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Biao He, Xin-Sheng Jiang, Guo-Rui Yang, Jian-Nan Xu. *A numerical simulation study on the formation and dispersion of flammable vapor cloud in underground confined space*. Pages 1-11.

A transient numerical study on the formation and dispersion of fuel vapor clouds in confined space was conducted. A liquid–gas phase-change model for fuel vapor formation was developed to better understand safe methods for fuel operation and storage. A liquid fuel leak was exposed to air, and a flammable fuel vapor–air mixture was formed. The simulation of the low-speed flowing and plum-like fuel vapor clouds was based on large eddy simulation. A typical case of gasoline leakage in underground fuel storage was also analyzed in detail. The results showed that following a gas leak in an underground storage tank, the vapor–air mixture will fill the space from the edges to the tank chamber exit and from the bottom up. In addition, the volume fraction at the top of the tank chamber remained below the 20% low explosion limit (LEL). The volume change in the vapor–air mixture with a volume fraction above 20% LEL can be divided into three periods: linear growth, space constraints, and critical increasing. This study provides an important insight for assessing flammable atmosphere risks after fuel leakage in a confined space and for determining the proper rescuing means and time.

- **Keywords:** Flammable vapor cloud; Confined space; Numerical simulation; Phase change; Dispersion

Ján Janošovský, Matej Danko, Juraj Labovský, Ľudovít Jelemenský. *The role of a commercial process simulator in computer aided HAZOP approach*. Pages 12-21.

Process safety is one of the key pillars of sustainable industrial development. In combination with the increasing use of computer aided process engineering, the demand for an appropriate model-based safety analysis tool capable to identify all hazardous situations leading to a major accident has increased. Commercial process simulators are equipped with extensive property databases and they employ high accuracy mathematical models providing the capability to simulate real behavior of a process operated within the area of the mathematical model validity. The main focus of this work is to improve standard hazard identification methods by the combination of hazard and operability (HAZOP) study and process simulation in commercial process simulator Aspen HYSYS. Software tool consisting of modules for computer simulation and complex analysis of simulation data will be proposed. The developed tool was applied to modern chemical productions exhibiting strong nonlinear behavior, where proper prediction of

consequences can be very difficult. In the first case study, hazard identification in continuous glycerol nitration employing user-dependent analysis is presented. Mathematical methods of simulation data analysis independent of the user is demonstrated in the second case study of ammonia synthesis. Possibilities and limitations of the proposed tool are revealed and discussed in this work.

- **Keywords:** Computer aided hazard identification; HAZOP study; Aspen HYSYS; Process safety; Chemical reactors; Mathematical modeling

Muddu Madakyaru, Fouzi Harrou, Ying Sun. *Improved data-based fault detection strategy and application to distillation columns*. Pages 22-34.

Chemical and petrochemical processes require continuous monitoring to detect abnormal events and to sustain normal operations. Furthermore, process monitoring enhances productivity, efficiency, and safety in process industries. Here, we propose an innovative statistical approach that exploits the advantages of multiscale partial least squares (MSPLS) models and generalized likelihood ratio (GLR) tests for fault detection in processes. Specifically, we combine an MSPLS algorithm with wavelet analysis to create our modeling framework. Then, we use GLR hypothesis testing based on the uncorrelated residuals obtained from the MSPLS model to improve fault detection. We use simulated distillation column data to evaluate the MSPLS-based GLR chart. Results show that our MSPLS-based GLR method is more powerful than the PLS-based Q and GLR method and MSPLS-based Q method, especially in early detection of small faults with abrupt or incipient behavior.

- **Keywords:** Multi-scale PLS models; GLR hypothesis testing; Data uncertainty; Process monitoring; Distillation Columns; Fault detection

Rita R. Zapico, Pablo Marín, Fernando V. Díez, Salvador Ordóñez. *Performance of a cell-foam trickle-bed reactor for phenol wet oxidation: Influence of operation parameters and modelling*. Pages 35-43.

The homogeneous wet oxidation of phenol, catalysed by Cu(II), has been studied in a trickle-bed reactor. The reactor bed consisted of a ceramic foam made of alumina with a cell density of 20 ppi. This bed is especially suited to promote mass transfer between phases with very low pressure drop. The gas phase (oxygen at 0.6 MPa) was circulated continuously, while the liquid phase (40 mol/m3 phenol in water) was circulated in discontinuous mode, i.e. with total recirculation of liquid. The experiments were planned to determine the influence of the main operating conditions, i.e. liquid superficial velocity (0.9–3.3 × 10−3 m/s), Cu(II) concentration (0.41–0.945 mol/m3) and temperature (110–143 °C). Temperature and liquid superficial velocity were found to have the most marked influence in phenol conversion. The use of the foam packing, particularly at high liquid superficial velocities, enhances oxygen mass transfer between phases and increases the efficiency of the process (higher phenol conversion). A mathematical model, based on conservation equations applied to the bulk liquid and liquid film, has been proposed and validated with the experimental results. It has been found that the model is able to predict the experiments within an error of ±10%.

- **Keywords:** Reticulated structures; Phase contact; Mass transfer; Multiphase reactor; Wastewater treatment; Wet-air oxidation

Sami Mnif, Alif Chebbi, Najla Mhiri, Sami Sayadi, Mohamed Chamkha. *Biodegradation of phenanthrene by a bacterial consortium enriched from Sercina oilfield*. Pages 44-53.

The phenanthrene (PHE) degradation by a halotolerant bacterial consortium enriched from production water of Sercina oilfield in Tunisia was investigated. The consortium PHMM utilized PHE (200 mg/L), as a sole carbon source, in the presence of a wide range of NaCl concentrations, from 1 to 5% (w/v). The maximum growth rate was obtained at 500 mg/L of PHE. A PHE metabolism was assayed by using FTIR, UV and GC–MS analyses. Results revealed that the consortium PHMM metabolized PHE via protochatechuate pathway since intermediates such as naphthalenol and phthalic acid were detected. Phylogenetic analysis showed that the adapted consortium PHMM was composed by two dominant bacterial strains, identified as Pseudomonas sp. (strain PH1) and Staphylococcus sp. (strain PH2). All the results indicated that the microorganisms from the Tunisian oilfield have a promising application in bioremediation of petrochemical contaminated environments and could be potentially useful for the study of PAHs biodegradation.

- **Keywords:** Phenanthrene; Biodegradation; Oilfield; Consortium; Pseudomonas; Staphylococcus

Maryam Mahjouri, Mohd Bakri Ishak, Ali Torabian, Latifah Abd Manaf, Normala Halimoon, Jamal Ghoddusi. *Optimal selection of Iron and Steel wastewater treatment technology using integrated multi-criteria decision-making techniques and fuzzy logic*. Pages 54-68.

Selecting the optimal wastewater treatment technology (WTT) is one of the biggest challenges in the sustainable management of industrial wastewaters. In Iran's economy, the strategic role of the steel sector highlights its importance in sustainability assessments. Using Iran's steel industry as a case study, this paper develops an integrated methodology for determining the most appropriate WTT. Since, the most common approach for technology evaluation, in both developed and developing countries, is expert judgment, this issue is studied by means of a multi-dimensional approach that considers the sector characteristics; the interaction of the technical, environmental and economic aspects; and the specific preferences in developing countries. The proposed modelling framework presents a rational decision-making process based on two multi-criteria decision-making (MCDM) techniques including the Analytic Hierarchy Process (AHP) and the Technique for Order Preference by Similarity to Ideal Solution (TOPSIS) in combination with fuzzy logic to make use of the combined benefits of several methods The methodology is carried out as a stepwise procedure and the fuzzy concept is introduced in both the weighting and ranking procedures. The most commonly used industrial WTTs in the steel industry are identified and ranked with respect to the six evaluation criteria and their thirty associated indicators. Finally, the results from different models, with crisp and fuzzy values, are compared to propose a straightforward and pragmatic operational decision tool. The study indicates that a hybrid model of AHP, TOPSIS and fuzzy logic offers better results and provides a higher degree of confidence for sophisticated judgments. According to the findings, the experts largely prefer the more advanced treatment systems, such as "Electrolytic splitting with Reverse osmosis and Evaporation in addition to the conventional technologies" because of their high system efficiency and compatibility with environmental impact criteria. This approach can be applied for other sectors at any industry level of decision-making—from the level of individual plants to national.

- **Keywords:** Optimal technology; Wastewater treatment; Iron and Steel industry; AHP; TOPSIS; Fuzzy logic

Luca Marmo, Daniela Riccio, Enrico Danzi. *Explosibility of metallic waste dusts*. Pages 69-80.

Among the industrial sectors that are affected by dust explosions, the metal working industry is one of the most frequently involved. Metal dusts are often the by-products of

mechanical workings. Dust producing machines are widely distributed, small in size and are generally located in workplaces. Abatement plants are also often located in the working area. The companies that are involved in these explosions are often small, and thus often have limited resources. These factors generally lead to difficulties in managing the risk of explosions. This paper has the aim of investigating the flammability of waste dust produced by metal workings, and to define the dust properties that are more likely to lead to an explosion. For this purpose, a simple and fast flammability test has been used as a cheap way of characterise the flammability of the samples. The test has been called the Speedy Esplosibility Test (SET), and it is similar to the procedure suggested in the new ISO/IEC standard (ISO/IEC 2016) that came into force recently. SET is composed of 4 different tests, derived from standard procedures, each of which represents a different ignition mechanism:

- High voltage continuous arc ignition and glowing wire ignition in a Hartman 1.2 l tube (based on UNI EN 13821:2004);
- Dust cloud ignition in a G-G furnace and dust layer ignition on a hot plate (based on UNI EN 50281:1999).

The SET results are compared with the standard flammability classification obtained according to ISO, 2016ISO/IEC 80079:2016, with the standard KSt measurement in the 20-L Siwek Sphere, and with tests in the 20-L sphere with 2 × 1 kJ igniters, respectively according to the UNI EN 14034: 2011 part 2 and part 3. Moreover, the morphology and chemical nature of the dusts have also been determined and their effects on dust explosibility are discussed.

- **Keywords:** Flammability test; Speedy explosibility test; Mechanical workings; Metallic Dust; Dust Esplosibility; Dust Explosion

Shan-Fei Fu, Xiao-Hui Xu, Meng Dai, Xian-Zheng Yuan, Rong-Bo Guo. *Hydrogen and methane production from vinasse using two-stage anaerobic digestion*. Pages 81-86.

Vinasse is mainly produced during the brewing or liquor production, which is an potential substrate for biogas production. However, due to the rich content of easily degradation components in vinasse, the fermentation system during the initial AD stage of vinasse is easily acidifying, which leads to the fermentation system unstable, even failed. In this study, mesophilic hydrogen and methane production from vinasse through two-stage anaerobic digestion was investigated. In addition, one-stage anaerobic digestion of vinasse was also conducted to compare with two-stage anaerobic digestion. During two-stage anaerobic digestion, the hydrogen and methane yield were 14.8 and 274 ml/g VSsubstrate, respectively. The methane yield from two-stage anaerobic digestion was 10.8% higher than that of one-stage. During the methane production process, the lag-phase of two-stage anaerobic digestion was 9.1 days less than that of one-stage. In addition, the VS removal efficiency and energy recovery of two-stage anaerobic digestion were 10.4% and 12.9% higher than those of one-stage. Two-stage anaerobic digestion for hydrogen and methane production could efficiently improve the substrate utilization efficiency and energy recovery of vinasse.

- **Keywords:** Vinasse; Two-stage anaerobic digestion; One-stage anaerobic digestion; VS removal efficiency; Substrate utilization; Energy recovery

Vytenis Babrauskas. *Phosphorus explosions*. Pages 87-93.

Phosphorus is a highly reactive substance and numerous accidents have been reported due to phosphorus reactions with diverse chemicals. Yet, it has generally been considered that phosphorus does not explode when O2 (or air) is the only available

reaction partner. A chemical explosion requires that a bulk volume of reactant be available to react abruptly. Thus, a substance which is highly reactive is likely to participate in an explosion only if rapid, local consumption of reactant can be avoided and a sizable volume becomes capable of reacting precipitously. Since reactions of P with O2 are rapid, explosions have rarely been encountered and most chemical safety treatises warn of explosive P reactions only in connection with substances other than air. Despite this background, a series of P explosions is described which occurred in molecular beam epitaxy equipment. Earlier known incidents are also discussed. In each case, the details of the environment allowing precipitous reaction of a sizable volume of P have not been well understood, and additional research is warranted. Reference works should make clear that explosions in the system P + O2 are possible, and that neither additional reactants nor elevated temperatures are required for this.

- **Keywords:** Combustion; Explosions; Molecular beam epitaxy; Oxidation; Phosphorus; Industrial accidents

Hamideh Nouri, Sattar Chavoshi Borujeni, Ramkrishna Nirola, Ali Hassanli, Simon Beecham, Sina Alaghmand, Chris Saint, Dennis Mulcahy. *Application of green remediation on soil salinity treatment: A review on halophytoremediation*. Pages 94-107.

The salinity of soil and water resources is one of the economically expensive challenges to achieve sustainable development across the world. Salinity, which is a major environmental issue for both arid and semi-arid regions, is highly stressful for vegetation and adds to other stresses including water scarcity, nutrient deficiencies and soil alkalinity. Remediation is a strategy to clean up pollutants from the plant root zone in order to reduce vegetation stress and enhance productivity. This strategy involves biological management of soil and water which often leads to increased soil infiltration and leaching of excess salts out of the root zone. Several methods of soil and water remediation have been proposed that can be classified into the two main groups of engineering-based remediation and green remediation. Green remediation is the use of vegetation to remove or contain environmental contaminants such as heavy metals, trace elements, organic compounds and radioactive compounds in soil or water. There has recently been increased interest in green remediation using halophytes, particularly in developing countries. This paper reviews the different methods of phytoremediation and their application in green remediation. It also describes how halophytes are an emerging means of desalination and how they can be used for phytoremediation of heavy metals.

- **Keywords:** Soil and water remediation; Green clean-up; Salinity; Phytoremediation; Halophyte; Desalination

T. Li, R.P. Lindstedt. *Thermal radiation induced ignition of multipoint turbulent explosions*. Pages 108-121.

The severity of vapour cloud explosions is typically correlated with the peak over-pressure or, more accurately, with the total impulse caused by the pressure waves. The flame speed arising from strong (e.g. quasi-stable) turbulent deflagrations is frequently used to provide an indication of potential damage. However, conventional flame propagation mechanisms can present difficulties in terms of explaining the resulting damage. For example, the over-pressure in the Buncefield vapour cloud explosion was much higher than that predicted by conventional models. Alternative propagation mechanisms include intermittent localised strong explosions or detonations potentially supported by forward thermal radiation causing multi-point ignition of dust particles ahead of the advancing flame front. Such mechanisms are here explored using particles coated with acetylene black as the radiation target due to their relationship with soot emissions. A continuous wave laser operating in the near infrared was used as the

radiation source with experiments performed in a flame tube using fuel lean CH4/H2/Air mixtures. It is shown that ignition kernels caused by irradiated particles can successfully be entrained into the main flow and/or recirculation zones formed around obstacles and cause multipoint explosions. The resulting relationship between fuel consumption ahead of the advancing flame and the evolution of the strength of the explosion is shown to be complex and typically lead to increased explosion durations with reduced peak pressures. It is also shown that chaotic pressure wave interactions can substantially increase both the explosion duration and the peak pressure depending on the timing of the radiation induced ignition.

- **Keywords:** Turbulent explosions; Particle ignition; Thermal radiation; Natural gas; Hydrogen enrichment; Pressure impulse

Roohan Rakhshaee, Javad Darvazeh. *Comparing performance of three forms of hematite in fixed bed reactor for a photocatalytic decolorization: Experimental design, model fitting and optimization of conditions*. Pages 122-137.

α-Fe2O3 in three forms of bulk, bare nanoparticles and stabilized nano particles by pectin were used in a fixed bed reactor with changeable diameter of flexible wall and two lamps inside column as a novel design for photocatalytic decolorization of methylene blue (MB) in aqueous solution. At first, the portion of photo degradation as one of the MB removal mechanisms was determined due to comparing performance of reference and experimental reactors. Three parameters of fixed bed reactor containing initial effective diameter of reactor (DE), inlet flow rate (F) and residence time (τ) were analyzed, experimentally, and the obtained results using three photocatalyst agents were compared. The experimental data was fitted as a function of the independent variables and proposed by the final equations in the terms of coded and actual factors as the linear models for nano α-Fe2O/pectin and bare nano α-Fe2O, and the quadratic model for bulk α-Fe2O3. The most decolorization (C0MB 100 mg l−1) as the experimental and predicted responses were obtained (99.2% and 99.9284%), (98.5% and 99.8849%) and (82.4% and 92.2101%) using nano α-Fe2O3/pectin at DE = 1.7387 cm, τ = 93.073 min and F = 3.219 ml/min, using bare nano α-Fe2O3 at DE = 1.000 cm, τ = 95.125 min and F = 2.033 ml/min, and using bulk α-Fe2O3 at DE = 1.000 cm, τ = 99.999 min and F = 2.000 ml/min, as optimum conditions, respectively.

- **Keywords:** Photocatalytic decolorization; Fixed bed reactor; Experimental design; Model fitting; Optimization; Hematite

Rubia Zahid Gaur, Surindra Suthar. *Nutrient scaling of duckweed (Spirodela polyrhiza) biomass in urban wastewater and its utility in anaerobic co-digestion*. Pages 138-146.

The study aimed to investigate the biochemical up gradation of duckweed (DW)—Spirodela polyrhiza biomass cultivated in wastewater and then its further utility in anaerobic digestion (AD). For chemical scaling of DW biomass, a batch-scale duckweed reactor was designed using urban wastewater (WW) and changes in WW characteristics were recorded at the end. The WW showed the significant reduction (p < 0.05) in pH-16.9; electrical conductivity (EC)—67.6%; biochemical oxygen demand (BOD)—62.6%; nitrate nitrogen (NO3−-N)—76.5%; orthophosphate (PO4−3-P)—76%; sulphate (SO4−2)—86.9%; sodium (Na+)—12.0%; calcium (Ca+2)—75.9% and, potassium (K+)—53.6% after duckweed treatment. After treatment, the DW biomass was harvested and analysed for biochemical properties. Results showed an increase in carbohydrate (45.5%), starch (40.8%), lipid (46.4%) and, protein (56.4%) contents. In the second stage of experiments, the harvested DW biomass was mixed (v/v) with waste activated sludge (WAS) and inoculum—acclimatized anaerobic granular sludge (AAGS) to produce

four anaerobic batch setups: T1—DW/WAS/AAGS (50:10:40), T2—DW/WAS/AAGS (40:20:40), T3—DW/WAS/AAGS (30:30:40) and, T4—AAGS (100%) and production of methane was recorded for 35 d. The methane production was recorded in the ranges of 3001 (T3)—5491 (T1) mL. The rate of methane generation in all batch reactors was in the order: T1 (24.01) > T2 (15.13) > T3 (9.55). Results thus, revealed that the high content of DW in reactor caused positive effect on methane generation. During the process, soluble chemical oxygen demand (SCOD) and volatile solids (VS) also reduced 36.8–79.7% and, 42.9–70.9%, respectively. Gompertz model validates the experimental methane yield in all setups. Our study indicates that DW can be sustainable tool to solve two major problems: wastewater treatment and renewable energy production under clean development approach.

- **Keywords:** Methane; Wastewater treatment; COD; Duckweed; Waste activated sludge; Acclimatized anaerobic granular sludge

Bing Xu, Lunjian Chen, Baolin Xing, Zhengxin Li, Le Zhang, Guiyun Yi, Guangxu Huang, Manoj K. Mohanty. *Physicochemical properties of Hebi semi-coke from underground coal gasification and its adsorption for phenol*. Pages 147-152.

Groundwater pollution caused by underground coal gasification (UCG) as well as its purification is a great concern for scientific and engineering community. In the present study, a UCG model test of Hebi coal was carried out by air/steam two-stage gasification method. The physicochemical properties of UCG residual semi-coke samples were characterized by SEM, nitrogen adsorption at 77 K and FTIR, respectively. Adsorption experiments of phenol onto semi-coke samples were also performed. The results can be summarized as follows: (a) obvious cracks and small voids were observed in semi-coke samples; (b) compared with raw coal, semi-coke presented a larger BET surface area of 21.6 m2/g, larger pore volume of 0.087 cm3/g and wider pore size distribution with micro pores in size of 1.5–2 nm; (c) surface functional groups such as hydroxyl and carbonyl were partially preserved after gasification; (d) and the maximum removal rate of phenol approximately reached 35%. The dispersion forces between π electrons of aromatic nucleus in semi-coke and phenol ring and the formation of electron donor-acceptor complex make it work for phenol adsorption.

- **Keywords:** Underground coal gasification; Groundwater pollution; Semi-coke; Structural properties; Phenol adsorption; Self-remediation

Seyed Mostafa Hosseini Asl, Mojtaba Masomi, Morteza Hosseini, Hamedreza Javadian, Montserrat Ruiz, Ana Maria Sastre. *Synthesis of hydrous iron oxide/aluminum hydroxide composite loaded on coal fly ash as an effective mesoporous and low-cost sorbent for Cr(VI) sorption: Fuzzy logic modeling*. Pages 153-167.

The aim of this research was to estimate the possibility of using synthesized hydrous iron oxide/aluminium hydroxide composite loaded on coal fly ash (FA3) as an efficient sorbent for Cr(VI) sorption from aqueous solution. In this regard, dissolution and precipitation processes were performed to rearrange and load the intrinsic iron and aluminum on the surface of fly ash. Different characterization techniques including XRD, XRF, FT-IR, SEM, LPS and BET surface area were applied to analyze the sorbent properties. Moreover, sorption kinetics were studied using Morris–Weber intra-particle diffusion, Lagergren pseudo-first-order and pseudo-second-order models. The kinetic analyses indicated that pseudo-first-order model controlled the sorption process. In order to estimate the sorbent capacity, Langmuir, Freundlich and D–R models were applied. The thermodynamic parameters of Cr(VI) sorption were also studied. In addition, removal efficiency of Cr(VI) was predicted using the developed fuzzy logic model. The fuzzification

of four input variables including pH, contact time, adsorbent dose and initial Cr(VI) concentration versus removal efficiency as output was carried out using an artificial intelligence-based approach. A Mamdani-type fuzzy interface system was employed to fulfill a collection of 24 rules (If-Then format) using triangle membership functions (MFS) with seven levels in fuzzy sets. The proposed fuzzy logic model demonstrated high predictive performance with correlation coefficient (R2) of 0.95 and acceptable deviation from the experimental data, confirming its suitability to predict Cr(VI) removal efficiency. Based on experimental data and statistical analysis, the synthetized sorbent was effective for treating wastewater containing Cr(VI).

- **Keywords:** Fly ash; FeOOH/Al(OH)3; Sorption; Cr(VI); Isotherm; Fuzzy logic modeling

Hai Nguyen Tran, Ya-Fen Wang, Sheng-Jie You, Huan-Ping Chao. *Insights into the mechanism of cationic dye adsorption on activated charcoal: The importance of π–π interactions*. Pages 168-180.

The mechanism and capacity of methylene green (MG5) adsorption onto commercial activated-charcoal (CAC, Norit RB4C) were investigated in batch experiments. The microporous CAC material was found to exhibit a large specific surface area (1026 m2/g) and high total pore (0.502 cm3/g) and micropore (0.347 cm3/g) volumes. The point of zero charge (9.81 ± 0.07) of CAC was determined by the "drift method" and found to be insignificantly dependent on the varying operation conditions. The dye adsorption process was low relative to the solution pH (2.0–10) and ionic strength (0–0.5 M). Kinetic studies indicated that the adsorption equilibrium was quickly reached based on low activation energy required for adsorption (Ea; 4.12 kJ/mol). CAC can remove 53–64% of the MG5 concentration from solution within 1 min. The maximum adsorption capacities determined from Langmuir model at 10 °C, 30 °C, 40 °C, and 50 °C were 361 mg/g, 489 mg/g, 543 mg/g, and 581 mg/g, respectively. Desorption studies demonstrated that the MG5 adsorption was irreversible. The MG5 adsorption process was found to be spontaneous (−ΔG°), endothermic (+ΔH°), and increased the randomness (+ΔS°) in the system. Oxygenation of the CAC surface through a hydrothermal process with acrylic acid resulted in a decrease in MG5 adsorption and identified the importance of π–π interactions to the adsorption process. The analysis of Fourier transform infrared spectroscopy revealed that the aromatic CC bonds decreased in intensity and upshifted after MG5 adsorption, which additionally confirms the significant contribution of π–π interactions. The combined results of our studies highly indicated that the primary mechanisms in MG5 adsorption were π–π interactions and pore filling, while hydrogen bonding and n–π interactions were minor contributors.

- **Keywords:** Activated carbon; Methylene green 5; Adsorption mechanism; π–π interaction; Pore filling; Oxygenation method; Point of zero charge

Sajad Mobini, Fereshteh Meshkani, Mehran Rezaei. *Synthesis and characterization of nanocrystalline copper–chromium catalyst and its application in the oxidation of carbon monoxide*. Pages 181-189.

Nanocrystalline Cu–Cr mixed oxides catalysts with different molar ratios of Cu/Cr were synthesized by the hydrothermal method and employed in the catalytic CO oxidation. The physicochemical properties of these catalysts were characterized by powder X-ray diffraction (XRD), N2 adsorption (BET), temperature programmed reduction (TPR), scanning and transmission electron microscopy (SEM and TEM) methods Also, for a better comparison of catalysts the reaction rate and TOF values were calculated at two different temperatures. The results represented that the powders were mainly consisted of macropores with wide pore-size distribution. The catalytic results showed that the activity of the sample with a Cu/Cr molar ratio of 2 was significantly higher than the

other samples due to the formation of $CuCr_2O_4$ spinel structure, which was more active than the CuO and Cr_2O_3 phases in CO oxidation reaction.

- **Keywords:** CO oxidation; Spinel structure; Copper chromite; Hydrothermal synthesis; Nanocrystalline; Stability

Abdullah M. Al-Hamdi, Uwe Rinner, Mika Sillanpää. *Tin dioxide as a photocatalyst for water treatment: A review*. Pages 190-205.

Many phenols, phthalates and other toxins are released into the environment from industrial or agricultural processes, or household waste. These compounds are often stable and difficult to degrade in wastewater facilities, thus posing a serious long-time risk. The development of novel and efficient technologies for the environmentally sustainable removal of these dangerous compounds from different sources is of crucial importance. The photocatalytic oxidation of organic pollutants in the presence of semiconductors such as tin(IV) oxide (SnO_2) is a green technology and seems to be a highly promising technique for water treatment and for the removal of recalcitrant compounds. The photocatalytic efficiency of SnO_2 can be enhanced via modifications in the design of the metal oxide, resulting in a lower recombination rate of electron–hole pairs and an increase in the efficiency of the semiconductor during the excitation state, which allows the degradation process of toxins to proceed under UV or visible light irradiation. This review article summarizes some of the most relevant investigations and fundamental aspects related to SnO_2 and its activity and discusses recent achievements in the modification of SnO_2 as a photocatalyst for phenol degradation.

- **Keywords:** Tin(IV) oxide; Photodegradation; Photocatalysis; SnO_2 doping

A. Brink, C.M Sheridan, K.G. Harding. *The Fenton oxidation of biologically treated paper and pulp mill effluents: A performance and kinetic study*. Pages 206-215.

The Fenton oxidation (Fe^{2+}/H_2O_2) of bio-recalcitrant organics, which are present in biologically treated paper and pulp mill effluents (BTME), were investigated in this study. This study primarily focused on the performance and kinetics involved in the Fenton oxidation of BTMEs. A biologically treated recycle mill effluent (RME) and a neutral sulfite semi-chemical (NSSC) mill effluent were used for the experiments. The impact of $FeSO_4 \cdot 7H_2O$ and H_2O_2 dosages on chemical oxygen demand removal (COD) was evaluated. The Fenton oxidation experiments were carried out at 25 °C and a pH value of 3.8. The initial COD of the biologically treated NSSC and RME effluents were 3756 mg/L and 436 mg/L, respectively. The maximum COD removal was found at a Fe^{2+}/H_2O_2 ratio of 2.22 and 0.32 for the RME and NSSC effluents, respectively. The optimal COD/H_2O_2 for the RME and NSSC effluents was found to be 0.96 and 1.19 respectively. After a 60 min reaction, the maximum COD removal efficiency for the NSSC and RME effluents were found to be 44% and 63%, respectively. The maximum reaction rates obtained for the RME and NSSC effluents were 18 mg COD L^{-1} min^{-1} and 48 mg COD L^{-1} min^{-1}, respectively. The experimental results demonstrated that bio-recalcitrant organics, such as phenols and lignin, were readily degraded into organic acids. The applicability of the first order, second order, Behnajady–Modirshahla–Ghanbery (BMG) and a newly developed two staged first-order (TSF) kinetic model were evaluated. Both the BMG and TSF models yielded high correlation coefficients (r^2). For extended reaction times, it was found that the TSF model best described the COD removal. In addition, the TSF kinetic constants (k_{12}, k_{13}) revealed that a rapid initial degradation reaction is followed by a slower secondary degradation reaction. This performance and kinetic study demonstrated that the conventional Fenton process can effectively remove bio-recalcitrant organics that are found in BTMEs.

- **Keywords:** Fenton process; Recycle mill effluent; Neutral sulfite semi chemical mill effluent; Chemical oxygen demand; Bio-recalcitrant organics; Kinetics

Helen Adetoun Lawal-Akinlami, Palaniyandi Shanmugam. *Comparison of biochemical methane potential and methanogen morphology of different organic solid wastes co-digested anaerobically with treatment plant sludge*. Pages 216-226.

This paper describes biomethanation of tannery limed fleshing (TLF), fruits and vegetables (FVW), and sugarcane juice residue (SJR) with pre-fermented tannery-based common effluent treatment plant sludge (CETP), as an inoculum. The BMP, microbial morphology and other bioprocess efficiency parameters were evaluated using a laboratory scale batch reactor, with a substrate/inoculum ratio of 3:1 under a mesophilic anaerobic (35 ± 2 °C) condition and mixed at 100 rpm in orbit shaker. Maximum cumulative biogas yield was observed in FVW (2468.50 ± 0.44 Nm mL/d) followed by TLF and SJR comparatively to the inoculum. The specific methane yield observed ranged from 0.169 ± 0.05 to 0.478 ± 0.00 Nm L/g VSr for the wastes, against 0.204 ± 0.01 Nm L/g VSr for control treatment. The mixture of all the three wastes (CLFS) benefitted to yield more biogas compared to the mono-digestion. The highest VSr and sCODr efficiency of 62.44 ± 0.32 and 93.46 ± 1.04% obtained in FVW compared to other wastes, coincides with the methanogenic microbial count and densities. A good correlation (R2 = 0.82) was also observed between the experimental BMP and stoichiometric methane potential of the various organic solid wastes.

- **Keywords:** Organic solid wastes; Common effluent treatment plant sludge; Anaerobic digestion; Biochemical methane potential; Methanogens

Dariush Ranjbar Vakilabadi, Amir Hessam Hassani, Ghasemali Omrani, Bahman Ramavandi. *Catalytic potential of Cu/Mg/Al-chitosan for ozonation of real landfill leachate*. Pages 227-237.

Landfill leachates contain various refractory contaminants that pose potential threats to the environment and human health. In this study, Cu/Mg/Al-chitosan was synthesized by decorating chitosan with Cu (0.89 mmol/L), Mg (4 mmol/L), and Al (2 mmol/L) using a precipitation method. The catalytic potential of Cu/Mg/Al-chitosan for ozonation of real landfill leachate was examined (COD = 40,700 mg/L; BOD5 = 2100 mg/L; pH 9.1; BOD5/COD = 0.052). A significant catalytic potential of 51% was obtained for chemical oxygen demand (COD) removal in the catalytic ozonation process (COP) with 20 mg/L of catalyst and a reaction time of 50 min. The COD removal rate of the COP with Cu/Mg/Al-chitosan was 5.3 and 3.77 times greater than that with the established catalysts activated carbon and MgO, respectively. A pseudo-first order kinetic model fit the heterogeneous decays of ozone the best. The tert-butanol was employed as a radical scavenger in the experiments. GC/MS analysis was used to determine the organic compounds before and after the treatment. Thus, Cu/Mg/Al-chitosan is a promising and affordable catalyst for use in COPs to attenuate the COD of landfill leachates.

- **Keywords:** Catalyst; Landfill leachate; Cu/Mg/Al-chitosan; Catalytic potential; Ozonation; Chemical oxygen demand

Umra Khan, Rifaqat Ali Khan Rao. *A high activity adsorbent of chemically modified Cucurbita moschata (a novel adsorbent) for the removal of Cu(II) and Ni(II) from aqueous solution: Synthesis, characterization and metal removal efficiency*. Pages 238-258.

Remarkable adsorption potential towards Cu(II) and Ni(II) ions from wastewater under competitive sorption conditions was shown by alkali treated Cucurbita moschata biomass

(ATCMB). The improvement in the adsorption properties of Cucurbita moschata biomass on treatment was because of the increase in the acidic functional groups on the surface of the adsorbent due to the chemical reaction taking place between sodium carbonate and lignocellulosic material. The alkali treatment of the adsorbent is simple and less time consuming as compare to other methods like physical activation such as the steam pyrolysis, etc. The influence of independent parameters, viz contact time, initial metal ion concentration, pH and adsorbent dosage on the process was investigated. The equilibrium equations were extensively investigated and found to be efficiently represented by Langmuir, Freundlich and Temkin isotherm models at different temperatures. Kinetic studies showed better applicability of second order kinetic model. The thermodynamic parameters (ΔH^0 and ΔG^0) suggest that adsorption of Cu(II) and Ni(II) ions was endothermic and spontaneous. The practical efficiency of ATCMB was demonstrated by removing Cu(II) and Ni(II) from single and binary-metal systems by column process. The breakthrough capacities of Cu(II) and Ni(II) ions in single metal system were higher than in binary-metal system. The desorption studies of Cu(II) and Ni(II) ions with 0.1 M HCl were conducted by column process. Therefore, these methods were further used for the extraction and pre-concentration of Cu(II) and Ni(II) ions from solutions of these metal ions prepared in DDW and in tap water for their determination using Atomic absorption spectrometry. Hence the highly efficient alkali treated Cucurbita moschata biomass showed rapid uptake of Cu(II) and Ni(II) indicating that it could be an excellent alternative for the removal of heavy metals by sorption process.

- **Keywords:** Cucurbita moschata; Chemical modification; Heavy metal; Isotherm; Thermodynamics; Kinetics

Mohamad Ali Fulazzaky, Maria Nuid, Azmi Aris, Khalida Muda. *Kinetics and mass transfer studies on the biosorption of organic matter from palm oil mill effluent by aerobic granules before and after the addition of Serratia marcescens SA30 in a sequencing batch reactor*. Pages 259-268.

Kinetic and mass transfer aspects of biosorption of oxidisable organic matter (OOM) from wastewater are important for better understanding of the mechanisms of granules initiation and development. The modified mass transfer factor models were used to predict the liquid–solid mass transfer rates of OOM biosorption from palm oil mill effluent (POME) attached to aerobic granular sludge (AGS) in a sequencing batch reactor (SBR). The variations of [kLa]g, [kLa]f and [kLa]d pursuant to time were verified to have a zigzag pattern due to the organic loading rate varies with a change in the quality of POME feeding the SBR. The influence of added Serratia marcescens SA30 on the rates of mass transfer would be very remarkable due to the effects of metabolites and biomass growth this can lead to a rapid utilisation of OOM accumulated into AGS. The maximum efficiencies of SBR reaching 48% for CODt removal at [kLa]g value of 3.054 h−1 and 68% for CODs removal at [kLa]g value of 21.012 h−1 were verified before the addition of S. marcescens SA30 and those reaching 68% for CODt removal at [kLa]g value of 1.229 × 1063 h−1 and 94% for CODs removal at [kLa]g value of 7.152 × 1064 h−1 were verified after the addition of S. marcescens SA30. The resistance of mass transfer could be dependent on external mass transfer, which controls the movement of organic molecules along the experimental period of POME fed the SBR without and with added S. marcescens SA30. The performance of SBR would increase with increase of [kLa]g value, and this provides new insight into dynamic response of the aerobic digestion to AGS development.

- **Keywords:** Biosorption; Mass transfer kinetic; Oxidisable organic matter; Palm oil mill effluent; Sequencing batch reactor; Serratia marcescens SA30

Vishal Kumar Sandhwar, Basheshwar Prasad. *Terephthalic acid removal from aqueous solution by electrocoagulation and electro-Fenton*

***methods: Process optimization through response surface methodology*. Pages 269-280.**

The present work deals with the treatment of terephthalic acid (TPA) and chemical oxygen demand (COD) from synthetic aqueous solution. Initially the aqueous solution was treated by acid precipitation at different pH (2–5) and temperature (15–60 °C). Approximately 87.1% of TPA and 68.85% of COD were removed by acid precipitation treatment at optimum conditions. After acid precipitation, the filtered supernatant was further treated by electrocoagulation (EC) and electro-Fenton (EF) techniques separately. Operating parameters viz. pH—(4–12), current density (A/m2)—(15.24–45.72), Na2SO4 concentration (mol/L)—(0.02–0.04) and time (min)—(10–70) for EC treatment and pH—(1–5), current density (A/m2)—(15.24–45.72), H2O2 concentration (mg/L)—(50–250) and time (min)—(10–70) for EF treatment were optimized and modeled by Central Composite Design (CCD) in response surface methodology (RSM). Maximum removal of TPA—82.76%, 91.87% COD—79.56%, 89.68% with electrical energy consumption (kWh/kg COD removed)—22.65, 18.11 were obtained through EC and EF treatment respectively at optimum conditions. Sludge generated at optimum conditions via electrochemical treatments was characterized by FTIR, XRD, SEM/EDX and TGA/DTA techniques.

- **Keywords:** Terephthalic acid; Electrocoagulation; Electro-Fenton; Graphite cathode; Sludge analysis; Optimization

Yong Sun, Gang Yang, Lian Zhang, Zhi Sun. *Preparation of high performance H2S removal biochar by direct fluidized bed carbonization using potato peel waste*. Pages 281-288.

The biochar was produced by fast pyrolysis of potato peel waste (PPW) using the fluidized bed. The response surface methodology (RSM) and the central composite design (CCD) were employed for determining optimal adsorbents with the maximum H2S removal capacity. The operational parameters e.g. carbonization temperature (°C), duration (min) and space velocity (SV-L min−1 kg−1) were chosen as independent variables in the CCD. The statistical result indicates that the carbonization temperature is significant to the H2S removal capacity. The optimal condition for achieving the maximum H2S adsorption capacity of biochar is obtained as the followings: carbonization temperature (500 °C), duration (5 min), and SV (8000 L min−1 kg−1) with the H2S removal reaching 53 mg/g. The equilibrium adsorption indicates the heterogeneity of adsorption sites. The advantage of fluidized bed reactor in process intensification by significantly reducing carbon footprint during adsorbent preparation shows prosperous future.

- **Keywords:** Biochar; Potato peel waste; H2S; CCD; Fluidized bed; Fast carbonization

M. Sheikhalishahi, A. Azadeh, L. Pintelon. *Dynamic maintenance planning approach by considering grouping strategy and human factors*. Pages 289-298.

This paper proposes a novel maintenance planning approach by considering grouping strategy as well as human factors. The proposed approach describes various steps from boundary definition to execution of maintenance plan. Positive and negative economic dependencies are considered for series and parallel components, respectively. In this work, a special attention is paid to human factors during maintenance planning. In order to show the applicability of the proposed approach a power plant is selected as a case study. Two human factors including time pressure and fatigue are identified and quantified through an extensive data mining. According to the results of the case study, grouping maintenance activities by considering human factors provides a considerable

cost saving. Also, it is shown that ignoring human factors could decrease the cost saving. The proposed approach suggests the importance of human factors in maintenance planning, however, for various cases and in different industries this impact may be different. The proposed approach would minimize maintenance costs while human error as well as risks of delaying maintenance activities are taken into account.

- **Keywords:** Human factors; Dynamic grouping strategy; Multi-component system; Genetic algorithm; Time pressure; Fatigue

Agnès Janès, Jérôme Lesage, Benno Weinberger, Douglas Carson. *Experimental determination of minimum ignition current (MIC) ratio of hydrogen/methane (H2NG) blends up to 20 vol.% of hydrogen*. Pages 299-308.

In the context of planning a decarburization of the European Union energy sector, in order to reach a reduction of carbon emissions up to 95% by 2050, several studies on the compatibility of the existing gas networks with blends of natural gas/hydrogen up to 20% of hydrogen have been tested in industrial scale projects. In relationship to the European Union ATEX directive 2014/34/EU covering equipment and protective systems intended for the use in potentially explosive atmospheres, gases and dusts are classified according to their ignition properties. The explosion group for gases and vapors is determined by the maximum experimental safe gap (MESG) and/or minimum ignition current (MIC) ratio values, both defined in the IEC 60079-20-1 (Explosive Atmosphere—Part 20-1: Material characteristics for gas and vapour classification—Test methods and data) standard. This paper reports the results of the experimental determination of MIC of methane/hydrogen mixtures up to 20 vol.% of hydrogen. We present the ratios of MIC for hydrogen/methane blends to the MIC of pure methane as well, in order to classify these mixtures into gases groups. The interpretation of our results would lead us to conclude that methane/hydrogen mixtures containing 16 vol.% of hydrogen or more should be Group IIB gases. However, other results available in scientific literature and standards lead to the conclusion that these concentrations would still remain within the Group IIA classification. This issue was recently discussed in the IEC subcommittee 31 M of the International Electrotechnical Commission, in order to resolve this contradiction.

- **Keywords:** Minimum ignition current; Maximum experimental safe gap; Ignition sensitivity of gases; Classification in gas groups; Methane/hydrogen mixtures; Explosive Atmosphere

A.M. Na'inna, H.N. Phylaktou, G.E. Andrews. *Explosion flame acceleration over obstacles: Effects of separation distance for a range of scales*. Pages 309-316.

The influence of obstacle separation distance on explosion flame acceleration was studied for 10% methane–air mixtures using two 20% blockage obstacles with variable number and width of bars (variable obstacle length scale) were investigated in a 162 mm diameter 4.5 m long tube with ignition on the centre of the closed end and flame propagation towards the open end. The spacing between the obstacles was varied from 0.25 m to 2.75 m. It was observed that the maximum overpressure and flame speed increased with the reduction in number of flat-bars (i.e. with increasing obstacle length scale). A maximum overpressure of 129 kPa at 2.25 m obstacle spacing was achieved with 1-flat-bar obstacles, followed by 118 kPa and 110 kPa for 2 and 4-flat-bars respectively at 1.25 m and 0.5 m obstacle separation. Turbulent to laminar burning velocity ratios downstream of the second obstacle at the optimum spacing for maximum interaction were in the range of 62–122. These are the magnitudes of flame acceleration required to explain overpressures in vapour cloud explosions in the presence of obstacles. It is worth appreciating that two obstacles of lower blockages but spaced

optimally could generate higher explosion severity in terms of overpressure, flame speed and turbulence level similar to real gas explosion incidents.

- **Keywords:** Explosions; Flame acceleration; Obstacle separation distance; Obstacle scale; Turbulent flames

Long Shi, Jinhui Wang, Guomin Zhang, Xudong Cheng, Xianbo Zhao. *A risk assessment method to quantitatively investigate the methane explosion in underground coal mine*. Pages 317-333.

Methane explosion in underground coal mine is one of the most deadly hazards to the miners and the surrounding environment. An improved analytical hierarchy process (IAHP) was developed to investigate the influencing factors of methane explosion quantitatively. IAHP was validated by statistical data, showing its advantages in reducing bias. Both IAHP results and statistical data indicated that electrical spark, blasting and friction spark were the leading ignition sources. Blasting operation, digging process, explosive charge and gas detect procedure showed the highest influencing weights to methane explosion. A case/example was provided to determine the safety level of an underground coal mine. Implementations were provided to avoid methane explosion in underground coal mines, such as avoiding high methane concentration (10–15 vol.%), taking care of rocks with more than 30% quartz and larger than 70 μm particle size, and using high melting point tool/equipment, and limiting coal pick speed within 1.5 m/s.

- **Keywords:** Risk assessment; Methane explosion; Underground coal mine; Analytic hierarchy process; Spark ignition; Fault tree analysis

Shraboni Mukherjee, Madhumanti Mondal, Soumya Banerjee, Gopinath Halder. *Elucidation of the sorptive uptake of fluoride by Ca2+-treated and untreated algal biomass of Nostoc sp. (BTA394): Isotherm, kinetics, thermodynamics and safe disposal*. Pages 334-345.

The present study explores the sorption mechanism of fluoride from aqueous solution on to live biomass of Nostoc sp. (BTA394). Adsorptive efficiency of the algal biomass both as Ca2+-treated and without Ca2+-treatment were studied in varying fluoride concentration. The influence of several parameters like initial fluoride concentration (5–20 mg/L), time (0–14 h), temperature (283.15–303.15 K) and calcium concentration (50–200 ppm) were considered. The effect of pH (1–11) was taken into account only for the untreated biomass. Instrumental analysis of the algal biomass was studied for better understanding of the adsorption mechanism. The removal process was found to follow Langmuir isotherm model (R2 = 0.9962 and 0.9945) with maximum adsorptive uptake of 4.72 mg/g and 3.49 mg/g by Ca2+-treated and Ca2+-untreated algal biomass respectively. The sorption process obeyed pseudo second order kinetic model. Thermodynamic study revealed the process to be endothermic, spontaneous and feasible in nature. The spent algal biomass was further modified which could be used as an ingredient in road construction or brick making thereby preventing the problems associated with waste disposal. Therefore, Ca2+-treated live algal biomass of Nostoc sp. (BTA394) could be a promising biosorbent for fluoride removal from aqueous solution.

- **Keywords:** Biosorption; Nostoc sp.; Defluoridation; Isotherm; Kinetics; Thermodynamics

Suvendu Manna, Debasis Roy, Prosenjit Saha, Deepu Gopakumar, Sabu Thomas. *Rapid methylene blue adsorption using modified lignocellulosic materials*. Pages 346-356.

Lignocellulosic matter was grafted with neem oil–phenolic resin for developing a highly efficient adsorbent capable of capturing dye rapidly from water. Methylene blue was used for demonstrating the removal efficacy of the treated lignocellulosic biomatters. Effect of adsorbent dose, pH, time and temperature on removal efficiency was investigated. The data indicate that after modification, methylene blue removal efficacy of lignocellulosic matter increased from 455 mg/g to 2000 mg/g. The removal efficiency of the treated biomatters was unaffected for the pH range between 2 and 8. The treated biomatters rapidly captured above 95% of the initial methylene blue content from water within 5 min. The kinetic and thermodynamic study indicated that MB removal was pseudo second order endothermic process. The chemical characterization indicated that MB was captured on the surface of the biomatters through electrostatic interaction, hydrogen bonding and van der Waals forces. The study also indicated that the materials could be regenerated and reused for more than five cycles with slight decrease of the removal efficiency. This treated lignocellulosic biomatters based process was found to be comparable or better than their available alternatives.

- **Keywords:** Lignocellulose; Methylene blue; Neem oil–phenolic resin; Dye; Adsorption; Biomass modification; Recycle

Manuela Stan, Ildiko Lung, Maria-Loredana Soran, Cristian Leostean, Adriana Popa, Maria Stefan, Mihaela Diana Lazar, Ocsana Opris, Teofil-Danut Silipas, Alin Sebastian Porav. *Removal of antibiotics from aqueous solutions by green synthesized magnetite nanoparticles with selected agro-waste extracts*. Pages 357-372.

The present work highlights on efficacy of three types of green synthesized magnetite nanoparticles (Fe3O4 NPs) for the removal of a mixture of seven antibiotics, namely piperacillin (PIP), tazobactam (TAZ), sulfamethoxazole (SUL), tetracycline (TET), trimethoprim (TRI), ampicillin (AMP) and erythromycin (ERY) from aqueous media. Fe3O4 NPs were prepared through an environmentally friendly, facile and economical synthetic route which uses aqueous peel extracts of lemon (Citrus limon), black grapes (Vitis vinifera) and cucumber (Cucumis sativus), and were denoted as Fe3O4(lem), Fe3O4(grp) and Fe3O4(cum), respectively. The magnetic nanoparticles were characterized by XRD, FTIR, SEM, TEM, BET, XPS, and VSM techniques. A Box-Behnken design approach was employed in order to identify the optimum conditions for removal of selected antibiotics. The concentration of antibiotics was determined using high-performance liquid chromatography coupled with diode array detector and mass spectrometer (HPLC-DAD–MS) analysis. The Langmuir, Freundlich and Temkin adsorption isotherm models were used for description of the adsorption equilibrium of studied antibiotics and kinetic studies were conducted. Overall, Fe3O4 NPs synthesized with extracts exhibited high removal (>90%) of studied antibiotics, excepting SUL and TRI, and likewise demonstrated higher efficiency for the purpose of antibiotics removal than Fe3O4 NPs synthesized by a previously reported conventional method.

- **Keywords:** Environmental pollution; Antibiotics; Box-Behnken design; Magnetite nanoparticles; Green synthesis; Vegetal extracts

Swaroopa Rani Dasari, Vaibhav V. Goud. *Simultaneous extraction and transesterification of castor seeds for biodiesel production: Assessment of biodegradability*. Pages 373-387.

The objective of this study was to investigate single step trans-esterification with integration of Soxhlet order to find the effect of various reaction variables on the conversion of castor oil methyl ester (COME) via conventional optimization method. Based on the results obtained from the conventional method, a three-level-three factorial central composite design (CCD) was employed to study the effect of three significant

variables on COME conversion. The optimum conditions to maximise the methyl ester conversion inferred from the RSM (Response Surface Methodology) were: reaction time—6.3 h, oil/methanol molar ratio—1:400, catalyst concentration—1.5 wt%, seed weight—20 g, stirring speed—1000 rpm, and temperature—65 °C. At this condition methyl ester conversion could reach as high as 95%. The co-solvent (hexane) showed insignificant effect on methyl esters conversion. The fuel properties of produced COME conform to the ASTM standards. Biodegradability of prepared COME tested using bio-kinetic model was found to be 51% in 28 days. The lower biodegradability attributed to the higher COME viscosity.

- **Keywords:** Free fatty acid; Reactive extraction; Castor oil methyl ester; KOH; Response surface methodology; Biodegradability

Sandip Mondal, Kaustav Aikat, Kumar Siddharth, Krishna Sarkar, Rachana DasChaudhury, Gulshan Mandal, Gopinath Halder. *Optimizing ranitidine hydrochloride uptake of Parthenium hysterophorus derived N-biochar through response surface methodology and artificial neural network*. Pages 388-401.

The present study investigated the feasibility of utilizing Parthenium hysterophorus derived activated N-biochar (PH-ANB) as a potential low cost adsorbent for the effective removal of micro-pollutant and water-soluble cationic pharmaceutical ranitidine hydrochloride (RH) from simulated aqueous system. The structural characteristic features of PH-ANB were analysed using FTIR, SEM, BET and point of zero charge (pHPZC). The process of RH removal was conducted under the influence of varying parameters viz. adsorbent dose (0.01 g–0.1 g), contact time (5 min–180 min), pH (2–10), speed of agitation (40–240 rpm), temperature (293–313 K) and initial RH concentration (25–200 mg L−1) by performing a sequence of single parametric batch sorption experiments. The parametric conditions at which more than 99% removal of RH achieved were: adsorbent dose 0.05 g L−1, agitation speed 120 rpm, pH 2, equilibrium time 90 min and temperature 20 °C. The isothermal Langmuir model was well fitted with the equilibrium adsorption data while kinetic data suggested pseudo second order kinetics. The effects of process parameters on the removal efficiency of RH was optimized following the experimental matrix developed through a 23 full factorial central composite design (CCD) method of response surface methodology (RSM). The ideinvestigational data was then used to train artificial neural network (ANN). Results showed that ANN has superior predictability than RSM in optimization of RH removal. The study suggested that PH-ANB could be a reasonable and promising adsorbent for the elimination of RH from aqueous solution.

- **Keywords:** Parthenium hysterophorus; N-Biochar; Ranitidine hydrochloride; Modeling; Response surface methodology; Artificial neural network

Biao Sun, Kaihua Guo, Vishnu K. Pareek. *Hazardous consequence dynamic simulation of LNG spill on water for ship-to-ship bunkering*. Pages 402-413.

The significant hazards associated with LNG ship-to-ship bunkering could involve LNG vapour dispersion and LNG pool fires. The boil-off LNG vapour initially behaves as a denser-than-air vapour due to its cryogenic temperature and then is dissipated, as the vapour cloud heated up by surrounding environment. LNG pool fires occur due to either the source ignites immediately or a flash fire burns back to the source. It could cause thermal radiation damage to the surrounding properties or people. Due to different LNG discharge locations, i.e. below waterline, at waterline and above waterline, three possibilities of lumped LNG vapour source planes were compared to investigate the vapour dispersion behaviours and fire radiation hazards in different cases. The present

study is aimed at capturing the features of different hazards, analysing the potential hazardous area and investigating a possible mitigation method by applying computational fluid dynamics. Thermal radiant heat flux and temperature were utilised to analyse the material effectiveness on both the LNG bunker and the cargo vessel. The water curtain, which is commonly used to prevent material stress cracking in case of LNG leakage, were considered appropriately to mitigate the radiation hazard.

- **Keywords:** LNG spill; Bunkering; CFD; Dense gas dispersion; Pool fire radiation; Hazard mitigation

Maryam Moradi, Mohammad Haghighi, Somaiyeh Allahyari *Precipitation dispersion of Ag–ZnO nanocatalyst over functionalized multiwall carbon nanotube used in degradation of Acid Orange from wastewater*.. Pages 414-427.

A series of Ag–ZnO/CNT nanophotocatalysts with different multiwall carbon nanotubes loadings were prepared by precipitation–decomposition method. The samples properties were well-characterized by XRD, FESEM, EDX, BET, FTIR and DRS measurements. The results indicated that the loading of multiwall carbon nanotubes to nanocomposites has significant influences on morphology, surface area, hydroxyl and carboxylic functional groups and the absorption of visible light region. The catalytic performance was evaluated by the photocatalytic degradation of Acid Orange 7 dye under visible light. The results revealed that the Ag–ZnO/CNT(5) nanophotocatalyst with 5 wt.% loading of functionalized multiwall carbon nanotubes possessed superior photocatalytic activity than that of Ag–ZnO nanocomposite and the pure ZnO. The enhanced photocatalytic activity was attributed to the effective separation of electron–hole pairs on Ag–ZnO/CNT. The effect of operational parameters such as the initial pH, amount of photocatalyst and dye concentration on photo mineralization of AO7 dye has been analyzed, which efficient degradation was observed at pH 3–9. Furthermore, Ag–ZnO/CNT(5) nanophotocatalyst exhibited good recycling stabilities over several separation cycles in photocatalytic reaction system. Finally, a mechanism for photocatalytic degradation of AO7 dye is suggested.

- **Keywords:** Ag–ZnO/CNT; Nanophotocatalyst; Precipitation; Acid Orange; Wastewater treatment; Advanced oxidation

Nusrat Parveen, Sadaf Zaidi, Mohammad Danish. *Development of SVR-based model and comparative analysis with MLR and ANN models for predicting the sorption capacity of Cr(VI)*. Pages 428-437.

Environmental pollution due to heavy metals has become a global concern. Among all existing processes such as chemical precipitation, electro-dialysis etc., biosorption has been recognized as an efficient treatment for the wastewater containing heavy metals like Cr(VI). In this study, the soft computing technique support vector regression (SVR), has been used for predicting the sorption capacity of Cr(VI) with the independent parameters including contact time, initial sorbate concentration, pH of the medium and temperature using agricultural waste 'maize bran' as a low cost biosorbent. The developed SVR-based model has been compared with multiple linear regression (MLR) and artificial neural network (ANN) in terms of statistical evaluation parameters. The correlation coefficient (R) for the SVR, ANN and MLR model are 0.9986, 0.9331, 0.8955 while the average absolute relative error (AARE) are obtained as 1.30%, 9.52% and 13.16% respectively. The SVR model is found to be superior than the MLR and ANN models for predicting the sorption capacity of Cr(VI). Furthermore, the effects of the input parameters on the sorption capacity of Cr(VI) employing the MLR, ANN and SVR-based models have been simulated and the obtained results revealed that the SVR-based model is the most accurate, precise, and highly generalized.

- **Keywords:** Biosorption; Low cost biosorbent; Support vector regression (SVR); Multiple linear regression (MLR); Artificial neural networks (ANN); Heavy metals removal

Xiangkui Gao, Yanping Yuan, Xiaoling Cao, Hongwei Wu, Xudong Zhao. *Coupled cooling method and application of latent heat thermal energy storage combined with pre-cooling of envelope: Sensitivity analysis and optimization*. Pages 438-453.

Cooling system for mine refuge chamber provides comfortable environment for miners to avoid heat damage. The existing cooling systems have their own application scopes and limitations. The coupled cooling method of Latent Heat Thermal Energy Storage (LHTES) combined with pre-cooling of envelope (PE) is a new free cooling method which is suitable for high-temperature, passive, impact and other harsh environment. Then, to improve the thermal comfort and reduce energy consumption, the effect of the pre-cooling temperature, melting temperature of PCM, aspect ratio and amounts of PCM unit on the indoor temperature are investigated in a systematic manner. Furthermore, the system is optimized and the generalized results for the evaluation parameter are given. Analysis of the results may lead to following main conclusions: (i) the method really controls the indoor temperature and the saving amount of PCM is more than 50% compared to the traditional LHTES systems; (ii) the temperature control (TC) performance of PCM would drop significantly if it melts more than 80%; (iii) under current operating conditions, the optimal melting temperature is about 29 °C and the aspect ratio of PCM unit is 60:500; (iv) per 1 °C the pre-cooling temperature dropped, 19% the actual amount of PCM decreased for the case studied.

- **Keywords:** Coal mine accident; Refuge chamber; Cooling method; Latent Heat Thermal Energy Storage; Surrounding rock; Thermal analysis

S.M. Ashekuzzaman, Jia-Qian Jiang. *Strategic phosphate removal/recovery by a re-usable Mg–Fe–Cl layered double hydroxide*. Pages 454-462.

Excess phosphorus (P) in freshwater bodies is one of the major causes of eutrophication. The regulations for removing phosphate from wastewater treatment plant (WWTP) are becoming more stringent and thus the alternative technologies are sought to enhance the P removal efficiency. In this study, Mg–Fe–Cl based layered double hydroxide (LDH) compounds were synthesized and used for phosphate removal. Implementing LDH as a tertiary treatment process for the removal and recovery of phosphate is proposed. Results show that LDH dosage of 2 g/l can reduce phosphate concentration down to 0.1 mg/l from an initial value of 10 mg/l at an equilibrium contact time of 2 and 3 h, respectively. The adsorption kinetics of phosphate onto Mg–Fe–Cl LDH is well governed by the pseudo-second-order kinetic model, and adsorption data fit well to the Langmuir and Freundlich isotherms. The study on pH effect of adsorbate solution suggested that pH range between 3–7.5 is suitable for unaffected phosphate removal. The repeated use of this LDH by both batch and fixed bed column experiment showed that total phosphate reduction was about 95% and desorption percentage was about 91% through six cycles of adsorption–desorption processes. It is likely that this LDH compounds can be applied to remove and recover phosphate from secondary effluent of domestic wastewater treatment plant and thereby, to meet future stringent discharge regulations.

- **Keywords:** Layered double hydroxide; Phosphate removal; Sorption; Desorption

Z.L. Li, L. Cheng, L.W. Zhang, W. Liu, W.Q. Ma, L. Liu. *Preparation of a novel multi-walled-carbon-nanotube/cordierite composite support and its immobilization effect on horseradish peroxidase*. Pages 463-467.

Immobilization of enzyme is important for its application in wastewater treatment and its reuse. A novel multi-walled-carbon-nanotube (MWCNT)/cordierite composite support was designed. MWCNTs were successfully loaded on cordierite matrix with noncovalent self-assembly method through the amination of N-β-aminoethyl-γ-aminopropyl-trimethoxysilane. MWCNTs were loaded on both the surface and the inner holes of the cordierite matrix. Horseradish peroxidase (HRP) was successfully immobilized on the composite support by physical adsorption. The activity of the immobilized HRP increased linearly with the increase of MWCNT content on the composite support because the MWCNTs provided more loading sites. The loading content of HRP on the composite support was as high as 1.34 mg g^{-1} and its absolute activity reached as high as 1643.2 U g^{-1}, which were much higher than those reached on simple cordierite support. The storage stability, thermo-stability, catalytic stability and acid–base stability of the immobilized HRP were far better than those of free HRP. The immobilized HRP also had good reusability. The good stabilities provided good tolerance under the fluctuant conditions. Such a design and preparation method provide a new route for the design of composite support with ceramics matrix for enzyme catalysts.

- **Keywords:** Composite support; Cordierite; Horseradish peroxidase; Immobilization; MWCNTs; Self-assembly

Nikodem Szlązak, Dariusz Obracaj, Marek Korzec. *Analysis of connecting a forcing fan to a multiple fan ventilation network of a real-life mine*. Pages 468-479.

The important role of ventilation in underground mines is to guarantee safety and proper environmental conditions in all accessible areas of a mine by applying national mining laws and regulations. A mining ventilation network changes all the time as a result of moving working areas. It frequently results in an increased length of primary intake and return routes, which in turn increases the equivalent resistance of a complex ventilation network. It is necessary to undertake activities to maintain needed airflow rates in branches of ventilation network. In the conditions that prevail in copper mines in Poland, the number of downcast shafts is usually greater than that of upcast shafts. Developing new mining areas in a mine is released by subsurface roadways. If developing of mining areas is realised by shafts the most commonly used ones are downcast shafts. It is difficult to obtain demanded air distribution in ventilation network of the mine due to the large distance between the downcast and upcast shafts. In one of the Polish copper mines, installing a subsurface main fans' station at a downcast shaft, aimed at increasing airflow rates in the ventilation network, is being considered. The paper is devoted to the analysis of the possibility of increasing airflow rate in a ventilation network in this mine. The first example of building in a forcing fan in the ventilation system with a single downcast shaft and one upcast shaft is shown to illustrate the complexity of the issues in the real ventilation network of the mine. Then the impact of embodying the forcing fan to the ventilation network of the real copper mine with a multiple-fan network is analysed. Computer software can be used to solve the ventilation system for such an analysis. Most of the software is based on the model of air distribution in the ventilation network known as The Hardy Cross procedure. The principles governing such a procedure have been discussed in the article. The results of the analysis let us draw a conclusion that a significant increase in the total air supplied to the mine with a complex structure of the ventilation network is difficult to obtain using underground forcing fans. The only tangible benefit of the presented solution is a change in air distribution in excavations located a short distance from the downcast shaft at which a forcing fan could be installed. An increase in airflow rates in mining districts located near this shaft is possible. However, it must be remembered that connecting the forcing fan in one downcast shaft of the multi-shaft network decreases airflow into other downcast shafts.

- **Keywords:** Mine ventilation; Push–pull ventilation network; Main fan station; Ventilation network analysis; Optimization of ventilation network; Energy efficiency

Xuewei Li, Qiwu Zhang, Xinzhong Liu, Xiaowen Zhou, Fumio Saito. *Mechanochemical processing K2CO3/Cs2CO3-cellulose and kaolinite for the formation of water-insoluble Cs-compound*. Pages 480-485.

The aim of this work is to develop a novel method for the immobilization of radioactive cesium (Cs) compound, and this can be applied to the treatment of real biomass items contaminated with Cs which had spread over a wide area from the Fukushima Daiichi Nuclear Power Station in March 2011 in Japan. In the same group of alkali metal Cs, potassium (K) was first used for optimizing experimental conditions. The chemical composition of Cs in the contaminated biomass is believed to be similar to Cs2CO3, so that K2CO3 was used as a model starting sample added to cellulose, called as CK mixture, and further with kaolinite, as CKK mixture. Both CK and CKK mixtures were separately ground by a planetary ball mill, and the ground products were heated at different temperatures in air. Heating both mixtures at 600 °C enables us to reduce their weights effectively, due to mainly decomposition of cellulose. Finally, the mixture containing cellulose, kaolinite and Cs2CO3, as CKC mixture was investigated under the optimized conditions. As a result, the formation of water-insoluble Cs compound in the calcined sample with kaolinite addition after milling operation was achieved.

- **Keywords:** Ball-milling; Biomass; K2CO3; Cs2CO3; Kaolinite; Radioactivity

Mohammad Kavand, Neda Asasian, Mansooreh Soleimani, Tahereh Kaghazchi, Raoof Bardestani. *Film-Pore-[Concentration-Dependent] Surface Diffusion model for heavy metal ions adsorption: Single and multi-component systems*. Pages 486-497.

The present experimental work was performed in order to investigate the adsorption of several heavy metal ions including lead (Pb2+), cadmium (Cd2+) and nickel (Ni2+) onto a commercial kind of activated carbon (AC) in single and multi-component aqueous batch systems. Working on the equilibrium experimental data led to obtain the best-fitted isotherm model: Langmuir. The kinetic series of adsorption experiments were also performed to investigate the effects of several parameters like initial concentration, agitation speed and adsorbent dosage. In order to explain the adsorption kinetics and evaluation of the mass transfer coefficients, a diffusional kinetic model with some new suppositions was developed: the Film-Pore-[Concentration-Dependent] Surface Diffusion model (FPCDSD); a comprehensive model which could be easily reduced to describe other simplified ones. The FPCDSD model showed a high degree of correlation with the experimental data. The detailed calculation methods to determine the contribution of each resistance against mass transfer were addressed in the paper. The model with a single set of mass transfer parameters (with the order of magnitude of Dp ≈ 10−10 m2 s−1, Ds ≈ 10−15 m2 s−1 and kf ≈ 10−5 m s−1) was found successful in correlating adsorption data in ternary system under different operating conditions.

- **Keywords:** Adsorption; Kinetic model; Mass transfer; Diffusion; Activated carbon; Heavy metal

Ilda Vergili, Z. Beril Gönder, Yasemin Kaya, Gülten Gürdağ, Selva Çavuş. *Sorption of Pb (II) from battery industry wastewater using a weak acid cation exchange resin*. Pages 498-507.

This study investigates the removal of Pb (II) from a real battery industry wastewater by batch and column studies using a weak acid cation (WAC) resin. Batch experiments

carried out under different conditions yielded optimum conditions of t = 360 min and m = 0.1 g (2 gL−1). The mechanism of ion exchange was studied using kinetic and thermodynamic models. The temperature had a limited effect on the diffusion kinetics. The Gibbs free energy change (ΔG°) values were negative, corresponding to a spontaneous process of Pb (II) ion sorption onto the WAC resin. The plots obtained from the first loads of the column studies show the typical "S" shape of a packed-bed system with gradual breakthrough for both flow rates. Breakthrough was reached at 360 bed volume (BV) and 83 BV for flow rates of 1 m h−1 and 3 m h−1, respectively. Capacity losses of 77% and 87% were obtained after regeneration. WAC resins were characterized based on Fourier Transform Infrared Spectrum (FTIR), thermogravimetric analysis (TGA) and Environmental Scanning Electron Microscopy (ESEM) images before and after column studies.

- **Keywords:** Battery industry wastewater; Lead; Kinetics; Thermodynamics; Column studies; Weak acid cation resin

Mohammad Mehdi Amin, Amir Rahimi, Bijan Bina, Heshmatollah Nourmoradi, Mohammad Sadegh Hassanvand, Fazel Mohammadi-Moghadam, Samira Norouzi, Mohsen Heidari. *Biodegradation of n-hexane as single pollutant and in a mixture with BTEX in a scoria/compost-based biofilter*. Pages 508-517.

This study evaluated the biodegradation of n-hexane as single pollutant, and in a mixture with benzene, toluene, ethylbenzene, and xylenes (BTEX) in a scoria/compost-based biofilter. Initially, the biofilter was fed with n-hexane and maximum elimination capacities (ECmax) of 10.7 and 8.1 g m−3 h−1 were obtained for inlet loading rates (ILR) of 14.0 and 11.6 g m−3 h−1 at empty bed retention times (EBRT) of 138 and 108 s, respectively. Michaelis–Menten kinetic model was well fitted to the experimental EC of n-hexane in the single pollutant condition. In the presence of BTEX, the removal efficiency of n-hexane dramatically decreased from 76 to 21% at EBRT of 108 s. In this condition, BTEX was easily degraded with an ECmax of 110.6 g m−3 h−1 for ILR of 119.1 g m−3 h−1. A competitive inhibition kinetic well described the n-hexane removal in the presence of BTEX with an inhibition constant of 0.151 g m−3. Moreover, the interaction index of benzene with the addition of BTEX was −0.702, indicating the significant inhibitory effect of BTEX on n-hexane biodegradation. This study revealed that, in the biofiltration of n-hexane/BTEX mixture, a significant decrease in BTEX concentration is a prerequisite for the efficient removal of n-hexane.

- **Keywords:** Biofiltration; VOCs; n-Hexane; BTEX; Inhibitory effect; Elimination capacity; Removal efficiency

Salawu Omobayo Adio, Mohamed Hussein Omar, Mohammad Asif, Tawfik A. Saleh. *Arsenic and selenium removal from water using biosynthesized nanoscale zero-valent iron: A factorial design analysis*. Pages 518-527.

Environmentally friendly method is reported for the synthesis of nanoscale zero-valent iron using plant extract as a reducing agent. The biosynthesized nanoparticles were characterized using FESEM, EDS, XRD, FT-IR and TGA. A factorial design analysis was conducted to determine the influence of different factors affecting the removal of arsenic (As) and selenium (Se) from water using biosynthesized nanoscale zero-valent iron. The factors investigated include; pH, adsorbent dosage, initial concentration, contact time and shaker speed. It was observed that the effect of adsorbent dosage was most significant for the removal of arsenic from water. At 95% confidence level, dosage variation showed more than 30% increase in removal efficiency when it was varied between 10 mg and 100 mg. About 95% of arsenic removal was recorded using 100 mg adsorbent at solution pH 3. For selenium removal, the effect of adsorbent dosage showed

a relatively positive influence. About 90% removal efficiency was recorded at Se solution of pH 3 which signifies the applicability of the material for real water samples.

- **Keywords:** Biosynthesis; Nanoparticles; Arsenic and selenium removal; Nanoscale zero valent iron; Adsorption

Fatemeh Aghili, Ali Asghar Ghoreyshi, Ahmad Rahimpour, Mostafa Rahimnejad. *Coating of mixed-matrix membranes with powdered activated carbon for fouling control and treatment of dairy effluent*. Pages 528-539.

A novel membrane configuration consisting of a powdered activated carbon mixed-matrix membrane (PAC-MMM) and PAC loading onto its surface was fabricated via a combination of wet-phase inversion and pressure deposition technique for treatment of cheese whey wastewater (CWW) as a dairy effluent. The structural and mechanical properties of the PAC-MMMs with different concentrations of PAC were characterized using field emission scanning electron microscopy, atomic force microscopy, and tensile strength analysis. Characterization of the fabricated PAC-MMMs indicated that the filtration properties were improved by increasing the PAC concentration up to 0.5 wt.%. On the basis of this result, the 0.5 wt.% PAC-MMM was selected for further modification by PAC loading on the membrane surface. The experimental results revealed that the PAC-coated MMM at optimum surface PAC loading of 30 g m^{-2} could remove almost 95% of the chemical oxygen demand (COD) at the initial stage of filtration. The CWW flux was 125 L m^{-2} h^{-1}, while the irreversible fouling was significantly decreased compared to an un-coated MMM. High permeation flux, high mechanical properties, high organic matters removal, low fouling, and low investment costs, make the 30 g m^{-2} PAC-coated MMM a good candidate for treatment of dairy effluents.

- **Keywords:** Powdered activated carbon; Mixed-matrix membrane; Cheese whey wastewater; Irreversible fouling; Chemical oxygen demand