium have technologically important uses. The increasingly short half-lives that are seen in the elements heavier than californium pretty much guarantee that the heaviest actinides will never assume an important role in technology. In this presentation, features of the chemistry of these elements will be discussed in the context of the challenges presented by life in the 21st Century.

I&EC 42

The forgotten silent heroes

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During my career in chemistry for sixty years, I published a number of articles, wrote books and obtained patents. Some of my research projects resulted in industrial applications. A new discovery is always exciting. Sometimes the results may be a lucky accidental discovery, but is rare. Most of the time it is the result of a tedious series of experiments carried out by a number of persons whose contributions played parts in the development of ideas. The theory, which appears to be the starting point for the successful achievements, is impressive and we applaud the perseverance, which made the discovery possible. The fame of the discovery frequently surrounds one or perhaps two persons, even though in most of the cases it is the result of a team effort when the team is composed from a junior chemist to a well-known scientist. Our system is built in such way that it is unavoidable that generally the person who gets credit and recognition is the one heading the effort. When that person presents the findings or accepts some award, it is customary to give thanks in 1-2 sentences to the supporting staff. However the role of the silent heroes deserve better recognition. The lecture will discuss the problems and suggest possible better ways to spread the fame.

I&EC 43

Science, service, and the ACS: Becoming an ACS Fellow from the I&EC Division

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I was honored by the I&EC Division as a nominee for designation as an ACS Fellow in the first year that the ACS developed that program. I believe my selection was a result of work inside and outside of the Society and would like to share how the I&EC Division provided me the opportunities to be successful. This presentation will detail my
involvement with the ACS and the Division over the past 35 years or so from student affiliate to Editor of Crystal Growth & Design.

I&E 44

Cleavage of acetyl groups from northeast hardwood for acetic acid production

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This paper discusses the recovery of acetic acid in kraft pulp mills. Acetyl groups in wood hemicelluloses can be hydrolyzed using alkali to form alkali acetate which is a precursor to acetic acid. The objective of the study reported here is to identify the optimum conditions for cleavage of acetyl groups from wood hemicelluloses for conversion to acetic acid. Experimental data are presented for the extraction of northeast hardwood using alkali streams that are available in kraft pulp mills; caustic, green liquor and white liquor. In the work, the effects of extraction time, chip soaking temperature, alkali concentration, extraction temperature, and chip thickness are discussed. A comparison is made to previous literature data. The data being developed will be used to design a process for recovery of acetic acid from kraft pulp mills.

I&E 45

Methacrylated lignin model compounds as monomers for use in high-performance polymers

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Lignin is a copious pulp and paper industry waste product that has the potential to be a vital next-generation biorefinery feedstock that could yield valuable macromolecular and low molecular weight aromatic chemicals when strategically depolymerized. The high aromatic content found in lignin would be ideal for the development of high-performance, bio-based polymers for a wide range of applications since the incorporation of aromaticity to the chemical structure of a polymer is known to drastically improve its strength and increase its glass transition temperature. Methacrylated lignin model compounds synthesized and employed as alternative, bio-based monomers for use in high-performance polymers are presented. Specifically, methacrylated versions of guaiacol, eugenol, phenol, creosol, 4-ethylguaiacol, 4-propylguaiacol, catechol, and 4-methoxycatechol were incorporated either individually as potential styrene replacements or as a functionalized, synthetic bio-oil into vinyl ester resins. Additionally, vanillin was utilized in a green-oriented one-pot, two-step resin synthetic scheme that, when cured, produced a highly bio-based thermoset. Monomer properties, in situ free
Thermoplastic elastomeric block copolymers via controlled radical polymerization of soybean oil

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This contribution presents — for the first time — the controlled radical polymerization of a vegetable oil into thermoplastic rubber, and the incorporation thereof into triblock copolymers with polystyrene to form thermoplastic elastomers. Increased costs of petrochemically-derived monomeric feedstocks such as butadiene has made biopolymers not only more environmentally friendly but also economically competitive. Over the past two decades, the production of bio-based polymers from plant oils has successfully brought forth thermoset materials through traditional free radical polymerization routes to yield highly crosslinked polymers; crosslinking beyond the gel point is to be expected owing to the inherent multifunctional nature of triglyceride-based monomers. We have discovered, however, that under the appropriate conditions controlled radical polymerizations such as Atom Transfer Radical Polymerization can sufficiently limit the polymerization of triglyceride so that it terminates at a desired molecular weight and block composition. Here we present multiple synthetic methods for these bio-based elastomeric block copolymers comprised of poly(acrylated epoxidized soybean oil) (PAESO) and polystyrene (PS). The properties of these materials range from toughed glassy to tacky rubbers to resilient elastomers at room temperature but are amenable to common processing techniques at elevated temperatures, making them suitable for a wide range of applications. Finally, we investigate the viability of these materials in the specific application of bitumen modification, commercially representing a vast fraction of the thermoplastic elastomers market. Our findings have concluded thus far PS/PAESO-based block copolymers can match and even exceed the performance of petroleum-based polymers such as those of the Kraton(R) family.

Transparent stretchable conducting films of single walled carbon nanotubes and PEDOT:PSS for next generation sensors and solar cells

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In this work we demonstrate stretchable transparent electrodes made from single walled carbon nanotubes (SWNTs) and the conducting polymer poly-(3,4-ethylenedioxythiophene) (PEDOT). The SWNT films accommodated strains of up to 150% and demonstrate conductivities as high as 2,200 S cm\(^{-1}\) in the stretched state, which is the most conductive film in the stretched state found in the literature. We also used the SWNT films as electrodes in arrays of transparent, stretchable capacitors, which behave as pressure and strain sensors, and can potentially be used as sensors in biofeedback devices. We also produced highly conductive stretchable PEDOT films. The conductivity of the PEDOT:PSS films were improved using a fluorosurfactant. In addition, the fluorosurfactant improved the wetting properties of the PEDOT:PSS solution, which enabled the facile deposition of highly conducting PEDOT:PSS films on stretchable and flexible buckled poly(dimethylsiloxane) substrates. These flexible films were used as anodes in the demonstration of the first intrinsically stretchable organic solar cell, which can accommodate strains of 27%, reversibly.

I&EC 48

Synthesis of ceramic nanofibers with negative coefficient of thermal expansion

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Zirconium tungstate (ZrW\(_2\)O\(_8\)) is a ceramic material having a negative coefficient of thermal expansion (NCTE) over a wide range of temperature from 0.3 to 1050K. In this study, by adopting a new low temperature synthesis approach, phase pure nanoparticles of ZrW\(_2\)O\(_8\) were prepared. After a series of size distribution homogenization and filtering steps, recovered nanoparticles were electrospun with a polymer. A two-step burnout procedure was used to produce ZrW\(_2\)O\(_8\) nanofibers with diameters around 250nm.

I&EC 49

Multifunctional nanoparticles for drug and mRNA delivery in cancer therapeutics

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Advanced drug/gene delivery based on nanoparticles hold great promise to improving cancer therapeutics. Due to high robustness and amenability to chemical modifications for specific targeting cells, polymeric nanoparticles are great candidates as efficient drug and gene delivery carriers. However, their synthesis often requires laborious processes and stringent synthesis conditions, therefore, not amendable for industrial
scale manufacturing. Here, we report a simple yet versatile approach to synthesize vesicular nanoparticles for drug/gene delivery. The nanoparticles were assembled from random copolymers synthesized in one-step photopolymerization of acryloyl chloride (AC). The polymer was partially self-crosslinked, leading to amphiphilicity in an organic solvent (e.g. acetone), a unique characteristic of block copolymers and surfactants. Depending on solvent quality and photoexposure dosage, the average particle size could be varied conveniently from 20 nm to half a micron. The particles were hydrolyzed in an aqueous solution, followed by functionalization with polycations, poly(ethyleneimines) (PEI), which were commonly used in drug/gene delivery. We show that the PEI modified nanoparticles effectively delivered both model anticancer drug and RNA to HEK 293T cells at a low cytotoxicity level. The simplicity in particle synthesis, tunable particle size and chemistry, and high stability in drug/gene loading shown in our system will offer an attractive platform to develop smart nanoparticles in industrial and biomedical applications.

I&EC 50

Light-management in ultrathin conjugated polymer films on metallic ground planes

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Nanophotonics, encompassing plasmonics, metamaterials and functional photonic materials, has emerged as a rapidly expanding new field for materials and devices research in the past few years. As a result, important advances in fields such as photovoltaics, nano-optical sensors, enhanced information storage, light-emitting devices and photocatalysis have benefitted from a deeper understanding and improved control of light-matter interactions on the nanoscale. In particular, optical nanoantennas are capable of concentrating and enhancing optical fields to the nanometer-scale and receiving and transmitting optical signals in a highly directional way, which challenges existing technological limits such as ground-breakingly pushing the hard-disk storage densities into 1Tb/inch². Monopole-nanoantennas, which consist of quarter-wavelength-long vertically oriented metal rods placed on a conductive ground plane, are of great interest due to their ease of fabrication and large signal directivity and gain.

Here, we demonstrate how the design of gold monopole-nanoantenna arrays affects the enhancement and localization of optical frequency electric fields in underlying semiconducting conjugated polymer(poly(3-hexylthiophene), P3HT) films, both experimentally and theoretically. We successfully fabricate a gold nanoantenna/P3HT/silver film monopole-nanoantenna array system where the silver film acts as the conductive ground plane. Significant absorption enhancement in polythiophene is obtained which is also validated by agreement with full-field electromagnetic simulation data. Under longitudinally polarized excitation, light is strongly localized both at the tip of the gold nanoantenna and in the underlying P3HT thin film compared with the fact that light is only localized on the surface of the nanoantenna.
under transverse polarization. We also suggest that there is an image plane effect between the nanoantenna and the underlying metal ground plane which causes the system to behave like a dipole antenna with large field intensity enhancement in the P3HT "gap" region when light is polarized longitudinally.

I&EC 51

R&D towards recovery of uranium from seawater in Japan

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The recovery of uranium has been carried out by adsorption method. In this method, the adsorbent needs the high selectivity and capacity for uranium adsorption in the seawater. It was found that hydrous titanium oxide was noble material for the recovery of uranium from seawater. Then, screening researches were carried out to evaluate the many kinds of uranium adsorbents and concluded that the amidoxime was a promising functional group for recovery of uranium from seawater. We have developed the high performance adsorbent having amidoxime with radiation-induced graft polymerization and the collection of 1 kg uranium from seawater was demonstrated. In the recovery system, the stacks of fabric adsorbent were changed to a braid type adsorbent to improve the contact between the adsorbent and the seawater. The sea area being considered for the recovery of uranium was preliminary investigated on the conditions of seawater temperature and depth of the sea.

I&EC 52
Improving the chemistry of amidoxime-based uranium adsorbents

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The presence of 4 billion tons of uranium dissolved in Earth’s oceans has motivated a sustained effort to develop technology to sequester uranium from seawater over the past 40 years. A demonstrably successful approach has involved the use of poly(acrylamidoxime) adsorbents, which are able to extract and concentrate 3 ppb levels of uranyl carbonate under actual marine conditions. This talk presents research progress toward increasing uranium uptake from seawater through chemical modification of amidoxime-based adsorbent materials. The research entails a combined theoretical and experimental approach to (i) better understand how current these adsorbents function, (ii) identify binding site architectures optimized for uranyl cation interaction using state-of-the-art de novo structure-based design methods, and (iii) synthesize, characterize, and evaluate performance of promising candidates in the laboratory.

I&EC 53

Complexation of amidoxime-related ligands with uranium and transition metals: Potentiometric and spectrophotometric studies

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Extraction of uranium from seawater is very challenging, not only because uranium is in an extremely low concentration, but because it exists in seawater as very stable triscarbonato complexes in the presence of many transition metal ions, some of which are in concentrations higher than or comparable to that of uranium. Sorbents with amidoxime-type ligands were successfully used to extract kilogram quantities of uranium in marine tests in Japan. To improve the extraction efficiency and reduce the extraction cost, fundamental understanding of the coordination chemistry of the extraction process is necessary. Therefore, thermodynamic studies have been conducted to determine the stability constants and enthalpy of complexation with a combination of techniques including potentiometry, spectrophotometry and microcalorimetry. These data provide guidance for the design of ligands and the optimization of sorbent preparation.

I&EC 54

Amidoxime functionalized materials for the selective extraction of the uranium

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The selective extraction of uranium from the environment can lead to a variety of applications from waste remediation to the mining of $\text{UO}_2^{2+}$ from seawater. Several studies over the past sixty years has concluded that the amidoxime moiety, $\text{RC(NH}_2\text{)}=\text{NOH}$ is highly selective for the uranyl cation, even under such complex conditions as seawater. Despite these studies, only recently has solid-state structural data been acquired that supports the $\eta^2$ coordination of amidoxime to the uranyl ion. These recent results suggest a higher stability complex and are potentially linked to the selectivity of the amidoxime for the uranyl cation. We have modified both solid (small organic molecules and biopolymers) and liquid (ionic liquids) materials with this functional group and have applied them towards the separation of the uranyl cation. We will discuss the synthesis and modification of these materials and their applied separations of uranium.

**I&EC 55**

*Polymer-supported reagents for the selective removal of uranium from seawater*

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Crosslinked poly(vinylbenzyl chloride) is explored as a substrate onto which ligands are immobilized that can be used to remove the uranyl ion from seawater. The ligands are phosphorus-based and include phosphates, phosphonates, and bifunctional ligands.

**I&EC 56**

*Nanoporous sorbents for selective extraction of actinides*

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Advanced nanoporous sorbents are being developed for uranium extraction from seawater and other actinide elements from nuclear wastes. We have investigated mesoporous silica nanoparticles, mesoporous carbon nanoparticles, and other porous materials for selective actinide extraction. These materials provide highly tunable platforms for incorporating selective chelators, either by grafting or by direct incorporation into the structures. The porous structures of these materials are able to encapsulate chelators at high densities, allowing high actinide sorption capacities. Material properties such as sorption capacity, selectivity, uptake and elution kinetics, durability, and reusability are being optimized by controlling the morphology, pore size, and surface functionalization of nanomaterials.

**I&EC 57**
Functionalized carbon materials as uranium adsorbents

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The extraction of valuable materials from seawater provides a pathway for alternatives to terrestrial sources supporting future energy needs. Uranium extracted from seawater will be vital for future nuclear power as the terrestrial ore supply diminishes over time. While polymer-based sorbents have been actively developed for over 20 years, carbon-based sorbents have been neglected. Recently, the introduction of controlled porosity in porous carbons, specifically in the mesopore regime, has led to an increased interest in carbon materials in energy storage, catalysis, and separations. A focus on the functionalization of carbon materials is currently underway, directed toward surface polymerization inside the mesopores, where amidoxime ligands are grafted in high density to the pore walls. Comparisons between mesoporous carbons and other carbon-based materials will be discussed along with some of the challenges associated with achieving a deployable format.

I&EC 58

Electrospun chitin nanofibers for uranyl absorbant materials

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It has been recently shown that ionic liquids (ILs) allow the dissolution of biopolymers without the loss of the important high molecular weight of the natural polymer which leads to improved strength. Electrospinning polymers produces high surface area fibers which can be functionalized with selective ligands for preferential complexation of the uranyl ion. Here we will present our efforts to prepare electrospun nano and micron sized chitin fibers directly from the dissolution of shrimp shells in the IL 1-ethyl-3-methylimidazolium acetate. The results of this single step process suggest that chitin can be extracted with higher molecular weight and purity over current processes that result in chitin with a lower degree of polymerization. We will discuss the correlation of physical properties and electrospinning conditions with the surface morphology and size range of the fibers.

I&EC 59

Comparison of the crystal structures and transport properties of single crystals of three complex intermetallic Ln-M-Sn systems (Ln = Gd, Tb, or Y; M = Co or Ru)
Intermetallic compounds composed of complex unit cells have been studied as potential thermoelectric materials for many years, as lattice thermal conductivity is typically reduced as unit cell complexity increases. Here we present the growth, crystal structure, and physical properties of single crystals of three complex, tin-containing materials with similar structural features in the \( \text{Ln-Co-Sn} \) and \( \text{Ln-Ru-Sn} \) (\( \text{Ln} = \text{Gd}, \text{Tb}, \text{or Y} \)) phase space. The materials presented have varying unit cell complexities with primitive cell volumes of \( \sim 6700 \, \text{Å}^3 \), \( \sim 3300 \, \text{Å}^3 \), and \( \sim 1650 \, \text{Å}^3 \). Additionally, two of the compounds presented represent new structure types in the \( \text{Ln-Ru-Sn} \) phase space. We examine the effects of complexity on the compounds’ electronic properties and whether primitive cell volume relationship for lattice thermal conductivity is maintained for highly complex intermetallic compounds with comparable atomic mass elements and bonding characteristics.

Detection of hydroxyl radicals in living cells using rhodamine-based fluorescent dye

Reactive oxygen species (ROS) are associated with many diseases such as Parkinson's, Alzheimer's, cancer and diabetes. Among ROS, hydroxyl radical plays a significant role due to its high reactivity with biomacromolecules. Detection of the radical selectively, provides information about the localization, extent of damage and resulting cellular response. Therefore, methods that are sensitive, accurate and reproducible for the detection of hydroxyl radical are crucial for understanding pathophysiology in a host of inherited and acquired diseases. The synthesis, characteristics, and biological applications of a series of new rhodamine nitroxide fluorescent probes that enable imaging of hydroxyl radicals in living cells are described. These probes are highly selective for hydroxyl radical in aqueous solution avoiding interference from other ROS, and they facilitate hydroxyl radical imaging in biologically active samples. The robust nature of these probes (high specificity and selectivity, and facile synthesis) offer distinct advantages over previous methods for detection of hydroxyl radicals.
Intrinsic properties of the active sites for hydrogen production from alcohols without coke formation

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To address the challenges of energy production from fossil fuels, conversion of biomass into hydrogen alleviates the environmental impact of fossil fuels and enhances sustainable development.

We have studied the contribution from the catalyst support perspective in steam reforming of ethanol, and found that the synergistic interaction between Pt and oxygen vacancies in transition metal oxide nanoparticles provides the active sites for the reaction. Overall, the higher activity and better stability with less coke formation are seen over the catalyst that has stronger Pt and oxygen vacancy interaction and weaker surface acidity. Literature analysis suggests: (i) more systematic study for ethanol adsorption from the catalyst support perspective, (ii) an extension of these studies to diol molecule as EG. The present research is focused on the interaction between hydroxyl molecules with pure transition metal oxide particles and Pt nanoparticles supported on these oxides to provide insights for hydrogen production from bio-alcohols.

I&EC 62

Room-temperature ionic liquid-based solvent extraction systems for improved fission product separations

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A series of 1,3-dialkylimidazolium-based ionic liquids (ILs) have been evaluated as substitutes for the conventional organic solvents (i.e., n-alcohols) frequently employed in the extraction of alkali and alkaline earth cations from acidic aqueous phases by crown ethers. Insight into the fundamental aspects of metal ion extraction in these systems has been obtained by analysis of the acid and extractant dependencies of metal ion distribution ratios, measurements of the IL phase water content and of the solubility of the ILs in the aqueous phase, determination of the partitioning of the extractant and of inorganic ions, and consideration of the relative hydrophobicities of the ILs employed. In contrast to the single pathway (i.e., neutral complex extraction) observed using molecular diluents, metal ion extraction in these systems has been shown to proceed through as many as three competing pathways over a wide range of conditions. Despite this added complexity, the favorable physicochemical characteristics of the ILs (e.g., non-flammability and unprecedented structural tunability), along with the higher extraction efficiencies and selectivities for strontium over alkali metal cations.
sometimes observed with these solvents, suggests that they may have a role to play in various separations applications on both the industrial and analytical scale. In addition to their immediate practical utility, the results of these studies represent an important step toward developing guidelines for the rational design of IL-based metal ion separation systems.

I&EC 63

Investigation of polymer structure and properties of amidoxime-functionalized hydrophilic random copolymers on performance of uranium recovery from seawater

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Development of technology for recovery of uranium from seawater is crucial for satisfying future energy demand. Amidoxime-functionalized polymer adsorbents prepared via radiation-induced graft polymerization (RIGP) has been the most promising adsorbents for recovering uranium from seawater. RIGP adsorbent properties depend on chemical properties of graft chains on the graft copolymers. Especially the incorporation of hydrophilic groups in addition to amidoxime ligands was the key to obtaining high recovery and uptake rates of uranium. Due to insolubility of immobilized graft chains on a trunk polymer, the correlation between polymer properties of the graft chains and uranium uptake performance has been little investigated. Thus, this work aims to investigate polymer structure and properties of non-grafted amidoxime-functionalized hydrophilic random copolymers. Elucidating the effect of polymer structure and properties to uranium uptake performance will help in designing more efficient polymeric adsorbents for uranium recovery from seawater. Several amidoxime-functionalized hydrophilic random copolymers were synthesized and the effect of the polymer structure and properties including chemical composition, molecular weight, glass transition temperature, and solubility to uranium uptake from model seawater are investigated.

Sponsored by: Department of Energy – The Office of Nuclear Energy with Oak Ridge National Laboratory

I&EC 64

Uranium adsorbents based on crosslinked polymers

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The separation and purification of uranium has gained considerable importance with increasing demand of this element for clean energy applications. The storage of uranium in sea water is humongous due to its vast volume covering the earth’s surface (estimated around 4.5 billion tons), therefore, developing effective adsorbents for uranium extraction from seawater is very promising. So far, the most efficient uranium adsorbents were developed by Japanese based on grafting acrylonitrile and methacrylic acid on electron beam irradiated polyethylene fibers, followed by amidoximation with hydroxylamine and potassium hydroxide conditioning. To eliminate the high energy consumption step, electron beam irradiation, we focus on developing high surface area adsorbents based on crosslinked polymers. Divinylbenzene (DVB) as crosslinker and different monomers containing either nitrile group (-CN) or acid groups (-COOH, -SO$_3$H, -PO(OH)$_2$) were used to synthesize the crosslinked polymers. The effect of monomer types, monomer ratios, as well as crosslinking density on the surface area and uranium adsorption capacity of the polymeric adsorbents were systematically investigated and will be presented in this talk.

I&EC 65

Preparation of uranyl carbonate ions absorbent containing amidoxime groups via pre-irradiation induced grafting method

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Acrylonitrile is grafted onto polyethylene non-woven fabric and the amidoxime groups are introduced onto the non-woven fabric by the reaction of nitrile groups with hydroxylamine hydrochloride. The degree of grafting (DG) and the conversion of amidoximation are measured by gravimetric method and the kinetics is studied. The existence of the amidoxime groups is proven by Fourier transform infrared (FT-IR) spectroscopy analysis. Adsorption results show that the absorbent can extract uranyl carbonate ions when the concentration is lower than 3 ppb.
Radiation grafting of acrylonitrile to UHMWPE fiber for the preparation of uranium collection material

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In this work, we developed a novel amidoxime adsorbent using ultra-high molecular weight polyethylene (UHMWPE) fiber as grafting substrate. The fiber adsorbent was prepared by pre-irradiation under γ-ray, graft copolymerization in binary monomer solution and followed amidoximation reaction. The UHMWPE fibers were firstly irradiated in air at room temperature, and then reacted with the monomers in DMF solution purged by nitrogen at 60°C. The grafting degrees of acrylonitrile (AN) and acrylic acid (AA) reached 68.2% and 26.5%, respectively, on the UHMWPE fiber in a grafting period of 3 hr. The infrared analysis of UHMWPE-g-(PAN-co-PAA) fiber show C≡N stretching band at 2243 cm$^{-1}$ and C=O stretching band at 1732 cm$^{-1}$. The SEM micrograph of the non-grafted UHMWPE fiber exhibited a smooth surface and microgrooves along axial orientation. That of the UHMWPE-g-(PAN-co-PAA) fiber showed that the microgrooves were covered by the AN and AA co-grafted layer and the surface became rough.
An interest to improve capabilities for producing uranium adsorbents increased after an extensive survey of Japan's 10+ years of research on this technology. Significant efforts by Japanese researchers facilitated the development of protocols to design an absorbent to extract Uranium from seawater. Uranium is present in the seawater in very low concentrations, 3.3 parts per billion. The extraction of Uranium from such low
concentrations presents an economical challenge, where as the adsorbent method is not competitive with the actual method of In Situ recovery. For us, this is an opportunity to provide new investigations on extraction absorbents that conquer the economical challenges.

In order to enhance the performance of the material our efforts were first directed to better understand the technology implemented in Japan. We have been exploring the adsorbent synthesis and processing variables, as well as the correlation between chemical modification of the material and the Uranium absorption capacity. The synthesis variation research targets the understanding of each manufacturing step; radiation induced grafting of acrylonitrile, acrylonitrile to amidoxime functional group interconversion, and alkaline conditioning.

Sponsored by: The U.S. Department of Energy - The Office of Nuclear Energy with Oak Ridge National Laboratory.

I&EC 68

Enhancement of the extraction of uranium from seawater

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The amount of dissolved uranium in seawater far exceeds the amount available in terrestrial ores. In addition to contributing additional uranium to the nuclear fuel cycle, retrieving uranium from seawater greatly reduces the technological complexity and environmental impact associated with conventional uranium mining and milling. Although several methods of extraction have been developed and tested over the past several decades, significant interest has been generated in developing adsorbent fabrics using radiation-induced polymerization after over a kilogram of uranium was obtained by Japanese groups using similar methods. Despite their success, a need remains to develop more efficient adsorbents to make this technology commercially viable.

Advanced adsorbent materials are being developed using polymeric substrates with high chemical stability, excellent degradation resistance and improved mechanical properties. Fabrics include polypropylene, nylon and advanced Winged Fibers™ from Allasso industries featuring extremely high surface areas for improved grafting density. Using the University of Maryland's 100 kCi Co-60 gamma source and 1-10 MeV electron beam linear accelerator, the various fabrics have been irradiated over a wide range of dose rates, total doses and temperatures and subsequently analyzed with EPR for determination of free radical concentration.
Also being utilized are innovative vinyl phosphonate monomers with high distribution coefficients and selectivity for uranium with excellent potential for free radical polymerization. Optimization of the grafting procedure involves precise control over reaction temperature, duration and methodology. Attachment of the chelating adsorbent to the substrate polymer is maximized by use of high monomer concentrations and quantified by determination of the grafting density of the sample. Grafted samples are subsequently analyzed for uranium adsorption with ICP-AES. Preliminary results with the new adsorbent fabrics have yielded distribution coefficients ($k_d$) of around 1000. These results were obtained with real ocean water doped with approximately 10 mg/L uranium introduced in the form of uranyl acetate.

Current work includes optimization of irradiation conditions in addition to material characterization on the molecular level and analysis of the sample microstructure. Further testing in real seawater will be conducted to compare the selectivity of the adsorbent fabric towards uranium compared to that of other species, in addition to determining the loading and adsorption rates under various conditions such as pH, temperature and salt concentration. Experiments in seawater will also be performed to characterize the effects of organics on the adsorbent materials, test for durability and reusability and determine kinetics and efficiency of the uranium extraction as a function of the time of exposure to seawater in order to study the degradation of the sorbent in realistic environments.

I&EC 69

Uranium elution from amidoxime-based polymer sorbents using supercritical CO$_2$

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Amidoxime-based polymer sorbents have been extensively studied for sequestering uranium from seawater. Recovery of uranium from the sorbents is usually done by leaching with an acid such as 0.5 M hydrochloric acid. The aid leaching method is effective for recovering uranium but causes damage to the sorbent due to hydrolysis of the functional groups attached to the polymer. Supercritical fluid carbon dioxide (sc-CO$_2$) is a non-aqueous solvent which has been used to extract uranium from solid substances with CO$_2$-soluble ligands. Our initial results using this ligand-assisted sc-CO$_2$ elusion method to recover loaded uranium from an amidoxime-based sorbent are presented. Ligands tested in the initial experiments include beta-diketones, Cyanex reagents and TBP-HNO$_3$ complexes. Spectroscopic techniques, (fluorescence, Raman and FTIR) are used to measure uranium distributions and uranyl coordination environment in the sorbent.

I&EC 70

Marine testing of uranium adsorption from seawater
A polymeric adsorbent with amidoxime functional groups, developed at Oak Ridge National Laboratory (ORNL), is employed for marine testing. Laboratory experiments with seawater are conducted in batch 5-gallon tanks to provide kinetic and equilibrium data at temperatures ranging from 10 to 35 °C. Flow-through laboratory experiments are conducted using adsorbent beds and 110-gallon seawater tanks. In these experiments, seawater is continuously recycled through the adsorbent. Marine testing is currently conducted at two sites: (1) the Marine Sciences Laboratory of the Pacific Northwest National Laboratory (PNNL) at Sequim, WA, and (2) the Rosenstiel School of Marine & Atmospheric Science of the University of Miami, FL. The batch experiments indicated that six weeks were required for equilibrium, so a period of six weeks is allowed for equilibrium to be reached in all types of the experiments. The parameters investigated are temperature, amount of adsorbent, and flow rate. Results are compared with experimental data obtained in parallel with Japanese adsorbents. Initial results from the PNNL experiment showed that the capacity of the ORNL adsorbent is two to three times the capacity of Japanese adsorbent tested under identical conditions. Kinetic models coupled with mass transfer models and adsorption isotherm equations are used to analyze the experimental results.

I&EC 71

Life cycle cost and energy balance of uranium recovered by a braid adsorbent system

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Life cycle discounted cash flow and inventory analysis methods are used to estimate the production cost and energy return on investment (EROI) of uranium recovered from seawater via a polyethelene-based braid type adsorbent. The estimates are built on original assessments of the cost and energy intensity of materials, capital equipment, labor and other inputs to the uranium production chain. If fresh adsorbent achieves a capacity of 2 grams of uranium (g U) / kg ads, as in trials off the coast of Japan, and the adsorbent may be reused 6 times with capacity degradation of 5% per recycle, the U production cost is estimated at $1230/kg U with a 95% confidence interval of [$1030/kg U, $1430/kg U]. If this uranium is used in a once-through fuel cycle, the EROI is found to be 22. Improving the capacity of the multi-recycled adsorbent to 6 g U/kg ads would reduce the cost by approximately a factor of three, as would attaining a very high capacity -- 20 g U/kg ads -- in a single-use adsorbent.
Theoretical and experimental studies of double-effect direct contact membrane distillation on seawater desalination

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Abstract—A two-dimensional mathematical model was developed theoretically to predict the pure water productivity of double-effect Direct Contact Membrane Distillation (DCMD) processes. The DCMD device is a simple design of MD systems in which both the liquid feed and liquid permeate are kept in direct contact with the membrane. The advantages of DCMD lie in its simple configuration, the need for only small temperature differences and nearly 100% salt rejection. Seawater may be economical reclaimed by DCMD systems for producing drinking water. The DCMC process are performed at middle temperature operation (about 35 °C to 55 °C) of hot inlet stream associated with a constant cold stream inlet temperature. A concurrent flat-plate device was constructed and carried out to verify the theoretical prediction of pure water productivity on saline water desalination in this study. The numerical results from the mathematical modeling of the resultant partial differential equations were obtained using the finite difference technique of the fourth-order Runge-Kutta method. The results show theoretical prediction agreement with the measured values from the experimental runs. The influences of the inlet saline water temperature and volumetric flow rate on the pure water productivity as well as the hydraulic dissipated energy are also delineated.

Effect of plasma treatment on the surface morphology of silk fabric

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Plasma treatment is able to modify the surface structure of the treated substrate. In this study, silk fabric would be plasma treated under different treatment time and the change in surface morphology would be evaluated by Scanning Electron Microscopy (SEM). It is noted that plasma treatment is capable to modify the surface morphology of silk fabric. From the SEM images of the plasma treated silk fabric, it was found that the oxygen plasma would react with the fiber surface and pit and micro pores would be formed, thus making the fiber surface rougher. The longer the exposure time, the higher the surface roughness achieved.

Research on the treatment of AN wastewater using two-stage nanofiltration
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The study was conducted on the treatment of the acrylonitrile(AN) wastewater of high COD using two-stage nanofiltration. The effect of operation conditions including nanofiltration membrane species, concentration ratio, as well as operation temperature on the wastewater treatment performance were investigated in detail. With two stage nanofiltration, the COD removed rate of AN wastewater reached as high as 84.6%. Moreover, the coloration and turbidity decreased below 10° and 0.5NTU respectively. It was found that nanofiltration proved to be a very promising method for the AN wastewater treatment in industrial application.

I&EC 75

**Activated carbon-fenton reagent combination method for the treatment of AN wastewater**

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The study was conducted on the treatment of the acrylonitrile(AN) wastewater of high COD using the activated carbon-fenton reagent combination method. The effect of operation conditions including activated carbon species, dosage of activated carbon and fenton reagent, as well as the single activated carbon and the single fenton reagent on the wastewater treatment performance were investigated in detail. With the combination method, the COD removed rate reached as high as 50%. It was found that the activated carbon-fenton reagent combination method exhibited much better performance in the AN wastewater treatment than single activated carbon or single fenton reagent treatment method.

I&EC 76

**Study of soy-based polyurethane/ acrylic hybrid coatings**

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Bio-renewable materials are very important for deriving sustainable coatings. Aqueous polyurethane dispersions, also known as PUDs, have been synthesized using soybean oil - an inexpensive bio-renewable resource. In order to explore the potential of these PUDs, we have studied how these PUDs interact with different types of commercial acrylic latex by evaluation of their blends for stability, compatibility, and film properties. The key results of these hybrid coating systems will be presented.
Study of hydroxypropylmethylcellulose surface activity at the air-water interface

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The surface activity of hydroxypropylmethyl cellulose (HPMC) was studied at the air-water (A/W). Using a dynamic-surface-tension-measuring apparatus (model DCAT21), the surface tension was measured in different bulk concentrations and different pH. Results showed that the γ-C isotherm was presented inflexion and was like a “W” shape as the HPMC bulk concentration increases(see figure), and the γ-pH isotherm was also presented inflexion and was like a “V” shape with the pH increasing. Therefore, such biopolymer could exhibit different surface properties in different concentrations and pH.

![Surface tension of HPMC](image)

We gratefully acknowledge the financial support provided by the National 973 project (2010CB732201) and the National Natural Foundation of China (project 51043011).

Development of syngas utilization technologies in a demonstration waste gasifier

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A modified fixed bed gasifier (1.2m I.D. and 2.8m high) with water fluidized separator has been developed. To maximize the capture of soot or unburned carbon, the water fluidized bed and gas/solid separators are equipped in the modified fixed bed gasifier. The oxygen velocity was 45-70Nm³/hr and the feed rate of waste woodchips and RPF
were 1-3 ton/day. The experiments with 24-50 hours of operation were carried out to determine the effects of bed temperature, solid/oxygen ratio and oxidant on the gas composition, calorific value and carbon conversion. The calorific values of the produced gas decreased with an increase of bed temperature because combustion reaction more actively happened. The average gas composition of waste woodchips is CO: 33.1%, H$_2$: 11.8%, CH$_4$: 4.9%, CO$_2$: 50.1% and that of RPF is CO: 22.9%, H$_2$: 22.6%, CH$_4$: 4.1%, CO$_2$: 43.4%. To investigate the utilization of syngas from the gasifier, the combustion processes by using industrial boiler and gas engine and hydrogen production process were developed.

I&EC 79

Water remediation by removal of metal ions using poly(aminoamide) dendrimers

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In this study, removal of different Fe, Ni, and Cu metal ion concentrations from water was achieved by using fourth generation poly-aminoamide (PAMAM) dendrimer with terminal hydroxyl groups (G4-OH) in aqueous solution. Dendrimers are well defined and highly branched polymers with controllable architecture that consist of a core, interior and terminal branch units, and they can be used as a nanoscale container for toxic metals ions in aqueous solution. The chelation process between metals ions and the internal tertiary amine groups of the dendrimers was monitored visually and recorded using digital imaging. To quantify the results, time resolved UV-Visible Absorption Spectroscopy was used. Transmission Electron Microscopy and X-ray absorption spectroscopy were used to measure the size and distribution of the zerovalent metals after reduction of the coordinated metal ions to investigate the dispersion of the metal ions uptake by the usage of dendrimer. The results indicates the formation of mostly monodisperse metal clusters with diameter in the range of 1 to 1.5 nm (40-400 atoms/cluster), which is consistent with the mole equivalent of the original metal ion to dendrimer concentration. Here we report the complexation process between metals ions with the tertiary amines of PAMAM dendrimer and their subsequent reduction for further characterization. The dendrimer chelation process demonstrated to be a viable technique to remove metals ions from aqueous solution.

I&EC 80

Fabrication of copper/carbon core-shell nanoparticles using bio-inspired polydopamine
Recently, copper (Cu) nanoparticles have been considered as a promising candidate to substitute silver or gold nanoparticles in the electrically conductive ink application, due to their high electrical conductivity and low cost. However, Cu nanoparticles tend to be rapidly oxidized at the ambient air condition, therefore the oxidation protective coating should be accompanied with minimizing the electrical conductivity. Here, we utilized bio-inspired polydopamine as the encapsulating material on Cu nanoparticles. Polydopamine (pDop) mimics the catechol-amine structure in the mussel’s adhesive foot protein, mytilus edulis and it can be easily coated on the Cu surface at the nanometer scale. Furthermore, since pDop can be carbonized with high carbon yield by simple thermal annealing, the oxidation-resistive and electrically conductive Cu/C core-shell nanoparticles can be obtained.

I&EC 81

**Novel titanium complexes containing chiral tridentate Schiff base ligands for ring-opening polymerization of lactide**

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The selective synthesis of tri- and dichlorotitanium species containing chiral tridentate Schiff base ligands, derived from (1R,2S)-(−)-1-aminoindanol, was achieved by changing the solvent. Single-crystal X-ray analyses reveal that chlorotitanium complexes are monomeric and octahedral with the meridional occupation of the Schiff base. Although the chlorotitanium complexes lack typical initiating groups such as alkoxides or amides, they are effective catalysts for the controlled ring-opening polymerization of L-lactide (L-LA) as shown by the linearity of the molecular weight vs [L-LA]/[Ti] ratio plot as well as very narrow polydispersity index values.

I&EC 82

**Carbon dioxide capture with amines in nonvolatile solvents and the effect of sulfur dioxide on the absorbent**

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Building on previous research, diethylenetriamine (DETA) was studied in ionic liquids and polymeric solvents for its carbon dioxide capture capabilities. DETA reacts reversibly with CO$_2$ to form a zwitterionic adduct. The temperature at which CO$_2$ is released from the adduct was determined, using both a titrimetric method and TGA/MS, to be between 120-150°C. The DETA-CO$_2$ adduct is a solid material which introduces transport, storage and regeneration complications. By preparing mixtures of DETA with other amines, stable liquid products were obtained. The effect of a common flue gas contaminant (SO$_2$) on the DETA system was also investigated. In the presence of air, sulfur dioxide usually reacts with DETA to form sulfite salts, although this reactivity is slightly altered in ionic liquids. SO$_2$ also reacts with di-$n$-alkylamines to form bisulfates. SO$_2$ combines readily with tetraphenylphosphonium halide salts to form halosulfites. These reactions appear to be thermally reversible as the halosulfites release SO$_2$ when heated.

I&EC 83

Preparation, properties, and solubility of phosphonium ionic liquids as lubricant additives in synthetic base oils

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Phosphonium ionic liquids are unique materials that exhibit remarkable thermal stability, low flammability and high viscosity indices. These non-volatile materials reduce wear, exhibit high loading capacities and form effective boundary films for extreme pressure applications. The highly tunable nature of phosphonium ionic liquids provides them with an exceptionally diverse range of physical properties including variable viscosity, miscibility with base oils as well as compatibility with additives and materials. The ionic nature of the phosphonium salts also imparts electrical conductivity to the lubricant formulation. Here we report bulk physical properties of a number of novel phosphonium ionic liquids as well as their solubility data in synthetic base oils.

I&EC 84

Swellable glass sorbents: A new paradigm for industrial separation

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Swellable organosilica (Osorb®) is a sol-gel derived material that absorbs up to 8 times of its dry weight in neat organics and has high affinity for dissolved organic species. The absorption/swelling process is in part mechanically driven and is reversible. Osorb® was successfully used for partition of range of species from aqueous solutions, such as
produced waters, run off landfill recovery, and catalysis. This presentation will focus on the fundamental aspects of how Osorb removes organic from aqueous phases.

I&EC 85

**Syntheses of novel naphthalimide derivatives and their acidichromic and Hg-sensing properties**

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Two novel fluorescent naphthalimide-based sensors as ion sensor and acidichromic colorant are synthesized. This naphthalimide fluorophore is functionalized via a condensation reaction in which dithiodioxomonoaza-based crown-containing phenyl units are conjugated to the naphthalimide core as a trapper for detecting acids in the gas phase and heavy metal ions Hg$^{2+}$.

It shows a selective chromogenic behavior toward Hg$^{2+}$ ion by changing the color of the solution. It also can be found that both on a solid PC (polycarbonate) film and in solution show acidichromism, i.e. a reversible color change upon alternatively exposing the films or solution to HCl and NH$_3$ gases, respectively. In this study, the designed sensors have been developed for the colorimetric and fluorescent determination by UV-Vis and fluorescence spectroscopy, and visual detection by the naked-eye. The visual detection provides a simple, rapid and sensitive method and was used for the detection of gaseous acids and Hg$^{2+}$ ion in environmental applications.

I&EC 86

**Impregnated activated carbon materials with quaternary compositions as versatile toxic gas adsorbers for human respiratory protection**
The combinatorial method was employed to prepare and screen impregnated activated carbon (IAC) materials with up to four impregnated phases. Carbon impregnated with copper, zinc or manganese oxides is a good SO$_2$ and HCN adsorber and carbon impregnated with CuCl$_2$ is a good SO$_2$ and NH$_3$ adsorber. All four reagents were impregnated within activated carbon in varying proportions to screen for the most versatile adsorbent materials. Gravimetric analysis was used to evaluate the ability of the samples to remove acidic and basic gases. Based on the results of the gravimetric studies, ten samples were chosen and evaluated using mock industrial flow tests to determine the potential of the materials as versatile gas adsorbents for respiratory protection applications. An adsorbent material impregnated with 36% CuO, 48% ZnO, 12% CuCl$_2$ and 4.0% Mn$_3$O$_4$ provides a balanced gas adsorption performance with respect to SO$_2$, NH$_3$, HCN, NCCN and humid C$_6$H$_{12}$ gases.

I&EC 87

**Surface modification of cellulose acetate(CA) membranes by PVA coating**

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**INTRODUCTION**

With the demands for high efficiency and low energy consumption, concerns about forward osmosis technology have remarkably increased. Especially studies have been focused on forward osmosis membrane for seawater desalination. However, conventional research was focused on operation condition, development for effective draw solution and techniques for recovery of draw solute and researches about forward osmosis membrane were slightly developed. In this study, forward osmosis membrane was prepared using cellulose acetate and polyvinyl alcohol (PVA). Performance of membrane was tested through reverse osmosis device with preparation conditions of membrane, concentration of PVA and cross-linker, cross-linking time. Differences in water flux with rejection between RO and FO for prepared membrane were observed.

**EXPERIMENTAL**

**Materials** Cellulose acetate (CA), Polyvinyl alcohol(PVA), glutaraldehyde, acetone were used for membrane preparation. Sodium chloride (NaCl) was used for RO and FO performance test.
**Fabrication of CA membrane** Aqueous solutions with 23wt% CA was prepared. Then CA solution was poured onto the polyester non-woven fabric and casted using casting knife with 200µm. The casted film was immersed in water. Prepared membranes were then washed using deionized water for 8h to eliminate residual solvent.

**Membrane modification** PVA was used in modification of CA FO membranes by pressured coating methods. Aqueous PVA solution was prepared by dissolving the PVA polymer in distilled water completely. PVA solution was filled into the stirred cell in which a support membrane had been loaded, and was pressured through the membrane by using a nitrogen cylinder. During a pre-determined period of filtration, the PVA coated membrane was formed.

![Reaction scheme of cellulose acetate and PVA crosslinking.](image)

**Characterization of membranes** The chemical composition and structure of surface modified CA membrane were characterized by scanning electron microscope(SEM), X-ray photoelectron spectrooscope(XPS), Fourier transform infrared(FT-IR), Atomic force microscope(AFM), z-potential, contact angle.

**RO test** Experiments were conducted to evaluate the perm-selectivity of prepared membranes. Water flux and salt rejection were investigated using 2,000ppm of aqueous NaCl solution.

**FO test** 1M of aqueous NaCl solution was used as a draw solution. The water flux of prepared membranes were investigated using digital balance on permeate side.
CONCLUSION

In this study, we fabricated CA membrane by phase separation method. By pressured coating methods, the surface of CA membrane was modified with PVA successfully. The RO experiment with NaCl solution showed that the PVA coated membranes were showed decline of water flux as the concentration of coating solution increases. The PVA treated membranes showed better performances compared to unmodified CA membrane.

REFERENCES

Effects of seawater, salts, and air pollutants on the deterioration of stone cultural asset

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The effect of environmental factors such as sea salts and air pollutants on the deterioration of stone cultural asset has been evaluated using fresh granite. Dipping test of granite using sea salts and acidic solutions showed that initial dissolution rate of minerals was rapidly increased and then maintained constantly until 100 cycles. After sea salts and acid solution experiments, mineral compositions of a granite surface were changed and the density of the weathered granite was decreased to 2.56 g/cm$^3$ from 2.60 g/cm$^3$. However, dissolution rate of minerals over granite surface was retarded by TiO$_2$ coating which can block the penetration of chemicals. This implicates TiO$_2$ coating could be considered as a viable method to assist in the preservation of stone cultural asset from environmental contaminants.

I&EC 89

Comparing homogeneous and heterogeneous hydrogenation pathways of maleic anhydride to prepare succinic anhydride

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The hydrogenation of maleic anhydride (MA) is economically favored process to produce succinic anhydride (SA). Two hydrogenation pathways of MA to synthesis SA were investigated and compared. Homogeneous hydrogenation of MA to SA using Rh catalysts yielded high conversion of MA (99%) and high selectivity of SA (99%). Reaction was performed in 50 ml high pressure stirred autoclave under H$_2$ pressure 1.5–2.5 MPa at 350–380 K for 4-6h using RhCl(PPh$_3$)$_3$ and PPh$_3$ as catalyst and ethylene glycol dimethylether as solvent. Heterogeneous hydrogenation of MA in ethylene glycol dimethylether catalyzed by Ni/Sn/SiO$_2$ or Ni/Sn/Al$_2$O$_3$ (1-2 wt.% Ni, 0.5 wt.% Sn) was carried out in autoclave under H$_2$ pressure 0.5–1.0 MPa at 360–380 K for 2-8h. Heterogeneous hydrogenation yielded 98% conversion of MA, the product mixture consists of 85-95 % SA, 3-13 % gamma-butyrolactone and less than 2% unreacted MA.

I&EC 90

Styrene monomer production using alternative raw materials
Styrene monomer is used in the production of plastics and synthetic rubbers and has a global demand of 25 million MTA. It is currently produced via the dehydrogenation of ethylbenzene, a highly endothermic and thermodynamically limited reaction. Its production consumes about ten times the energy of similar chemicals and is a major contributor to GHG emissions.

The side-chain alkylation of toluene with methanol to yield styrene has been studied for many years. However, high rates of methanol decomposition and low yields of styrene have prevented the commercialization of this technology. Exelus has developed a styrene monomer production technology that achieves styrene selectivity of over 75%, far greater than previously reported results.

The greatest economic driver of this technology is a 20% reduction in feedstock costs. It also offers lower capital costs than conventional plants by eliminating the need to generate 900°C steam used to provide the heat of reaction.

I&EC 91

Testing adsorbents to extract uranium from ambient seawater

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A marine testing program has been initiated to test the ability of various adsorbent materials to extract uranium from ambient seawater. Adsorbents developed at Oak Ridge National Laboratory were exposed to filtered ambient seawater under controlled physical conditions (temperature and flow-rate) at the Marine Sciences Laboratory, a part of the Pacific Northwest National Laboratory. Ambient water quality (salinity, pH, dissolved organic carbon, trace element content) was monitored along with uranium content to interpret the adsorption of uranium. Uranium was determined directly in diluted ambient seawater by inductively coupled plasma mass spectrometry using the method of standard additions to correct for matrix interferences. Ambient trace element concentrations were determined by ICPMS following complexation by ammonium pyrrolidine-dithio-carbamate and reductive precipitation of an iron/palladium carrier to preconcentrate trace elements from solution. Determination of uranium and other metals on the adsorbents were conducted by ICPMS and ICPOES following acid extraction.

I&EC 92
Characteristics of urea utilization in a hybrid SNCR-SCR reaction using pilot scale flow reactor

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Urea utilization efficiency of hybrid SNCR-SCR reaction was measured with a variation of reaction temperature, NSR and additives using a pilot scale flow reactor. DeNOₓ efficiency of urea solution was 10~80% at 850~1,000°C with NSR = 1.0~2.5 and NH₃ concentration after the SNCR reaction was about 100~1ppm. DeNOₓ efficiency of hybrid SNCR-SCR reaction was about 50~92% and the utilization efficiency of urea was 46%. It should be noted that selectivity of slipped NH₃ over V₂O₅/TiO₂ catalyst was almost 1.0 and the utilization efficiency of urea in a hybrid SNCR-SCR reaction depends on the DeNOₓ efficiency of SNCR reaction. In our study, maximum utilization efficiency was found to be 98% at 940°C, NSR=1.1, and SV of catalyst=30,000hr⁻¹. At that time DeNOₓ efficiency was 54%.

I&EC 93

Ionic liquids for supercapacitor applications

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The need for improved energy storage capability in supercapacitors has prompted the use of ionic liquids (ILs) as alternatives to acetonitrile based solvents. Despite the advantages of supercapacitors, their use in transportation is not favorable because of the deterioration of organic solvents with increasing temperatures and their high vapor pressures. We report here on the synthesis and characterization of ionic liquids optimized for use in supercapacitors. ILs based on pyrrolidinium, imidazolium and dicationic ammonium cations bearing ether substituents and bis(trifluoromethylsulfonyl)imide [NTf₂] anions have been synthesized, purified and characterized for their physical properties. The structures of the salts were confirmed using H-1 and C-13 Nuclear Magnetic Resonance spectroscopy. The ILs were characterized for viscosity, conductivity and thermal profile. This work was supported in part at BNL by the DOE Office of Basic Energy Sciences, under contract # DE-AC02-98CH10886.
Effects of side chain branching on the structure and properties of ionic liquids

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This investigation focuses on synthesizing and characterizing ionic liquids (ILs) containing imidazolium and pyrrolidinium cations bearing branched alkyl chains and comparing the properties to their linear analogues to assess the effect of alkyl chain branching. The ILs were synthesized by reacting the amines with selected alkyl halides to generate the precursor halide salts. The associated anion was then converted to bis(trifluoromethylsulfonyl)imide [(CF₃SO₂)₂N]. Thermal profile, conductivity, density, and viscosity were measured for all ILs. The data indicates that viscosity increases with alkyl chain branching or increasing alkyl chain length, with a corresponding decrease in conductivity. The charge-ordered structures of straight and branched alkyl chain ILs were investigated using the wide-angle x-ray scattering technique. The x-ray diffraction data indicates that having branches on the side chain does not affect the charge-ordered structure. This work was supported in part at BNL by the DOE Office of Basic Energy Sciences, under contract # DE-AC02-98CH10886.

Cyclic phosphonium ionic liquids

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Phosphonium ILs have been less explored compared to their ammonium analogues, even though they offer the advantages of lower cost, lower viscosity, higher conductivity, better thermal stability, and wider electrochemical windows. Cyclic phosphonium ILs are thus far unreported. Recent reports on the physical properties of piperidinium and azepanium suggest that the analogous cyclic phosphonium compounds are expected to exhibit superior physical properties for battery applications. Cyclic phosphonium bis(trifluoromethylsulfonyl)imide (NTf₂) ILs bearing alkyl or phenyl...
substituents were synthesized, and their structures were confirmed using \(^1\)H, \(^{13}\)C and \(^{31}\)P Nuclear Magnetic Resonance spectroscopy. We report here on the conductivity, viscosity, self diffusion coefficients and thermal properties of the phospholanium and phosphinanium salts. The cyclic phosphonium salts appear to exhibit higher viscosities than their ammonium analogues and higher thermal decomposition temperatures. This work was supported in part at BNL by the DOE Office of Basic Energy Sciences, under contract # DE-AC02-98CH10886.

I&EC 96

**Greener vinyl ester resin from biowastes**

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Vinyl ester resin (VER) is a low-cost resin that can be processed at ambient temperature using Vacuum-Assisted Resin Transfer Molding (VARTM) into massive carbon-fiber-reinforced composite structures. Because VER production is dependent on oil it is subject to escalating prices and limitations in supply. The continued viability of this strategic material is further jeopardized by the use of hazardous materials, epichlorohydrin and styrene, in its manufacture. QNA has initiated a novel approach for VER production from renewable sources, which could eliminate dependence upon oil for manufacture of composites, replace toxic epichlorohydrin with non-toxic component. Non-petroleum biowastes in this approach could provide sustainable raw materials, and reduce biomass waste and its associated disposal cost.

I&EC 97

**Degradation of TNT and RDX by bioreduced iron bearing soil minerals**

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We demonstrated that reductive degradation of 2,4,6-Trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (Royal Demolition Explosive, RDX) can be enhanced by bio-reduced iron-bearing soil minerals (IBSMs) using *Shewanella putrefaciens* CN32 (CN32). The degradation kinetic rate constant of TNT by bio-reduced magnetite was the highest (0.0039 h\(^{-1}\)), followed by green rust (0.0022 h\(^{-1}\)), goethite (0.0017 h\(^{-1}\)), lepidocrocite (0.0016 h\(^{-1}\)), and hematite (0.0006 h\(^{-1}\)). The highest rate constant was obtained by bio-reduced lepidocrocite (0.1811 h\(^{-1}\)) during RDX degradation, followed by magnetite (0.1700 h\(^{-1}\)), green rust (0.0757 h\(^{-1}\)), hematite (0.0495 h\(^{-1}\)), and goethite (0.0394 h\(^{-1}\)). Significant increase of Fe(II) was observed during the reductive degradation of TNT and RDX by bio-reduced IBSMs indicating that
increased Fe(II) was a key factor to enhance the degradation of TNT and RDX in this study.

I&EC 98

Copper recovery from polishing wastewater by electrodialysis

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The environmental impact of copper contamination and higher water consumption are serious challenges facing for the semiconductor industries. Traditional wastewater treatments processes typically require high chemical consumption and generate heavy metal sludge volume. With the rising environmental awareness and high raw material cost, the reclamation processes have come into public attention.

This research focuses on the efficiency of an integrated water reclaim system with Ultrafiltration (UF) and Electrodialysis (ED) for treatment and reclamation of copper wastewater. In this work, the permeate flux for the ultrafiltration membrane are investigated using artificial solutions containing nano-scale silica particles and Cu ions. Using different operating parameters we studied the separation efficiency, produced water quality and the optimal conditions applied to SiO$_2$ and Cu raw material recovery. Experiments are conducted using commercial polyvinylidene fluoride (PVDF) membrane, ion exchange membranes (SKS-C• GSKS-A), and graphite electrodes in both batch and continuous operations with three parameters: concentration (SiO$_2$: 500, 1000 mgL$^{-1}$; Cu 10, 25, 50, 120 mgL$^{-1}$), pH (3, 4, 5) and voltage gradient (1, 1.5, 2.5 Vcm$^{-1}$). The UF membrane system could effectively separate the particles from the solution with a rejection rate over 99.7%, then the ED process would reclaim Cu ions from permeate solution. The removal efficiency of copper can reach above 95.6%, when the operating conditions in the well-stirred batch reaction process are constant voltage 50V and reaction time 2hr.
Results from the desorption experiment presented the release amount of 93.5% of copper from ion-exchanger membrane.

The improvement of adsorption efficiency by the modified ED system is an emerging technique for recycling heavy metal from chemical mechanical polishing (CMP) wastewater because it is capable to attenuate problems such as membrane fouling, block of ion exchange resin, and microbial activities in a batch reactor. The combination of membrane systems could treat the copper wastewater to the level that easily meets the Taiwan EPA’s effluent regulations (3 mgL$^{-1}$). With efficient desorbing solution, from this study presents the feasibility for removal and recovery of copper from wastewater.

I&EC 99

Interaction of uranium with poly(acrylamidoxime) adsorbents

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Acrylamidoxime polymers currently employed for extraction of uranium from seawater contain distinct chelating structures that are capable of forming metal complexes. Density functional theory is used to rank these chelates with respect to their relative affinity for the uranyl cation. The results yield further insight into how these adsorbents function and provide criteria for the design of improved adsorbents through chemical modification of the binding sites.
Development of rigid cyclic amidoximes for uranyl binding

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The ability to extract uranyl ([UO₂]^{2+}) from seawater would ensure a ready supply of uranium for nuclear power. Higher capacity adsorbents that are effective in the salinity and pH of seawater may be the quickest method to improve the gravimetric yield of uranyl extraction from seawater. We are developing rigid cyclic amidoximes of the type shown below. The progress on their synthesis, spectroscopic characterization and binding affinity for uranyl will be discussed.

![Chemical structure of amidoxime](image)

**R:** H, NH₂, Br, (CH₂)₄CH=CH₂

Amidoxime-grafted mesoporous carbon and porous organic gel sorbents for extraction of uranium from seawater

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Mesoporous carbon (MC) sorbents have gained much attention due to their inertness, high surface areas, and controllable pore sizes. In this study, pristine, activated, and oxidized MCs were synthesized by a soft template method. Free radical grafting of monomers under an electron beam irradiation or a chemical initiator, followed by amidoximation, yielded high surface area amidoxime (AO)-grafted MCs. In comparison to grafted MCs, porous AO-containing phenolic-formaldehyde monolithic gels were also prepared. The availability of various nitrile-containing phenolic precursors enabled the preparation of amidoxime and phthalimide dioxime (i.e., cyclic structure) sorbents. Results from uranyl sorption study, compared side-by-side with known uranyl sorbents, will be presented.

This research was supported by the Fuel Resources Campaign in the Fuel Cycle Research and Development Program, Office of Nuclear Energy, U.S. Department of Energy (DOE).

I&EC 102

Synergistic effect of sonochemical grafting and hierarchical porosity of carbons on uranium adsorption from seawater

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Here we report for the first time the synergistic effect of the sonochemical grafting and hierarchical porosity of carbons on uranium adsorption from seawater. Series of different carbon materials has been synthesized by combined soft- and hard-templated method. Typical soft-templating approach is based on the polymer-polymer interaction between a phenolic resin-type carbon precursor and a triblock copolymer used as soft template. The thermal decomposition of the latter creates uniform cylindrical mesopores ~8-10nm in diameter. The dissolution of silica colloids added the synthesis gel introduces porosity with spherical geometry, which can be easily tailored by the choice of silica colloids used. Our former studies suggest that the presence of tiny pores (up to 2nm) and large surface area is a key factor to improve degree of grafting. The goal of this work is to determine the role of mesopores and small macropores, and to discriminate the optimum porosity range for maximum uranium adsorption from seawater.

I&EC 103

Isolating trace seawater uranium with polymer functionalized porous carbon
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The volume of the world's oceans is so huge that seawater can almost provide limitless amounts of uranium - some around 4.5 billion tons, even though one ton seawater contains only about 3.3 mg Uranium. Therefore, developing effective adsorbents for uranium extraction from seawater is very promising. So far, the most efficient adsorbents are solid polymers containing amidoxime groups (-\((\text{NH}_2)\)=N-OH), which show high affinity and selectivity for uranyl ion, i.e. approximately ten fold greater than the conventional titanium oxide adsorbent. However, these polymeric adsorbents usually have lower Brunauer-Emmett-Teller (BET) surface area and low mechanical strength. To increase the surface area of the polymeric adsorbent, we copolymerized the amidoxime generating monomers on the surface of high surface area mesoporous carbon. With increasing the ratio of monomers/carbon, the uranyl ion adsorption capacity increases whereas the BET surface area decreases correspondingly. The capacities of uranyl ion adsorption from the best sample are 19.1 g U/kg and 63.3 g U/kg, respectively, for 50 mL and 250 mL uranium stock solutions. The results are higher than the Japanese sample under the same conditions (18.2 g U/kg and 35.4 g U/kg for 50 mL and 250 mL uranium stock solutions, respectively), indicating our sample has higher selectivity for Uranium. The real sea water test on the best polymer coated carbon composite adsorbent is under investigation.

I&EC 104

Influence of temperature on uranium adsorption from seawater

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Uranium recovery from seawater has been investigated over several decades. Although it has been reported that temperature has significant effects on uranium adsorption kinetics and equilibrium, further studies are needed to investigate these effects through thermodynamic and kinetic analyses. In this study, a polymeric adsorbent with amidoxime functional groups, developed at Oak Ridge National Laboratory, has been employed for batch experiments of uranium adsorption from seawater in 5-gallon tanks. A quantity of approximately 5 mg of adsorbent is typically used in each experiment, and a period of six weeks is allowed for the equilibrium to be reached. Adsorption kinetics and equilibrium are studied at different temperatures, ranging between 10 and 35 ºC. From the experimental data, the parameters of adsorption isotherms are obtained. Kinetic models coupled with mass transfer models and adsorption isotherm equations are used to analyze the experimental results. Changes in enthalpy, entropy, and free energy are also estimated through the van't Hoff equation to provide a better understanding of the adsorption thermodynamics. This study improves our
understanding of the influence of temperature on uranium adsorption from seawater by polymeric amidoxime-based adsorbents.

I&EC 105

Application of unusual metal speciation in ILs to f-element separations

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Ionic liquids (ILs) are unique in that they offer a high concentration of free ions at a temperature where many metal complexes and ligands are thermally stable. This has resulted in a number of reports on unusual metal chemistry, including the formation of metal-containing ILs. This also has important implications for liquid-liquid extraction of metals, a leading subfield of IL research. Since the behavior of metals in ILs can be unexpected, research on metal speciation in ILs is needed to design reliable separations and take advantage of the new synthetic opportunities of these materials. We have studied the speciation of uranium, thorium, and lanthanides in ILs due to the major relevance of separating these metals. Here we present our results in this area including the unusual coordination of f-elements to soft donors and attempts to incorporate f-elements into ILs.

I&EC 106

Extraction of uranium with regenerated chitin from the dissolution of shrimp shells in ionic liquid

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Ionic liquids (ILs) have the ability to dissolve large polysaccharides such as cellulose and chitin under mild conditions giving unprecedented access to high molecular weight biopolymers directly from biomass. We are interested in using this ability to dissolve chitin directly from shrimp shell waste and generate chitin-based resins for the extraction of uranium from seawater. In addition to being a strong, environmentally friendly, and renewable material, the easily accessible deacetylated derivative chitosan provides a useful tether for attaching any number of functional groups. While chitin and chitosan have been used to extract heavy metals from waste water streams, chitin processed by ILs has not been studied. We will present our efforts towards the “green” processing of shrimp shell waste to manufacture a uniquely high purity/high surface area absorbent chitin material for the extraction of uranium from seawater.
Advanced simulation of a transient gas solid reaction – the chlorination of silicon carbide

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Carbide-derived carbons (CDC) are an emerging class of carbon materials. They have been applied in many fields such as electro chemistry or catalysis. CDCs are produced by the reactive extraction of carbide materials (e.g. SiC, TiC) with chlorine. The reaction is a non catalysed gas solid reaction. Within this work different reaction engineering based models describing the transient reactive extraction were developed and kinetic data derived experimentally [1]. The 1-D and 3-D (finite elemente) models account for the shrinking core, pore diffusion in the product, particle size distribution of the technical powder and volume change of the gas phase. General conclusions, like critical product dimensions and regimes of complete chlorine depletion, were drawn for the production of CDC from SiC.


I&EC 108

Preparation of pigment microcapsules using polyamide as wall material for electronic ink

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The preparation of pigment microcapsules for electronic ink using polyamide is introduced. The wall of polyamide is synthesized from paraphthaloyl chloride and diethylenetriamine. Compared to the unmodified pigment, the dispersibility of phthalocynine green G modified with octadecylamine in tetrachloroethylene was improved by 66.7%. The modified particles migrated to the positive electrode under the direct voltage and were able to migrate reversibly as the anode and cathode were exchanged. The microcapsules that used OP-10 as emulsifier had narrow particle size distribution and complete morphology. The microcapsule yield reached 83.5% at the OP-10 concentration of 1.5wt%. With the reduction of the core/wall weight ratio from 1:6 to 1:10, the yield ascended to 87.6%. The particle size of the microcapsules obtained at 25°C was 327.4nm and was uniform. The average particle size decreased from 1049nm to 271nm while pH increased from 6 to 14. The formed microcapsules owned regular spherical shape.

I&EC 109

Fatty acid dispersant selection for inks used for digital fabrication of solid oxide fuel cells
Inkjet printing has recently emerged as a promising method for fabrication of solid oxide fuel cells. In order for this technology to achieve viability on the manufacturing scale, the ceramic nanoparticles comprising the inks must be stabilized to ensure long term colloidal stability. In the present work, a series of fatty acid dispersants are investigated to clarify how colloidal stability of NiO inks varies with fatty acid chain length, degree of unsaturation, and occurrence as a triglyceride or as an isolated fatty acid. Diffuse reflectance infrared spectroscopy (DRIFTS) indicates that the primary mechanism of dispersant-particle interaction involves the C=O bond of the dispersant. Settling tests show that ink stability does not vary with zeta potential, but does depend on dispersant chain length. The occurrence of the dispersant as a triglyceride also enhances stability, but not as strongly as increasing carbon chain length.

I&EC 110

Evaluation of relative importance of ultrasound reactor design parameters for the removal of estrogen hormones: ANN modeling

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The growing interest in Sonochemistry as a tool for environmental remediation leads to the need for process optimization. Ultrasound is a treatment technology, which could be considered as a significant contributor to green science. Several of these features are: (1) the process is carried out at room temperature and atmospheric pressure, (2) the unique use of electrical energy as a "reactant", allowing the consideration of ultrasound as a green-technology, (3) the energy consumption may be adjusted to match the contamination level.

Sonochemistry is a complex process, which depends on physical parameters and also on the process conditions. Physical parameters are interrelated and therefore a systematic approach has to be taken to optimize the process. The effect of physical parameters on the destruction of seven estrogen hormones (17α-estradiol, 17β-estradiol, estriol, 17α-ethinylestradiol, 17α-dihydroequilin, estrone and equilin) is presented in this study. Artificial Neural Networks (ANN) was used as a tool to identify the correlations between these process parameters. ANN enabled the establishment of relationship between sonication parameters such as power density, power intensity, ultrasound amplitude, as well as the reactor design parameters. The major significance was attributed to the area-specific power density and the volume-specific power intensity. The results of this work provide a sound basis to design pilot and full-scale ultrasound treatment systems. Process optimization lead to a 5-fold decrease in energy...
Combining chloride salt and mild thermal treatment to improve activated sludge settleability and dewaterability

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Mild thermal treatment combined with chloride salt was employed to improve the settleability and dewaterability of activated sludge. Sludge volume index and specific resistance to filtration were determined to evaluate the settleability and dewaterability, respectively. Results indicate that the settleability and dewaterability were deteriorated under thermal treatment, but enhanced markedly with some chloride salts. And combining thermal treatment could intensify this enhancement. Among these chloride salts, KCl, MgCl\(_2\), CaCl\(_2\) and FeCl\(_3\), CaCl\(_2\) was one of the most effective ones. It could ameliorate the settleability and dewaterability as soon as it was added. And notable improvement was observed by adding 37 mg/g DS CaCl\(_2\) at 80 °C. Microscopic observation shows that strong and compact flocs were formed during the treatment. The released polymer substances by thermal treatment are supposed to act as flocculants in the presence of cation, promoting particle contact and floc growth, and leading to strengthened settleability and dewaterability.

Exploring the physico-chemical properties of ionic liquids for carbon dioxide capture applications

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This study focuses on the impact of steric and electronic effects in ionic liquid CO\(_2\) solubility as well as cation core-based trends in thermal stability. A library of 17 ionic liquids was prepared to study the influence of structure through cation selection for CO\(_2\) capture. This is significant in that all physical property measurements are free from the potential influences of minor halide or metal containing species and truely represent only the properties of the IL studied. Two different trends were observed in the CO\(_2\) solubility which indicates both global and local effects of the cation core and core substitution. Here we report how molar volume effects are correlated across a wide
variety of cation core classes and structures while electronic effects are more prevalent in trends with core classes.

**I&EC 113**

**Synthesis of carbonaceous nanomaterials for the application of solid-phase extraction**

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This study aims to develop a solid-phase adsorbent based on carbonaceous materials embedded on silicon substrate or zirconia (ZrO$_2$) spherical carriers. This study used thermal chemical vapor deposition (TCVD) process at atmospheric pressure for growth of carbon nano-material, including carbon nanotubes (CNT), carbon nanosphere (CNS), carbon nanocapsule (CNC), carbon onion, and carbon fibers.

Wet impregnation and spin-coating processes were conducted to coat nickel (Ni) as catalyst precursor on the surface of substrates, followed by using TCVD process with methane as carbon source, argon as carrier gas, and hydrogen as initiator. The structural and physical characteristics of the carbon products were determined using scanning electron microscopy, transmission electron microscopy, energy dispersive spectrometry, X-ray diffractometry, and Raman scattering spectroscopy. The results of these micro-analyses were used to evaluate the effects of individual process parameter on the carbonaceous material characteristics. The ensuing solid-phase adsorption studies were then performed to characterize the sorption properties of the materials associated with their physical characteristics. In this work, phthalic acid esters (PAEs)
were used as the compounds of interest for the solid-phase adsorption studies. PAEs are commonly used in plastic industry, and are most widely used as plasticizer in products such as plastic toys, medical devices, food wrap, perfume and nail polisher. They are categorized as endocrine disrupting compounds (include sex hormone and the thyroxine) and some of them are suspected carcinogens. In Taiwan, PAEs reportedly exist in seawater and freshwater in very low concentration range (0.1 ∼ 300 μg/L). The work therefore uses a representative PAE, namely diethyl phthalate (DEP) as the testing compound. Preliminary adsorption test results indicate that CNC and carbon onion materials both achieved DEP adsorptivity in the range of 80 μg/g at DEP solution concentration of 5 mg/L, and 110 μg/g at DEP solution concentration of 10 mg/L. The web-like carbon structure attained approximately 50 μg/g at DEP solution concentration of 5 mg/L. Additionally, DEP adsorption capacities of CNC and carbon onions were both higher (12.0 μg) than that of commercial adsorbent Tenax TA (4.1 μg).

I&EC 114

Synthesis and characterization of nanosized Mn-TiO₂ catalysts and their application on removal of gaseous elemental mercury

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In order to prepare suitable materials for mercury capture from coal-fired flue gas, the nano-sized Mn-TiO₂ catalysts with different manganese loadings were synthesized with the assistance of the template agent. The catalytic oxidation performances of elemental mercury removal on these catalysts were tested in a wide range of temperature window (150-350 °C). Powder X-ray diffraction (PXRD), N₂ adsorption and transmission electron microscopy (TEM) were employed to characterize the catalysts. Results showed that Mn-TiO₂ with 10% manganese content could remove up to 95% of elemental mercury (balanced with air) at rather high gas space velocity (1.5×10⁶ h⁻¹). It was found that SO₂ inhabited the elemental mercury removal capacity of the synthesized catalysts while NO displayed a promotional effect. HCl was also observed slightly inhibiting the mercury conversion on the catalysts. Moreover, the loadings of manganese were observed playing important roles in catalytically oxidizing elemental mercury. With the increase of manganese content, the performance of the catalysts on elemental mercury removal improved. Mn-TiO₂ (10%) displayed up to 95% of elemental mercury removal efficiency through the test temperature window.

I&EC 115

Removal of 1,4-dioxane and volatile organics from contaminated groundwater using ozone based advanced oxidation processes

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1,4-Dioxane is classified as an emerging contaminant (EC), and its environmental regulations are becoming stringent. It is primarily used as a stabilizer for industrial solvents (chlorinated solvents or volatile organic compounds, (VOCs)) to prevent their breakdown during the manufacturing process. Releases of chlorinated solvents are considered to be the primary source of 1,4-dioxane in the environment. The USEPA has classified 1,4-dioxane as a Group B2 probable human carcinogen of low carcinogenic hazard. It has very high aqueous solubility, very low Henry's constant, and very low biodegradation coefficient. Due to these properties, it is difficult to efficiently remove 1,4-dioxane from water using air stripping, carbon adsorption or by biodegradation.

This project deals with laboratory-scale tests performed to evaluate the removal of 1,4-dioxane and volatile organics present in site groundwater using ozone based advanced oxidation process. The Naval Facilities Engineering Command Northwest (NAVFAC NW) had requested to conduct an investigation for 1,4-dioxane and VOC's removal at a site in Naval Air Station Whidbey Island (NASWI). The NASWI base has a region, which has contaminated groundwater. Currently, there is an existing groundwater treatment system in operation. This treatment system entails an equalization tank, particulate filters, and a packed tower air stripper to remove chlorinated VOCs such as trichloroethene, 1,1,1-trichloroethane, 1,1-dichloroethane, 1,1-dichloroethene, cis-1,2-dichloroethene, and vinyl chloride. However, the groundwater samples have had some detects of 1,4-dioxane in the recent past.

Ozone based advanced oxidation process was tested for the groundwater remediation. Due to very high iron and manganese content, the groundwater samples were raised to a pH of 10, aerated, filtered and then ozonated in the presence of peroxide. Experimental data showed ozonation in the presence of optimum dosage of peroxide reduced the concentration of 1,4-dioxane to below the desired level (≤ 3µg/L). Very high removal of VOCs was also observed.

I&EC 116

U.S. EPA’s Design for the Environment alternatives assessment program:
Selection of safer chemicals

Cal Baier-Anderson, Bridget Williams, williams.bridget@epa.gov, Emma Lavoie.
Design for the Environment, U.S. EPA, Washington, DC 20460, United States

The US EPA’s Design for the Environment (DfE) program works in partnership with industry, environmental groups, and academia to reduce risk to people and the environment by promoting the selection of safer chemicals. For more than 15 years, through partnership projects, DfE has evaluated human health and environmental concerns associated with traditional and alternative chemicals and processes in a range of industries, and empowered hundreds of businesses to select safer chemicals. To facilitate the identification of safer chemicals, criteria are needed to classify and compare chemicals. DfE has developed criteria to evaluate and compare chemicals based on a full range of human health and environmental information. DfE criteria are
applied in our Safer Product Labeling Program to help companies identify and use inherently safer chemicals in consumer and industrial products, and in our Alternatives Assessment Program to compare and contrast chemical options. Challenges in applying criteria include data gaps, emerging science, and uneven data. Progress is dependent on our ability to address these challenges in a manner that is rapid and cost-effective.

I&EC 117

Role of alternatives assessment in DuPont's ongoing journey to sustainability

Henry E Bryndza, henry.e.bryndza@usa.dupont.com, Catherine A. Barton, Catherine A. Barton, Mario W Chen, John Gannon, Robert Giraud, Robert W Rickard, Dawn G Rittenhouse, Carlonda R Reilly. Department of Central Research & Development, E I DuPont de Nemours & Company Inc., Wilmington, DE 19880, United States

Abstract: A description of DuPont's journey to sustainability from compliance towards proactive introduction of renewable materials will be discussed with special emphasis on the role of Green Chemistry in attaining DuPont's sustainability goals. The role of alternatives assessment and criteria for selection will be described in context of DuPont's overall managing processes including:

- DuPont's comprehensive Product Stewardship management process and considerations for introduction of and management of alternatives through the product lifecycle
- Tools, capabilities and processes for assessing multiple dimensions of sustainability throughout the product development and commercialization processes
- Live demonstration of the METIS desktop tool used in DuPont R&D for early assessment of candidates using multiple criteria
- An overview of technoeconomic selection of targets for replacement by renewable materials
- Special consideration of potential pitfalls for commercial success of alternatives including incumbency and scale
- Examples of successful development and launch of renewable materials within DuPont's portfolio

I&EC 118

Alternatives assessment: Going beyond hazard

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The ILSI Health and Environmental Sciences Institute (HESI), a global branch of the International Life Sciences Institute (ILSI), has recently initiated a sustainability-focused
With a vision of creating science-based solutions for a sustainable, healthier world, HESI recognizes sustainability as vitally important as it identifies and resolves global health and environmental issues through engagement with scientists from academia, government and industry. In the fall of 2011, HESI initiated the Emerging Issues Subcommittee on Frameworks for Alternative Chemical Assessment and Selection of Safer, Sustainable Alternatives. Objectives of the subcommittee include to: build understanding of existing approaches used to select safer, sustainable alternatives; identify strengths, weaknesses, and gaps in current approaches; develop a decision tree to guide key stakeholders through the alternatives assessment process; identify emerging needs/challenges for the future; and hold a workshop in fall of 2012 and publish recommendations aimed at improving the successful selection of safer, sustainable alternatives.

I&EC 119

Principles in design of alternative chemistries, and the need for alternatives to assess them

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Various regulatory programs have identified substances exhibiting Persistence, Bioaccumulation, and Toxicity (PBT) in the environment, as well as carcinogenic, mutagenic, reproductive toxicity (CMR), or other hazard characteristics in humans. Such substances are targeted for elimination and/or replacement with alternative chemistries. In designing of alternative chemistries, strategies which focus only on reducing hazard to human health, minimizing impact on the environment, or enhancing product performance will rarely achieve all of these desired attributes. This presentation will provide an overview of the physical/chemical, structural, and reactive properties which are associated with these hazard characteristics, to aid chemical researchers in design of reduced-hazard alternatives. Where reduced hazard and optimal product performance are competing goals, innovations in product packaging, delivery, and capture/recycle will be reviewed to illustrate the effectiveness of exposure control in alternatives innovation. Case studies will be used to illustrate how these concepts in molecular design and exposure control have resulted in development of novel alternative chemistries, the application of which cannot be directly compared against the chemistries they are intended to replace. Thus, the need for alternative approaches in chemical assessment will be illustrated as a necessary part of alternative chemistry development.

I&EC 120

Removal of emerging contaminants from aqueous solution by ozone–based processes
The presence of emerging contaminants (ECs) in water and wastewater systems has become a subject of significant concern worldwide. These emerging contaminants are complex organic molecules (e.g. pharmaceuticals) which potentially affect human health and environment. Conventional wastewater treatment plants are unable to completely remove these contaminants from water and therefore can discharge them into the environment. The need to develop effective methods for ECs removal, the combination of powerful chemical oxidants known as advanced treatment techniques has to be tested. The current study aims the assessment of the potential of ozone-based advanced oxidation processes (AOP) to oxidize number of persistent ECs, using various combinations of ozone with hydrogen peroxide and sodium persulfate. For this study perfluorinated compounds (PFCs), 1-4, dioxane, N,N-Diethyl-meta-toluamide, and three pharmaceuticals such as sulfamethoxazole, trimethoprim and carbamazepine has been selected. Experiments were conducted in a semi batch bubble column reactor setup (including an ozone generator, degassing unit and destruct unit). The effect of different process parameters such as reagents dosages, ozone weight percent, ozone flow rates, etc. on destruction of ECs was examined. During ozonation number of reactive species is formed. Basically, the types of oxidation reactions occurring during ozonation process can be classified as molecular ozone-driven and hydroxyl radical–driven. The experimental results revealed that some of the selected ECs were persistent to direct ozone reaction, however were easily oxidized by hydroxyl radical. These reactivity differences may be attributed to the structural differences and process conditions. The operational conditions were optimized for maximum removal of every compound and their influence on the degradation process was discussed.

I&EC 121

Enhanced oxidative sonochemical removal of 1,4-dioxane from water

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1,4-Dioxane is classified as an emerging contaminant (EC), and its environmental regulations are becoming stringent. It is primarily used as a stabilizer for industrial solvents (chlorinated solvents or volatile organic compounds, (VOCs)) to prevent their breakdown during the manufacturing process. Releases of chlorinated solvents are considered to be the primary source of 1,4-dioxane in the environment. The USEPA has classified 1,4-dioxane as a Group B2 probable human carcinogen of low carcinogenic hazard. It has very high aqueous solubility, very low Henry’s constant, and very low biodegradation coefficient. Due to these properties, it is difficult to efficiently remove 1,4-dioxane from water using air stripping, carbon adsorption or by biodegradation.
Application of ultrasound for the removal of 1,4-dioxane is presented in this study. The effect of pH and oxidizing agents such as H₂O₂, S₂O₈²⁻, SO₄²⁻ on the sonication process were examined. Results indicate that acidic conditions favor the sonication of 1,4-dioxane. The presence of peroxide showed a scavenging effect on the degradation of 1,4-dioxane. An overall degradation of 60% was obtained after 30 minutes of sonication in the absence of oxidizing agents. However, in the presence of sulfate radical (SO₄²⁻) and acidic conditions a removal of more than 99.6% was observed within 4 minutes. The presence of excess of peroxide inhibits the reaction, indicating that OH* radical is an important aspect in the degradation. A 98% reduction in electrical energy consumption per unit order was observed by using oxidants. Ultrasound proves to be an efficient and effective treatment technology for the removal of 1,4-dioxane.

I&EC 122

Structure-function study of CO₂ capture on covalently-tethered amines using combined volumetric adsorption-isothermal titration calorimetry

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With the increasing demand in energy, the influence of anthropogenic sources of CO₂ on global warming is also becoming a major environmental concern. Supported amine sorbents capable of capturing CO₂ within the current EPA standards (2-4 mmol CO₂/gram sorbent) are currently available; this study focuses on the fundamental structure-function relationship for CO₂ capture from dry and wet CO₂-containing gas streams. Numerous grafted amine samples were synthesized on SBA-15 silica supports by varying the loading density and amine precursor types (mono-, di-, tri-aminooalkyltrialkoxy-silanes). Combined volumetric adsorption and microcalorimetry studies were then performed on these samples by interfacing an automated volumetric adsorption apparatus with a differential scanning calorimeter. From these studies, the CO₂ uptake and corresponding heats of adsorption values on these aminated sorbents were obtained. These data provide important insight into the influence of surface amine densities and the local amine structure on CO₂ capture.

I&EC 123

Isotope separation using quantum tunneling

Joshua Schrier, jschrier@haverford.edu. Department of Chemistry, Haverford College, Haverford, PA 19041, United States

Quantum mechanical tunneling is widely used in electronics, but is unexplored for performing chemical separations. Recent theoretical work has revealed that quantum tunneling makes a substantial contribution to the transmission of helium atoms through nanoporous graphene sheets, even at room temperature. The mass-dependence of
quantum tunneling provides a new means for performing membrane-based gas separations of isotopes at much lower capital and energy cost than traditional cryogenic distillation and gas centrifuge methods. I will discuss the theory of quantum tunneling-based membrane separation and recent work on the design of improved nanoporous structures yielding $^3\text{He}/^4\text{He}$ selectivities of up to 19, with nanomole cm$^{-2}$ s$^{-1}$ flux rates. I will also discuss the design of bilayer-nanostructures exhibiting resonant tunneling transmission. Unlike classical membranes where permeance is inversely proportional to membrane thickness, the resonant tunneling states of the bilayer increases the flux rate by an order of magnitude compared to a single-layer structure, while also increasing the isotope selectivity.

**I&EC 124**

**Microwave catalytic degradation of dye wastewater by cobalt oxide modified activated carbon**

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Synthesized cobalt modified activated carbon was used in the catalytic degradation of dye wastewater. Parameters affecting degradation efficiency and chemical reaction kinetics were investigated. Ultrasonic impregnation and calcination were used as pretreatment process to obtain cobalt modified activated carbon. Thermal gravimetric analysis indicated that the weight loss temperature of cobalt modified activated carbon was 673.15K, which was 303.15K higher than activated carbon. X-ray diffraction analysis showed that cobalt modified activated carbon appeared characteristic peak when $2\theta$ is 20.9°, 37.1°, 43.0° and CoO appeared characteristic peak when $2\theta$ is 19.1°, 31.3°, 36.7°, 42.4°. The surface of activated carbon had polymorphs doped CoO cubic crystal diffraction peak. During the preparation, the doped cobalt presented in the activated carbon in the final form of CoO. Scanning electron microscopic analysis showed that the presence of the CoO introduced more crystalline defects and uneven to the cobalt modified activated carbon.

The influence of solution acidity, activated carbon dosage, dye concentration and microwave power to catalytic degradation of dye wastewater were further studied.

**Degradation of dye wastewater process parameters**—

<table>
<thead>
<tr>
<th>Dye species</th>
<th>pH</th>
<th>ACCO dosage (g.L$^{-1}$)</th>
<th>Initial dye concentration (mg.L$^{-1}$)</th>
<th>Microwave power (W)</th>
<th>Microwave time (S)</th>
<th>Color removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methylene blue</td>
<td>7.0</td>
<td>1.000</td>
<td>400</td>
<td>480</td>
<td>600</td>
<td>87.95</td>
</tr>
<tr>
<td>cationic red X-GRL</td>
<td>10.0</td>
<td>0.600</td>
<td>500</td>
<td>480</td>
<td>600</td>
<td>96.18</td>
</tr>
</tbody>
</table>
Degradation kinetic equation and parameters—

<table>
<thead>
<tr>
<th>Kinetic equation</th>
<th>methylene blue</th>
<th>cationic red X-GRL</th>
<th>acid light yellow G</th>
</tr>
</thead>
<tbody>
<tr>
<td>first order kinetics equation</td>
<td>( \ln(C_0/C) = 0.2038t + 0.1364 )</td>
<td>( \ln(C_0/C) = 0.3929t + 0.0118 )</td>
<td>( \ln(C_0/C) = 0.3077t + 0.0922 )</td>
</tr>
<tr>
<td>( k_1 (\text{min}^{-1}) )</td>
<td>0.2038</td>
<td>0.3929</td>
<td>0.3077</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9905</td>
<td>0.9977</td>
<td>0.9936</td>
</tr>
<tr>
<td>second order kinetics equation</td>
<td>( 1/C = 0.0017t + 0.0009 )</td>
<td>( 1/C = 0.005t - 0.0046 )</td>
<td>( 1/C = 0.005t - 0.0052 )</td>
</tr>
<tr>
<td>( k_2 (\text{min}^{-1}) )</td>
<td>0.0017</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9599</td>
<td>0.8733</td>
<td>0.8872</td>
</tr>
</tbody>
</table>

Key words: microwave, cobalt modified activated carbon, dye, kinetics

I&EC 125

Kilogram-lab-scale oxindole synthesis via palladium-catalyzed C–H functionalization

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A scalable, chromatography-free route for the preparation of an oxindole, a key intermediate en route to a drug candidate for raising HDL cholesterol, has been developed. This 3-step sequence takes advantage of Buchwald's palladium-catalyzed C-H functionalization (Hennessy, E. J.; Buchwald, S. L. J. Am. Chem. Soc. 2003, 125, 12084) to cyclize an α-chloroacetanilide to form the five-membered ring. This process has been successfully carried out in our kilo laboratory facility on 8 kg-scale in 76% yield.

I&EC 126

Copper C-arylation applied to the synthesis and scale-up of complex heterocycles
Direct copper C-arylations were relatively unknown reactions in the literature until only very recently. We will describe the direct copper catalyzed arylation to prepare highly substituted pyrazolo-pyrimidines and imidazo-pyridazines from thiazoles. The use of copper to replace palladium based direct arylation has a number of distinct advantages including green chemistry applications. We will examine the scope and scale-up of copper-C-arylations to produce complex heterocycles.

I&EC 127

Implementation of a kilogram-scale iridium-catalyzed redox-neutral alcohol amination

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The iridium- or ruthenium-catalyzed redox-neutral alcohol amination reaction is an attractive single-step alternative to traditional two-step processes for the synthesis of functionalized alkyl amines from aliphatic alcohols and a wide variety of amines. This chemistry has been implemented on kilogram-scale for the synthesis of diamine 1, a pharmaceutical intermediate. Of particular note, we determined that catalyst turnover is facilitated by the presence of water and a tertiary amine, allowing for catalyst loading to be reduced to below 0.1 mol% Ir. This presentation will describe our efforts and learnings from optimizing and scaling this chemistry.
I&EC 128

Process development of a triple reuptake inhibitor: Application and process safety evaluation of palladium catalyzed α-arylation of dihydroisoquinolinone

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Process development toward a triple reuptake inhibitor is discussed. During the evaluation of the original route two des-bromo impurities were observed in the palladium catalyzed α-arylation and palladium catalyzed Buchwald-Hartwig amination. The optimized route featured Eaton’s reagent mediated cyclization of a phenylacetamide, copper-mediated Buchwald-Hartwig coupling, and palladium catalyzed α-arylation of a dihydroisoquinolinone to construct the core structure. Safety studies by reaction calorimetry were performed for most of the stages and a delayed exotherm was observed during the palladium catalyzed α-arylation.