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Faisal Fadzil, Shariff Ibrahim, Megat Ahmad Kamal Megat Hanafiah. *Adsorption of lead(II) onto organic acid modified rubber leaf powder: Batch and column studies*. Pages 1-8.

This study evaluated the Pb(II) sorption capacities of two chemically modified biosorbents which are citric acid modified rubber leaf powder (CARL) and monosodium glutamate modified rubber leaf powder (MGRL). The raw rubber leaf powder (RLP) was modified to improve its effectiveness in removing the Pb(II) ions in an aqueous solution. CARL was prepared by esterification of citric acid onto the cellulose structure while MGRL was prepared by functionalising monosodium glutamate onto the epoxy activated rubber leaf powder. The sorption performance of the sorbents was examined by pH, kinetics and isotherm experiments. The adsorption of Pb(II) was much more favourable at higher pH. The rate limiting step in the adsorption process for both adsorbents was chemisorption and both adsorbents had a better fitting to the pseudo-second order kinetic model. The maximum capacities of Pb(II) calculated by the Langmuir isotherm by CARL and MGRL were 97.19 and 109.95 mg/g, respectively. In column experiments, the breakthrough time was found to decrease from 25 to 5 min for CARL and 37.5 to 10 min for MGRL with an increase in Pb (II) concentration from 20 to 60 mg/L. The Thomas and Yoon–Nelson models had a good fit with the fixed bed column data. Different column parameters such as column adsorption capacity and 50% adsorbate breakthrough were calculated. It was found that the adsorption capacity and performance of MGRL was superior to CARL in both batch and fixed bed column studies.

- **Keywords:** Organic acids; Rubber leaf; Adsorption; Lead(II); Column; isotherm

Abdul Hameed, Faisal Khan, Salim Ahmed. *A risk-based shutdown inspection and maintenance interval estimation considering human error*. Pages 9-21.

This paper presents a risk-based methodology to estimate shutdown inspection and maintenance interval by integrating human errors with degradation modeling of a processing unit. The methodology presented in this paper addresses to identify the number of shutdown intervals required to achieve a target reliability over a goal period. The proposed methodology is the extension of the previously published work by the authors to determine the shutdown interval considering the system's desired availability. The proposed work is novel in the sense that a concept of human error during shutdown inspection and maintenance is introduced while modeling the system failure. Selection of critical equipment is the most important aspect in obtaining the shutdown interval to

minimize overall operational risk. In order to achieve this, a risk criticality matrix is proposed to select the critical equipment for shutdown inspection and maintenance. Probability of human error induced during shutdown inspection and maintenance is estimated using Success Likelihood methodology (SLIM). The proposed methodology is composed of three steps namely, equipment selection considering criticality of operation, system failure modeling considering human error and finally a risk-based shutdown inspection and maintenance interval estimation. The proposed methodology is applied to a gas chilling and liquefaction unit of a hydrocarbon processing facility. The methodology is used to ensure the practicality of the proposed formulation to the real industry. The proposed methodology can be applied to any plant (process or non-process) such as those for LNG processing, petrochemicals, refineries or manufacturing plants. The key elements for the success of the proposed methodology are the identification and selection of critical equipment, breakdown of activities to estimate human error probability and plant-specific data for modeling system failures.

- **Keywords:** System reliability; Risk-based inspection and maintenance; Human error and shutdown inspection and maintenance; Failure probability; Consequence; Failure model

Fatemeh Kazemi, Habibollah Younesi, Ali Asghar Ghoreyshi, Nader Bahramifar, Ava Heidari. *Thiol-incorporated activated carbon derived from fir wood sawdust as an efficient adsorbent for the removal of mercury ion: Batch and fixed-bed column studies*. Pages 22-35.

The thiol-incorporated activated carbon (AC) was produced from fir wood sawdust by treating it chemically with phosphoric acid at five different impregnation ratios and used as adsorbent for Hg2+ ion in batch and fixed bed systems. The raw material and ACs samples were characterized by means of proximate and ultimate, FTIR, SEM, and BET analyses. The BET surface area of the prepared AC enhanced from 1273 m2/g to 1789 m2/g along with an increase in the impregnation ratio of H3PO4 from 1 to 1.5 g/g and then decreased to1593 m2/g. AC-H1.5 and the AC-S (modified AC) samples had the highest (1789 m2/g) and lowest surface area (1162 m2/g). The effects of various parameters such as contact time, adsorbent dose, pH and initial Hg2+ concentration for the removal of Hg2+ were studied in a batch process. The Hg2+ ion removal efficiency increased by increasing the adsorbent dosage from 0.25 to 2 g/L and the pH from 2 to 8. The equilibrium data fitted to the Freundlich, Langmuir and Redlich–Peterson isotherms, but gave a better fit to the Redlich–Peterson model. The maximum monolayer adsorption capacity of the mercury ion onto the AC-S sample (129 mg/g) was more than that onto the AC-H1.5 (107 mg/g). The results showed that the adsorption process fitted the pseudo-second-order kinetic models. In a fixed-bed column adsorption, the effects of bed height, flow rate and Hg2+ concentration on the breakthrough curve were investigated, on which the adsorption capacity predicted both by the Yan and Thomas models was found to be satisfactory with that determined by integrating the total area above breakthrough curves. The desorption of AC adsorbent was investigated with several acids (HCl, HNO3, H2SO4 and H3PO4) and bases (KOH, NaOH and NaCO3).

- **Keywords:** Mercury removal; Thiol-incorporated AC; Fir sawdust; Batch; Fixed-bed column

J. Kanagaraj, R.C. Panda, T. Senthilvelan. *Green remediation of sulfide in oxidative dehairing of skin and correlation by mathematical model: An eco-friendly approach*. Pages 36-48.

The dehairing of goat skin using sodium percarbonate has been attempted in place of conventional dehairing using lime and sodium sulfide. Conventional dehairing generates huge pollution loads to the maximum level in leather processing. The present method is

very simple that dehairs the goat skin with the help of 5% sodium percarbonate at an optimum level in combination with 4% sodium hydroxide and replaces hazardous material like sodium sulfide. The complete dehairing was achieved in 16 h duration. The pollution loads in terms of BOD, COD, Total Dissolved Solids (TDS), and Total Suspended Solids (TSS) were reduced up to the level of 56.3, 62.5, 68.1, and 52% in comparison with the control sample. Reduction of TOC values has been noticed. The advantage of the method lies with the fact that the processing time for leather making is considerably reduced by skipping reliming and deliming unit processes. A mechanistic mathematical model describing the diffusion reaction phenomena of dehairing agent through pores of skin has been developed that supports monolayer adsorption by Langmuir isotherm. Thermo gravimetric analysis and differential scanning calorimetry results explain that the present unit operation is dominated by exothermic process. Experimental samples show improved uptake of color with comparable leather qualities.

- **Keywords:** Oxidative dehairing; Sodium percarbonate; Mathematical modeling; Reduction of pollution loads; Replacement of hazardous chemical of sodium sulfide

Meftah Abuswer, Paul Amyotte, Faisal Khan, Syed Imtiaz. *Retrospective risk analysis and controls for Semabla grain storage hybrid mixture explosion*. Pages 49-64.

A continuation of the Quantitative Risk Management Framework validation is addressed in this paper. The explosion at the grain silo at the Semabla Company in Blaye, France in 1997 was considered as a hybrid mixture (Fermentation flammable gas/wheat and Maize dust) explosion. The risk analysis uses a Computational Fluid Dynamics modeling technique, which is represented in the Dust Explosion Simulation Code software and in conjunction with Probit equations to estimate the severity of consequences, and the Fault tree analysis technique to estimate the hybrid mixture explosion frequencies in a facility. Risk estimations (risk indices, individual risk, and societal risk) have been determined before and after the framework was applied. The results showed a great reduction in risk if the framework is applied before any expected explosion.

- **Keywords:** Dust explosion; Hybrid mixture explosion; Quantitative risk management; CFD modeling; Semabla grain storage

Cintia C. Lobo, Nora C. Bertola, Edgardo M. Contreras. *Approximate expressions of a SBR for wastewater treatment: Comparison with numeric solutions and application to predict the biomass concentration in real cases*. Pages 65-73.

Most industrial wastewater treatment systems often operate under transient conditions, causing several operational problems. An effective solution is the use of Sequencing Batch Reactors (SBR). In general, a great number of simulations are necessary to solve SBRs mathematical models in order to evaluate the effect of the operational conditions on the performance of the reactor. In this work, a set of analytical equations that represent the effect of the operational parameters on the performance of a SBR was developed. The obtained equations adequately represent the change of the organic substrate, ammonia, biomass, oxygen and soluble microbial products as a function of time within a single operation cycle of the SBR. The equations also predict the steady-state concentrations as a function of several operational parameters, avoiding the problem of performing a great number of simulations. Based on real SBR data, the biomass growth yield and the decay factor for two synthetic wastewaters were obtained. Using these coefficients, the proposed equations adequately predicted the biomass concentration in real cases.

- **Keywords:** Sequencing batch reactor; Modeling; Steady-state; Cheese whey; Phenol

Sadegh Rostamnia, Behnam Gholipour, Habib Golchin Hosseini. *Metal- and halogen-free hydrogensulfate ionic liquid/SBA-15 as catalyst in clean oxidation of aromatic and aliphatic organic sulfides with aqueous hydrogen peroxide*. Pages 74-79.

An efficient, and eco-friendly procedure for the oxidation of aromatic and aliphatic sulfides to sulfoxides using H2O2 catalyzed by hydrogensulfate ionic liquid/SBA-15 [IL-HSO4@SBA-15] has been developed. This atom-economical protocol affords the target products in good to high yields. The products can be separated by a simple extraction with organic solvent, and the catalytic system can be recycled and reused without loss of catalytic activity even after fourteen runs.

- **Keywords:** Hydrogensulfate ionic liquid; SBA-15; Sulfide oxidation; Sulfoxide; Mesoporous; Hydrogen peroxide; Green chemistry

Pham-Thi Huong, Byeong-Kyu Lee, Jitae Kim, Chi-Hyeon Lee, Meng Nan Chong. *Acid activation pine cone waste at differences temperature and selective removal of Pb2+ ions in water*. Pages 80-90.

This study reports potential application of pine cones (PC) and acids treated pine cone at as adsorbents for removal of Pb2+ ions in water. Two different types of acids were used for the treatment of PC at different activation temperature, with the following combination of hydrochloric -acid treated PC at 25 °C (PC-H25) and 50 °C (PC-H50); phosphoric-acid treatmented PC at 25 °C (PC-P25) and 50 °C (PC-P50). The basic physicochemical properties of PC, both before and after acid treatment, were characterized using scanning electron microscopy (SEM), Fourier-transformed infrared spectroscopy (FTIR) and elemental analysis (EA). Bath adsorption experiments on Pb2+ ions were optimized in term of pH, adsorbent dose, reaction time and initial concentration of Pb2+ ions. It was estimated through adsorption isotherm analysis that adsorption capacities of PC-H25, PC-P25, PC-H50 and PC-P50 on Pb2+ ions were 132.6, 108.2, 148.3 and 119.8 mg/g, respectively. Desorption studies revealed the promising regeneration potential of PC, PC-H25, PC-H50, PC-P25 and PC-P50. It was found that the percentage removal of Pb2+ was maintained at more than 60% as compared to the initial value, even after 5 adsorption–desorption cycles. Furthermore, the adsorption costs required for removal of Pb2+ ions using PC, PC-P25, PC-P50, PC-H25, PC-H50 were estimated to be 1.6, 11.5, 17.5, 6.7 and 8 US$/kg, respectively. Based on these findings, PC and acid-treated PC could be used as low-cost, eco-friendly and effective adsorbents for the Pb2+ removal from water.

- **Keywords:** Regeneration; Acid-treatment; Ion exchange; Adsorption cost; Lead; Pine cone

Prangya Ranjan Rout, Rajesh Roshan Dash, Puspendu Bhunia. *Nutrient removal from binary aqueous phase by dolochar: Highlighting optimization, single and binary adsorption isotherms and nutrient release*. Pages 91-107.

The viability of utilizing sponge iron industry based waste 'dolochar' as a proficient adsorbent for nutrient (phosphate and nitrate) removal and subsequent slow release of nutrient from the spent dolochar has been undertaken in this study. The efficacy of dolochar has been explored in both single and binary adsorption systems containing nutrients. The proposed experimentally obtained quadratic models for both the phosphate and nitrate removal were substantiated by analysis of variance (ANOVA) with high R2 values of 0.99 and 0.98, respectively. Response surface methodology (RSM) based optimization followed by experimental validation resulted in phosphate removal efficiency of 96.7% and nitrate removal efficiency of 57.1%. Single component

adsorption equilibrium data fitted well to pseudo-second order kinetic and Langmuir isotherm models with Langmuir maximum adsorption capacity, qm of 327.7 and 6.51 mg g−1 for phosphate and nitrate, respectively. Out of non-modified Langmuir, modified Langmuir, extended Langmuir and extended Freundlich, multi component isotherm models, binary adsorption equilibrium data fitted well to the extended Freundlich model. Thin layer funnel analytical test results reveals the slow nutrient release nature of spent dolochar. The results suggest that the dolochar has the potential to serve as a sustainable adsorbent for nutrient removal from wastewater along with the scope of utilizing spent dolochar as a slow release nutrient supplier.

- **Keywords:** Dolochar; Nutrient removal; Binary adsorption system; Response surface methodology; Multicomponent isotherms; Slow release of nutrient

Zhi Yuan, Nima Khakzad, Faisal Khan, Paul Amyotte. *Domino effect analysis of dust explosions using Bayesian networks*. Pages 108-116.

In most dust explosion accidents, a series of explosions consisting of a primary (dust) explosion and one or more subsequent secondary dust explosion(s) has been reported. Such chain of dust explosions can be referred to as a dust explosion domino effect (DEDE). DEDEs are capable of causing severe onsite and offsite damages to human, assets, and the environment, thus requiring a detailed understanding of the causes, consequences, probabilities, and escalation mechanisms thereof to prevent and mitigate the potential damages. In this research, we have developed a methodology for the probability estimation of DEDEs based on Bayesian network. The application and efficacy of the methodology have been demonstrated via a real-world case study. The results illustrate that the developed methodology can effectively portend the propagation of DEDEs while calculating the respective probabilities.

- **Keywords:** Dust explosion; Domino effect; Escalation probability; Bayesian network; Process industries

Luca Talarico, Genserik Reniers. *Risk-informed decision making of safety investments by using the disproportion factor*. Pages 117-130.

To improve risk informed decision making, a systematic approach is developed. The goal is to analyze and to evaluate safety investments aimed at mitigating and preventing major accidents involving e.g. hazardous materials that might trigger significant financial losses and fatalities. A formulation, explicitly using a disproportion factor, is proposed as a simulation exercise approach to this end. The disproportion factor can be used by any private and public investor to bias decision-makers toward safety. This is especially interesting for deciding about the prevention of high impact low probability (HILP) accidents. Furthermore experimental simulations have been performed on realistic data to test the proposed decision model and to provide general recommendations. Several types of accidents were considered and the impacts of technical and financial parameters on the disproportion factor, possibly making a safety investment profitable from an economic perspective, are also investigated and discussed in this paper.

- **Keywords:** Disproportion factor; Safety investment; Risk analysis; Decision model; Risk management; Cost–benefit analysis

J.P. Bassin, I.N. Dias, S.M.S. Cao, E. Senra, Y. Laranjeira, M. Dezotti. *Effect of increasing organic loading rates on the performance of moving-bed biofilm reactors filled with different support media: Assessing the activity of suspended and attached biomass fractions*. Pages 131-141.

In this study, two moving-bed biofilm reactors (MBBR1 and MBBR2) filled with different carrier media (Kaldnes K1 and Mutag Biochip, respectively) were subjected to increasing organic loading rates for 700 days. Regardless of the carrier used, both systems could withstand high organic loads up to 3.2 kgCOD/(m3 d), condition under which complete ammonium removal was achieved. However, the type of media influenced the quantity and distribution of attached biomass in the support, which in turn affected the activity of specific microbial functional groups in the biofilm. As the chemical oxygen demand (COD) input was gradually increased, the biofilm got thicker and the surface detachment rates were enhanced. Consequently, the amount of suspended solids has increased considerably to levels commonly found in hybrid bioreactors. Activity batch tests have shown that the contribution of the bulk phase biomass to the overall nitrification was very significant, being more relevant as the biofilm sloughing events became more intense. At constant organic loading rate, the hydraulic retention time (HRT) had a noticeable impact on the nitrification process, as it directly influenced the fraction of ammonium oxidized either by the attached or suspended biomass. Total nitrogen removal amounted up to 86 and 73% in MBBR1 and MBBR2, respectively.

- **Keywords:** COD removal; Nitrification; MBBR; Carrier media; Organic loading rate; Specific nitrification rate

Xiurong Ren, Qiang He, Ze Yang, Ting Li, Liping Chang, Weiren Bao. *Effect of temperature-programmed pyrolysis pre-treatment on desulfurization performance of Zn-based sorbent prepared by lignite as support*. Pages 142-149.

A series of Zn-based sorbents were prepared by high-pressure impregnation with lignite as precursor of support and zinc nitrate as the precursor of active component, followed by temperature-programmed pyrolysis of the impregnated lignite sample in a fixed-bed quartz reactor. The H2S removal performances of sorbents prepared under different pyrolysis conditions such as temperatures, holding time as well as heating rates were evaluated. The physical and chemical properties of sorbents were characterized by atomic absorption spectroscopy (AAS), X-ray diffraction (XRD), transmission electron microscope (TEM) and nitrogen adsorption techniques. The results show that the process of pyrolysis can improve the pore structure dramatically, which lead to the high specific surface area and large pore volume. The good desulfurization performance of sorbent was attributed to both of the proper porous structure of sorbents, the content and distribution of active component. The optimal operating conditions of temperature-programmed pyrolysis for the impregnated lignite sample were the heating rate of 10 °C/min, holding time of 180 min in N2 atmosphere and pyrolysis temperature of 550 °C. The sulfidation time could hold for over 720 min before reaching 1 ppm H2S in outlet gases and the sulfur capacity was up to 25.91 g S/100 g ZnO for sorbent prepared under this optimized condition.

- **Keywords:** Lignite; Temperature-programmed pyrolysis; Sorbent; Desulfurization; Hot coal gas; High-pressure impregnation

Horng-Jang Liaw, Chan-Cheng Chen, Nung-Kai Lin, Chi-Min Shu, Shang-Yi Shen. *Flammability limits estimation for fuel–air–diluent mixtures tested in a constant volume vessel*. Pages 150-162.

A model for estimating the flammability envelope of mixtures containing inert gases for a constant volume system was derived based on the energy balance equation and thermal radiation loss. The combustion products along the flammability boundaries were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) to verify the assumptions of the proposed model. The model was validated for acetone, methyl formate, methanol, and isopropanol with either steam or nitrogen as the inert gas. The heat loss effects on the

estimated flammability envelopes were small. The predicted lower flammability limits (LFLs) closely matched the measured limits, excluding those at the region approaching the limiting oxygen concentration (LOC). The estimated upper flammability limits also agreed well with the measured limits. The FTIR spectra indicated that the increase in the LFL around the LOC is attributed to the existence of unburned fuel, not the formation of CO as previously reported.

- **Keywords:** Energy balance equation; Flammability limits; Inert gas; Flame temperature; Combustion products; Fourier Transform Infrared Spectroscopy (FTIR)

Simona Golob, Mitja Kožuh. *Methodology for determining the risk acceptance criteria for the Seveso establishments*. Pages 163-172.

Accidents involving dangerous substances still happen and establishing an effective proactive methodology to provide safe daily operation remains a challenge. Findings about the limitations of the existing approaches with scenario presentation for the purpose of demonstrating that appropriate precautionary actions are taken to ensure a high level of protection, are the basis for the development of the new methodology, presented in this paper. The emphasis of the methodology is on effective daily operation, based on the identification of latent weaknesses; it takes into account that with dynamic processes safety changes from one moment to another. With the new approach, operators are encouraged to think continuously about the issues that have an impact on safety. Another challenge is the fact that understanding what effective daily operation means may differ from country to country and from legislation level to the operator. The guidance in this paper illustrates what effective daily operation means. The assessment of effective daily operation is also used as the risk acceptance criteria for Seveso establishments, and the presented approach is one of methodological guidance on how to implement the Article 19 of the Directive, 2012/18/EU of the European Parliament and of the Council (the Seveso III Directive).

- **Keywords:** Seveso; Risk acceptance criteria; Effective daily operation; Latent weaknesses; Seveso Directive; Risk assessment

Saranya Kuppusamy, Palanisami Thavamani, Mallavarapu Megharaj, Kadiyala Venkateswarlu, Yong Bok Lee, Ravi Naidu. *Potential of Melaleuca diosmifolia leaf as a low-cost adsorbent for hexavalent chromium removal from contaminated water bodies*. Pages 173-182.

The present study describes for the first time the utilization of dried twigs of Melaleuca diosmifolia, fallen off from the plant, to detoxify and remove hexavalent chromium or Cr(VI) from aqueous systems. Initial characterization by gas chromatography revealed that the selected biomaterial is one of the natural sources of eucalyptol. It constituted high concentrations of reducing compounds (iron, phenols and flavonoids). Batch studies revealed that the biosorbent (5 g L−1) was able to remove 97–99.9% of 250 mg L−1 Cr(VI) at wide-ranging pH (2–10) and temperature (24–48 °C). Adsorption kinetics was well described using the pseudo-second-order kinetic model, while the equilibrium adsorption data were interpreted in terms of the Langmuir isotherm model. The monolayer adsorption capacity was 62.5 mg g−1. Both inductively coupled plasma optical emission spectrometry and liquid chromatography analyses of the aqueous and solid phases revealed that the mechanism of Cr(VI) removal was 'adsorption-coupled reduction'. Scanning electron microscope, infrared spectroscopy and X-ray diffraction analyses of the biosorbent before and after adsorption also confirmed that both adsorption and reduction of Cr(VI) to Cr(III) followed by complexation onto functional groups of the active surface contributed to the removal of Cr(VI) from aqueous solution. The selected biomaterial effectively (99.9%) removed Cr(VI) in lake and sea water

samples, highlighting its potential for remediating Cr(VI) in real environmental conditions.

- **Keywords:** Melaleuca diosmifolia; Forest biomass; Biosorption; Chromium(VI) reduction; Kinetic model; Wastewater treatment

Selvaraj Munirasu, Mohammad Abu Haija, Fawzi Banat. *Use of membrane technology for oil field and refinery produced water treatment: A review*. Pages 183-202.

With the advent of modern drilling technology namely sand-tar, hydraulic fracturing and enhanced oil recovery, the amount of waste water to be treated before reuse and/or discharge to the environment has increased manifold in recent time. The treatment of produced water and refinery waste water from the oil industry has been traditionally done by physical as well as chemical processes. The use of membrane technology for the produced and refinery waste water treatment has been recent phenomenon and active research has been focused to enhance the efficiency and life time of the membrane during the operation of the waste water treatment. In this review we briefly focus on the produced and refinery waste water treatment by primary and secondary treatment in historical perspective followed by focusing on various membrane technologies starting from microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Finally we also focus on the membrane distillation (MD) in combination with forward osmosis (FO) as potential future technology.

- **Keywords:** Produced water; Oil refinery waste water; Membrane technology; Water reuse; Responsive surface; Oil–water separation

Majid Vafaeezadeh, Mohammad Mahmoodi Hashemi. *A non-cyanide route for glutaric acid synthesis from oxidation of cyclopentene in the ionic liquid media*. Pages 203-207.

The current work deals with the catalytic application of bis(1-butyl-3-methylimidazolium) tungstate ([BMIm]2WO4) for green synthesize of glutaric acid (GA) through oxidative cleavage of cyclopentene. In this method, 30% hydrogen peroxide (H2O2) was used as oxidant with water as the sole by-product of the reaction. Compared to the current synthetic procedures, this protocol is significantly improved in the environmental point of view. Moreover, the effect of the various parameters was investigated on the reaction efficiency. It was found that high yield of GA could obtain without using special methodologies or precautions. The catalytic system is reusable for several times.

- **Keywords:** Glutaric acid; Clean oxidation; H2O2; Ionic liquid; Green chemistry; Cyclopentene

Gabriele Baldissone, Davide Fissore, Micaela Demichela. *Catalytic after-treatment of lean VOC–air streams: Process intensification vs. plant reliability*. Pages 208-219.

This paper compares two different processes for the treatment of a gaseous stream containing small amounts of volatile organic compounds (VOCs), namely a traditional plant, where a heat exchanger is used to recover heat from the hot gas obtained after VOCs combustion, and a plant with a reverse-flow reactor, where the catalyst is used for VOC removal and for a regenerative heat recovery. The analysis is focused on the reliability and the safety of both plants: the recursive operability analysis (ROA) is firstly used for hazards identification, pointing out that the sintering of the catalyst and the discharge of a gas with high VOCs concentration are the most critical top events. The fault trees are then extracted and quantified. Finally, an integrated dynamic decision

analysis (IDDA) is carried out, with the goal of evaluating in more detail the plant behavior, for both cases, in the event of failure. Results show that the probability of occurrence of catalyst sintering is higher in the traditional plant, due to the fact that the control system used in the reverse-flow reactor is more complex and with more redundancies. With respect to the release of VOCs, this event is more probable in the reverse-flow reactor than in the traditional plant, but the associated risk is lower, although the difference is not very large.

- **Keywords:** Reverse-flow reactor; Process intensification; VOC after-treatment; Risk analysis; Recursive operability analysis; Fault tree; Integrated dynamic decision analysis

Fouzi Harrou, Farid Kadri, Sofiane Khadraoui, Ying Sun. *Ozone measurements monitoring using data-based approach*. Pages 220-231.

The complexity of ozone (O3) formation mechanisms in the troposphere makes the fast and accurate modeling of ozone very challenging. In the absence of a process model, principal component analysis (PCA) has been extensively used as a data-based monitoring technique for highly correlated process variables; however, conventional PCA-based detection indices often fail to detect small or moderate anomalies. In this work, we propose an innovative method for detecting small anomalies in highly correlated multivariate data. The developed method combines the multivariate exponentially weighted moving average (MEWMA) monitoring scheme with PCA modeling in order to enhance anomaly detection performance. Such a choice is mainly motivated by the greater ability of the MEWMA monitoring scheme to detect small changes in the process mean. The proposed PCA-based MEWMA monitoring scheme is successfully applied to ozone measurements data collected from Upper Normandy region, France, via the network of air quality monitoring stations. The detection results of the proposed method are compared to that declared by Air Normand air monitoring association.

- **Keywords:** Anomaly detection; MEWMA statistic; MSPC; Principal components analysis; Ozone pollution; Data-driven strategy

Agnès Janès, Guy Marlair, Douglas Carson. *Testing of gas flow measurement methods to characterize substances which emit flammable or toxic gases in contact with water*. Pages 232-241.

Selecting the most appropriate flow measurement techniques with related devices to characterize potentially hazardous chemicals which emit flammable or toxic gases due to their hydro-reactivity poses a difficult but required task for official classification of such materials. This paper offers a careful examination of three such potential methods that differ from each other by the flow rate measurement device which includes one manual and two automatic systems. Experiments for comparative testing and validation limits have been defined and carried out for two known hydro-reactive chemicals: aluminum chloride and sodium borohydride. The main conclusions are reported here. From the results obtained, the possible selection of the best investigated methods is suggested according to performance based criteria.

- **Keywords:** Dangerous when wet; Water-reactivity; Reaction with water; Hazardous hydro-reactive properties; Classification-testing protocols; Flammability and toxicity of released gases

M.D. Víctor-Ortega, J.M. Ochando-Pulido, A. Martínez-Ferez. *Performance and modeling of continuous ion exchange processes for phenols recovery from olive mill wastewater*. Pages 242-251.

A continuous-flow ion exchange (IE) process for phenols recovery from olive mill wastewaters was examined through both strong-base and weak-base anion exchange resins. The effect of initial pH showed that phenols removal efficiency increased with an increase in the pH value up 7 and efficiency remains constant at higher pH values for Amberlyst A26. On the other hand, phenols removal efficiency for Amberlite IRA-67 also increased with an increase in the pH value up 7, reaching phenols removal efficiencies close to 57%. In addition, Thomas, Yoon–Nelson and Clark models were applied to the experimental data to predict the breakthrough curves. The simulation of the best-performing operational condition was used to evaluate the process performances for different inlet phenols concentrations (5, 25 and 100 mg L−1). The results showed an increase in initial phenols concentration improved the adsorption capacity. In both cases, the Thomas model was found to give best fit to experiment data for the three initial phenols concentrations, followed by the Yoon–Nelson and Clark models. Finally, column regeneration studies showed almost 100% phenols recovery efficiencies were obtained. IE process led to a phenols solution susceptible to be concentrated and used in food, cosmetic or pharmaceutical sectors.

- **Keywords:** Breakthrough curves; Industrial effluents; Phenols recovery; Strong-base anion exchange resin; Weak-base anion exchange resin

Swaroopa Rani Dasari, Venu Babu Borugadda, Vaibhav V. Goud. *Reactive extraction of castor seeds and storage stability characteristics of produced biodiesel*. Pages 252-263.

In the present study, oil was extracted from a single castor seed by eppendorf vial method, and the oil yield was compared with the yield obtained from Soxhlet method. The oil yield from both methods was about 55% and comparable. Free Fatty Acid (FFA) content of extracted castor oil was found to be lower (<1 mg KOH/g oil). Therefore, single step transesterification (reactive extraction) was carried out to study the effect of various reaction variables on the conversion of castor oil biodiesel. The optimum biodiesel conversion of ~93% was achieved under following conditions: 4 h, 1:250 oil to MeOH molar ratio, 1 wt.% NaOH, 40 °C, 0.75 mm particle size, 20 g seed, 600 rpm and 10 (vol.%) co-solvent. The estimated fuel properties of biodiesel obtained with NaOH, KOH and NaOH (with co-solvent) were found to be similar and within the limits of ASTM standards. Similarly, storage stability of prepared biodiesel was evaluated over a six-month storage period (180 days) under three different storage conditions. The results showed a sharp decrease in fuel stability over time in terms of increase in density from 0.878 to 0.984 g/cm3, kinematic viscosity (10.59–16.18 cSt), acid value (0.52–5.15 mg KOH/g) respectively. While, iodine value significantly decreased from 82.5 to 54.57 g I2/100 g oil over time. Biodiesel sample stored in the open air degraded faster than samples stored in other storage conditions.

- **Keywords:** Reactive extraction; NaOH; Castor oil biodiesel; Storage stability; Castor seed; Free Fatty Acid

Arezoo Dadrasnia, Mohammed Maikudi Usman, Kelvin Swee Chuan Wei, Rita Devi Velappan, Hossein Jamali, Nooshin Mohebali, Salmah Ismail. *Native soil bacterial isolate in Malaysia exhibit promising supplements on degrading organic pollutants*. Pages 264-271.

A novel strain was isolated from an agricultural soil in Malaysia. After morphological and genetic characterization, the novel strain showed the highest similarity to Bacillus species. The ability of biostimulation (waste tealeaf) and bioaugmentation (Bacillus salmalaya 139SI) activities was investigated on soil polluted with 6% (w/w) waste crude oil for duration of 60 days. Strain 139SI was able to decrease the surface tension to 35 mN/m. Degradation of the initial petroleum hydrocarbon by 70% was achieved in the

treatments involving B. salmalaya strain 139SI and tealeaf compared to the sterilized polluted soil (15%), which served as a control for this study. The aerobic utilizing bacteria counts and dehydrogenase activity were significantly increased during the period of study. Analysis of residual waste crude oil monitored by gas chromatography spectrophotometer indicated 80–95% degradation of n-C8 to C12 followed by a 40% removal ratio of C22. Kinetic model showed that treatment amended with both tealeaf and strain has indicated the highest level of biodegradation rate, with rate constant of 0.107 day−1, while the biodegradation rate was 0.08 day−1 in treatments amended with only tealeaf. The finding showed the potentiality of tealeaf and Bacillus salmalaya 139SI toward the degradation/decomposition of crude oil in contaminated soil.

- **Keywords:** Bioaugmentation; Biostimulation; Bacillus salmalaya; Contaminated soil; Organic waste; Waste crude oil

Pham-Thi Huong, Byeong-Kyu Lee, Jitae Kim. *Improved removal of 2-chlorophenol by a synthesized Cu-nano zeolite*. Pages 272-280.

This study was conducted to investigate advanced removal characteristics of toxic 2-chlorophenol in water by copper supported nano zeolite (Cu-nano zeolite). The surface area and surface positive charged of the nano zeolite were increased after doping with copper ions, leading to enhance in 2-chlorophenol adsorption capacity. Advanced adsorption characteristics of 2-chlorophenol by Cu-nano zeolite were evaluated studying the effect of pH, reaction time, adsorbent dose, initial solution concentration, regeneration of adsorbent and even adsorption cost and the process was applied to the direct treatment of wastewater. The maximum adsorption capacity for 2-chlorophenol by Cu-nano zeolite was 204.68 mg/g at optimum pH 6.0 with 150 min of reaction time. Regeneration characteristics of 2-chlorophenol loaded adsorbent were also analyzed. Even after 9 cycles of adsorption–desorption, the percentage removal of 2-chlorophenol was maintained at more than 80% of the initial value. The adsorption cost required for removal 2-chlorophenol by Cu-nano zeolite was 0.58 US$/g, which is lower by 14% than those of activated carbon. The Cu-nano zeolite method was applied to treat industrial wastewater containing high concentration of toxic 2-chlorophenol (420 mg/L) collected from chemical plants. The result showed that 81.8% of 2-chlorophenol was removed from wastewater. Based on these findings, Cu-nano zeolite can be used for effective and economic removal of 2-chlorophenol from wastewater.

- **Keywords:** Adsorption cost; Regeneration; 2-Chlorophenol removal; Cu-nano zeolite; Wastewater; Adsorption isotherm; Kinetic

Deepak Pant. *Polycarbonate Waste Management using Glycerol*. Pages 281-287.

Recycling method of polycarbonate (PC) plastic using glycerol is proposed as a novel green method. Glycerol was found as an efficient reagent for chemical recycling of PC and gives upto 98% monomer recovery, which is compatible with any of existing chemical recycling methods. Recycling involves digestion followed by glycerolysis reaction of PC. The various products thus obtained are Bisphenol A (BPA); mono glycerol ether of BPA and di glycerol ether of BPA. Addition of urea improves the yield toward more alkoxylated products, controls the dehydration of glycerol to acrolein at reaction temperature and improves the application of glycerol as a reagent. Temperature programmed FTIR spectra study provides a mechanistic picture of the proposed chemical recycling. Glycerol carbonate and glycerol urethane was found as the important reaction intermediates. The process works well with industrial grade glycerol to improve the economy in this process. Furthermore, a working model of the recycling of post-user optical disc is also proposes.

- **Keywords:** Glycerol; Polycarbonate; Optical Disc; Chemical recycling; Green method

Jayachandra Reddy Nakkala, Rani Mata, Sudha Rani Sadras. *The antioxidant and catalytic activities of green synthesized gold nanoparticles from Piper longum fruit extract*. Pages 288-294.

In this study, we tested successfully a green method for the synthesis of gold nanoparticles using Piper longum fruit extract (PLFE) along with data on their in vitro antioxidant and catalytic activities. The formation of P. longum gold nanoparticles (PLAuNPs) was confirmed by UV–visible spectroscopy. The average size of the PLAuNPs was 56 nm as confirmed by the DLS particle size analyzer. The TEM-EDX revealed that PLAuNPs were spherical in shape and contained metallic gold. FTIR analysis indicated that the phenolic groups present in PLFE were involved in the reduction and capping of PLAuNPs. The thermal stability of PLAuNPs was analyzed by the TGA. PLFE and PLAuNPs exhibited moderate free radical quenching ability when analyzed by various in vitro antioxidant assays. The catalytic activity of PLAuNPs against four organic dyes namely methyl blue, methyl red, crystal violet and acridine orange was tested, which resulted in respective degradation of 65, 28, 39 and 34% after 28 h of mixing. Such green nanoparticles with potent catalytic properties might be useful in clearing the toxic dyes in industrial effluents.

- **Keywords:** Piper longum; Gold nanoparticles; Antioxidant; Catalytic activity

K.Y. Foo. *Value-added utilization of maize cobs waste as an environmental friendly solution for the innovative treatment of carbofuran*. Pages 295-304.

A new route for the conversion of maize cobs waste, a natural low-cost lignocellulosic biomass abundantly available from the food processing industries into an eco-friendly biosorbent (CC) via chemical treatment has been presented. The effectiveness for the adsorptive removal of a highly hazardous carbamate derivative pesticide, carbofuran from the aqueous solution was attempted. The operational parameters including the effects of modification agents and chemical impregnation ratio on the adsorption capability were investigated. The porosity, functionality and surface chemistry of CC were featured by means of low temperature nitrogen adsorption, elemental analysis, scanning electron microscopy, Fourier transform infrared spectroscopy, evaluation of surface acidity/basicity and zeta potential measurement. The effects of adsorbent dosage, initial concentration, contact time and solution pH on the adsorption performance were evaluated in a batch mode study. Equilibrium data were simulated by non-linear fittings using the Freundlich, Langmuir, and Temkin isotherm models. Kinetic modeling was fitted to the pseudo-first-order and pseudo-second-order equations. Langmuir isotherm model provided a better correlation to the experimental data, with a maximum monolayer adsorption capacity of 149.15 mg/g, while the adsorption kinetic was best fitted to the pseudo-second-order kinetic model. The results illustrated the potential of maize cobs waste derived biosorbent for the on-site remediation of pesticide contaminated wastewater.

- **Keywords:** Adsorbent; Adsorption; Carbofuran; Maize cobs waste; Pesticide; Biomass