

# Process Safety and Environmental Protection

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**Rais Ahmad, Anam Mirza. Adsorption of Pb(II) and Cu(II) by Alginate-Au-Mica bionanocomposite: Kinetic, isotherm and thermodynamic studies. Pages 1-10.**

The present investigation explores with the environmental degradation of Pb(II) and Cu(II) in single and binary system by novel ecofriendly synthesized Alginate-Au nanoparticles-Mica bionanocomposite. The bionanocomposite was characterized by SEM/EDX, TEM, FTIR, XRD and TGA techniques. Adsorption experiments were conducted to investigate the effect of pH, contact time, concentration, temperature on the removal process. The experimental data was best fitted by Freundlich isotherm model for Pb(II) in single and binary system whereas for Cu(II) by Langmuir isotherm model. The kinetic data was found to be best fitted by pseudo second order kinetic model in single and binary system. Adsorption process is endothermic and spontaneous as inferred from thermodynamic studies. The oxalic acid was found to be the best eluent for the desorption of metals. The breakthrough and exhaustive capacities were found to be 300 and 2000 mg g<sup>-1</sup> respectively. The nanocomposite can be applied successfully for sequestering heavy metals from industrial wastewaters.

- **Keywords:** Bionanocomposite; Characterized; Adsorption; Heavy metals; Desorption

**Xiaobin Liao, Rusen Zou, Bingxin Li, Tianli Tong, Shuguang Xie, Baoling Yuan. Biodegradation of chlortetracycline by acclimated microbiota. Pages 11-17.**

The wide presence of antibiotic chlortetracycline in the environment has aroused increasing ecological and human health concerns. Biodegradation can be a promising strategy to dissipate chlortetracycline. However, there is a paucity of knowledge on the biodegradation of chlortetracycline. The present study investigated the biodegradation of chlortetracycline by a microbial community in liquid culture, the potential intermediates, the influences of temperature, external carbon and nitrogen sources, and the composition of chlortetracycline-degrading microbial community. At the initial chlortetracycline level of 100 µg l<sup>-1</sup>, the average removal rates of 48.7% and 84.9% were achieved by acclimated microbial populations in one and four weeks, respectively. Four potential intermediates were identified using LC/MS/MS analysis. Moreover, microbial growth was observed with chlortetracycline biodegradation. Chlortetracycline could be used as sole carbon and nitrogen sources by the microbial community, while temperature rise and addition of external nitrogen source favored chlortetracycline

biodegradation. Illumina MiSeq high-throughput sequencing analysis indicated that bacterial community structure considerably changed with the degradation of chlortetracycline. Firmicutes, Proteobacteria and Bacteroidetes were the dominant phylum groups in chlortetracycline-degrading bacterial community.

- **Keywords:** Antibiotic; Biodegradation; Biological activated carbon; Tetracyclines; Chlortetracycline; Microbiota

**Swapnila Roy, Papita Das, Shubhalakshmi Sengupta, Suwendu Manna. *Calcium impregnated activated charcoal: Optimization and efficiency for the treatment of fluoride containing solution in batch and fixed bed reactor. Pages 18-29.***

The study of de-fluoridation was investigated using calcium impregnated activated charcoal (AC). The sorption efficiency of the modified charcoal was experimented through batch and fixed bed column reactor. Langmuir and Freundlich adsorption isotherm were utilized to study the mechanism of adsorption. The mechanism of adsorption process was illustrated by calculating Gibbs free energy, enthalpy and entropy from thermodynamic studies. The two-level, three-factor (23) Central Composite Design (CCD) expert Software was employed to find the optimum condition of batch process variables for maximizing the fluoride removal capacity of calcium activated hybrid activated charcoal. The optimum removal efficiency was obtained as 99.68%. Furthermore to confirm the practical applicability of this novel adsorbent, fixed-bed column reactor studies were done. The Thomas and BDST models were applied for the column study and it was observed that both model fitted satisfactorily with the experimental results. It can be concluded that calcium impregnated activated charcoal has potential to be a cost effective, environmentally safe adsorbent suitable for fluoride removal from water.

- **Keywords:** Fluoride adsorption; Calcium impregnated activated charcoal; Breakthrough; Equilibrium; Adsorption isotherm; Response surface methodology

**Ankita Swati, Subrata Hait. *Fate and bioavailability of heavy metals during vermicomposting of various organic wastes—A review. Pages 30-45.***

Vermicomposting process employing earthworms is increasingly being used for conversion of both municipal and industrial wastes to vermicast with reduced metals content. The aim of the paper is to review recent developments and approaches for determination of bioavailable metal fractions through speciation and consequently the fate of both essential and xenobiotic heavy metals during vermicomposting of various organic wastes. The review also provides a comprehensive summary on the occurrence of heavy metals in wastes vis-à-vis metals standards worldwide and the process efficacy in limiting the mobility of heavy metals. Past and present researches demonstrated a high-degree of agreement that vermicomposting results in effective reduction of both total and bioavailable metal contents owing to the formation of stable metal complexes and/or silicate fractions. Further, it has been concurred that earthworms and associated microbial communities during vermicomposting tend to decrease the mobility of metals by enhancing enzymatic activities in both gut- and cast-associated processes. In addition, the decrease in total metal content has been attributed to accumulation and immobilization of mobile metal fractions in earthworm tissues. In summary, it can be inferred that vermicomposting potentially converts various municipal and industrial wastes to nutrients-rich organic manure for agronomic applications with reduced metals bioavailability.

- **Keywords:** Waste stabilization; Earthworm; Gut associated processes (GAPs); Cast associated processes (CAPs); Metal speciation; Bioaccumulation

**Miguel Ángel Gómez García, Izabela Dobrosz-Gómez, Juan Carlos Ojeda Toro. *Thermal safety assessment for catalytic decomposition of hydrogen peroxide by dynamic analysis*. Pages 46-54.**

The goal of this research was to identify, characterize, and gain insight into the oscillatory thermal instability of hydrogen peroxide decomposition reaction. The experimental data, previously reported by Wirges (Chem. Eng. Sci., 35 (1980) 2141), were reexamined using a rigorous dynamic analysis. All possible bifurcation states were defined: the thermal stability regions (unique and multiple solutions), instability states (bifurcation points, saddle node bifurcations), and turning points (limit and oscillatory behavior). The geometric interpretation of each of these states, as they can be found in practical applications, was presented. The obtained results revealed a predominant thermal oscillatory behavior and high sensitivity to small fluctuation of dynamic parameters. Finally, complete information about the performance of this reactive system was ascertained and thermal sensitivity regions were fully discriminated

- **Keywords:** Hydrogen peroxide decomposition; Dynamic modeling; Bifurcation analysis; Thermal stability diagrams; Thermal runaway; Risk assessment

**Dison S.P. Franco, Jeanine M. Cunha, Gabriel F. Dortzbacher, Guilherme L. Dotto. *Adsorption of Co(II) from aqueous solutions onto rice husk modified by ultrasound assisted and supercritical technologies*. Pages 55-62.**

Rice husk was modified by ultrasound assisted (UA) and supercritical CO<sub>2</sub> (SCO<sub>2</sub>) technologies, to improve its adsorption characteristics regarding to Co(II). The Co(II) adsorption was studied with respect to the pH effect, kinetic curves and equilibrium isotherms. The UA and SCO<sub>2</sub> treatments provided increases of 7 and 4 times in the surface area, respectively. The maximum experimental adsorption capacities were 17.6, 20.8 and 35.0 mg g<sup>-1</sup>, for raw rice husk, SCO<sub>2</sub>-rice husk and UA-rice husk, respectively. These results demonstrated that mainly the ultrasound assisted technology was adequate to improve the rice husk characteristics for adsorption purposes.

- **Keywords:** Adsorption; BET model; Cobalt; Rice husk; Ultrasound assisted; Supercritical CO<sub>2</sub>

**Arvind Kumar, Hara Mohan Jena. *Adsorption of Cr(VI) from aqueous phase by high surface area activated carbon prepared by chemical activation with ZnCl<sub>2</sub>*. Pages 63-71.**

Prepared activated carbon from fox nutshell by chemical activation with ZnCl<sub>2</sub> in the N<sub>2</sub> atmosphere was used for Cr(VI) removal from aqueous solution. Activated carbon was produced at 600 °C activation temperature with a 2.0 impregnation ratio for 1 h of activation time has been found as 2869 m<sup>2</sup>/g, 1.96 and 1.68 cm<sup>3</sup>/g of highest BET surface area, total pore volume and micropore volume, respectively. Batch mode adsorption studies were carried out by varying agitation speed, pH, temperature, agitation time and initial Cr(VI) concentration. The adsorption of Cr(VI) was pH dependent and showed maximum removal efficiency of Cr(VI) at pH 2.0. Adsorption studies of 10–25 mg/L initial Cr(VI) concentration were conducted at pH of 2.0 and temperature of 30 °C. The equilibrium, kinetics, and thermodynamics of Cr(VI) adsorption were studied. The adsorption capacity of Cr(VI) from the synthetic wastewater was 43.45 mg/g. The experimental adsorption equilibrium data was fitted to Langmuir adsorption model with an adequate adsorption capacity of 46.21 mg/g.

- **Keywords:** Activated carbons; Fox nutshell; Chemical activation; Impregnation; Cr(VI); Adsorption

**Inès Mnif, Rihab Sahnoun, Semia Ellouz-Chaabouni, Dhouha Ghribi. *Application of bacterial biosurfactants for enhanced removal and biodegradation of diesel oil in soil using a newly isolated consortium.* Pages 72-81.**

One of the major environmental problems today is hydrocarbon contamination resulting from the activities related to the petrochemical industry. Bioremediation, involving the use of microorganisms to detoxify or remove pollutants is the most interesting strategy for hydrocarbon contamination depollution. In this aim, diesel oil biodegradation in soil was studied by four hydrocarbon degrading bacteria. A lipopeptide biosurfactant produced by *Bacillus subtilis* SPB1, confirmed to increase diesel mobility, was tested to increase diesel biodegradation along with co-inoculation with two biosurfactant producing strains. Culture studies revealed the enhancement of diesel biodegradation by the selected consortium with the addition of SPB1 lipopeptide and in the cases of co-inoculation by biosurfactant producing strain. In fact, an improvement of about 12.19% and 15.35% of diesel degradation were registered in the presence of 0.1% lipopeptide biosurfactant and when culturing *B. subtilis* SPB1 strain with the isolated consortium, respectively. Furthermore, the best improvement; evaluated to about 32.67% for soil contaminated with diesel was recorded when using the consortium cultured with *B. subtilis* SPB1 and *Acinetobacter radioresistens* RI7 strains. Gas phase chromatography analyses were correlated with the gravimetric evaluation of the residual hydrocarbons. Results suggested the potential applicability of the selected consortium along with the ex-situ and in-situ added biosurfactant for the bioremediation of diesel contaminated water and soil.

- **Keywords:** Biodegradation; Soil; Diesel oil; Biosurfactant; Bacterial consortia; *Bacillus* sp.; *Lysinibacillus* sp.; *Acinetobacter* sp.

**Kandasamy Kalimuthu, Chellasamy Panneerselvam, Chi Chou, Li-Chun Tseng, Kadarkarai Murugan, Kun-Hsien Tsai, Abdullah A. Alarfaj, Akon Higuchi, Angelo Canale, Jiang-Shiou Hwang, Giovanni Benelli. *Control of dengue and Zika virus vector Aedes aegypti using the predatory copepod Megacyclops formosanus: Synergy with Hedychium coronarium-synthesized silver nanoparticles and related histological changes in targeted mosquitoes.* Pages 82-96.**

The employ of nano-formulated biopesticides for mosquito control represents a promising strategy. Recently, it has been outlined that differences in the green reducing extracts used in nanosynthesis led to the production of nanoparticles with distinct bio-physical properties. In the present investigation, *Hedychium coronarium*-synthesized silver nanoparticles (AgNPs) were characterized by UV-vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), energy-dispersive X-ray diffraction (EDX), and transmission electron microscopy (TEM). The toxicity of *H. coronarium* rhizome extract and *H. coronarium*-synthesized AgNPs was assessed against larvae and pupae of the dengue vector *Aedes aegypti*, as well as against adults of the non-target copepod *Mesocyclops formosanus*. Then, the control of *A. aegypti* larval population was attempted using the predatory copepod *M. formosanus* in synergy with *H. coronarium*-synthesized silver nanoparticles, evaluating predation efficiency pre- and post-nanoparticle treatment. In presence of both predaceous copepods and nano-larvicides high control of the larval populations was obtained. Furthermore, histological changes in mosquitoes targeted with nanopesticides were studied by light microscopy, evaluating the impact on mid-gut epithelial cells following treatment with LC50 of AgNP. Overall, this study highlighted the concrete potential of synergizing copepod-based control programs with highly effective green nano-larvicides in the fight against dengue and Zika virus vectors.

- **Keywords:** Biological control; Biosafety; Dengue; Nanosynthesis; Biosynthesis; Zika virus

**Hannatu Abubakar Sani, Mansor B. Ahmad, Mohd Zobir Hussein, Nor Azowa Ibrahim, Aminu Musa, Tawfik A. Saleh. *Nanocomposite of ZnO with montmorillonite for removal of lead and copper ions from aqueous solutions*. Pages 97-105.**

The clay minerals montmorillonite (MMT) was combined with ZnO to form efficient nanocomposite which was used as an adsorbent. Zinc oxide nanoparticles (ZnO-NP) were successfully incorporated into the layers of montmorillonite by green simple heat method using zinc nitrate and sodium alginate as zinc oxide precursor and stabilizer respectively. The XRD and FESEM measurements revealed the presence of ZnO nanoparticles with hexagonal wurtzite structure in the ZnO/MMT nanocomposites. The role of the ZnO in enhancing the adsorption efficiency of the ZnO/MMT nanocomposite for the removal of copper and lead ions from aqueous solutions was investigated. The effects of different parameters such as contact time, dosage, initial concentration, and pH were investigated. Kinetics of adsorption were studied using pseudo-first-order and pseudo-second order. The efficiency of the nanocomposites was studied by Langmuir and Freundlich isotherms. The material showed high efficiency in a wide pH range, for the adsorption of Pb and Cu ions. Kinetic studies showed that the adsorption followed the pseudo-second-order and equilibrium best described by Langmuir isotherm. The regeneration results show that the nanocomposites can be utilized for at least three times because of its stability and durability. Thus, it can serve as a promising adsorbent for the removal of copper and lead ions from aqueous solutions.

- **Keywords:** ZnO/MMT nanocomposite; Sodium alginate; Copper; Lead; Water; Nanotechnology

**L. Simão, J. Jiusti, N.J. Lóh, D. Hotza, F. Raupp-Pereira, J.A. Labrincha, O.R.K. Montedo. *Waste-containing clinkers: Valorization of alternative mineral sources from pulp and paper mills*. Pages 106-116.**

Waste streams generated from pulp and paper mills show high potential to be used as alternatives raw materials for production of clinker. In this context, this work aims to evaluate the use of such materials to obtain hydraulic binders, which are referred to as Ecoclinkers and Ecocements. Lime mud, wastewater treatment process sludge and biomass ashes were characterized, and five formulations (F1–F5) were developed by applying the Bogue equations. These compositions were processed at three different clinkering temperatures (1350, 1440 and 1455 °C). The formulated Ecoclinkers and a reference hydraulic binder were characterized by X-ray diffractometry to identify the crystalline phases, which were subsequently quantified by the Rietveld method. The results showed that crystalline phase characteristics of clinkers and cements, and compression strengths of ~20 MPa after 28 days curing time were obtained, confirming the potential use of the investigated waste as alternative materials for production of clinker.

- **Keywords:** Pulp and paper mill; Waste; Clinker; Recycling; Alternative materials; Valorization

**Sabino De Gisi, Antonio Molino, Michele Notarnicola. *Enhancing the recovery of gypsum in limestone-based wet flue gas desulfurization with high energy ball milling process: A feasibility study*. Pages 117-129.**

The most common system for flue gas desulfurization (FGD) is the wet scrubbing process in which, the contact between the flue gases to be treated and an alkaline sorbent such

limestone is realized with the correspondent production of gypsum. The production of gypsum represent a perfect example of how is possible to obtain a new product for the market starting from the need of environmental protection (the sulphur dioxide (SO<sub>2</sub>) removal). Today, limestone is ground in long drum mill reaching a size in the range 5–10 mm. With the intent of increasing the specific surface area of limestone and consequently the gypsum production, the raw limestone was treated in a high-energy mill. The performance of such micronized limestone in terms of gypsum production and SO<sub>2</sub> removal were then evaluated by means of a bench scale desulfurization test. Subsequently, a feasibility study with the goal to verify the possible advantages simulating the application of the micronized limestone on a full-scale Waste-to-Energy (WtE) plant was realized. Results showed how the micronization process occurred securely, with a greater production of gypsum and better performance in terms of SO<sub>2</sub> removal. Additionally, the micronization solutions tested in the present study showed the suitability also from economic and environmental point of view. Since there are many power plants or WtE plants worldwide and, in many cases, they adopt a wet FGD, this study may be attractive for plant operators. The greater production of gypsum through the use of micronized limestone may help reduce the consumption of raw materials, which increased in recent years due to growing demand of the building industry.

- **Keywords:** Gypsum; High-energy mill; Mechanochemistry; Multi-criteria analysis; Sulphur dioxide; Waste-to-energy plant

**J.J. García-Sánchez, M. Solache-Ríos, V. Martínez-Miranda, R. Enciso-Perez, N.V. Arteaga-Larios, M.C. Ojeda-Escamilla, I. Rodríguez-Torres. *Experimental study of the adsorption of fluoride by modified magnetite using a continuous flow system and numerical simulation. Pages 130-139.***

This study used fixed-bed column experiments to examine the potential and effectiveness of modified magnetite with aluminum or lanthanum to remove fluoride ions from fluoride solutions and drinking water. A fixed bed column test was conducted to simulate the actual condition of adsorption in a continuous manner in a filtration process. Fixed-bed column experiments were carried out at a bed depth of 1.3 cm and a flow rate of 1 mL min<sup>-1</sup>. The breakthrough curves obtained for fluoride ion adsorption from aqueous solutions and drinking water were fitted to Thomas, Bohart–Adams, Yoon and Nelson, and Yan models. The significant influence of bed height, flow rate, empty bed contact time, and initial fluoride concentration on removal were used for simulation of breakthrough curves. The impact of common ions present in drinking water on the adsorption of fluoride was investigated. The regeneration of the column was performed by eluting with 0.01 M Ca(OH)<sub>2</sub>, NaCl, NaOH or Na<sub>2</sub>SO<sub>4</sub> solution after the adsorption studies. Thomas, Yoon–Nelson and Yan models were found suitable for the normal description of breakthrough curves in the experimental conditions, whereas the Adams–Bohart model was able to explain only the initial part of the dynamic behavior of the column system. Simulation results indicate that the breakthrough point (tp) decreases as the flow rate and initial fluoride concentration increase, and bed height is directly proportional to fluoride removal. It was concluded that modified magnetite can be effectively used as a sorbent for the removal of fluoride ions.

- **Keywords:** Adsorption; Simulation; Fixed bed; Fluoride; Drinking water

A. Ronda, A. Pérez, I. Iañez, G. Blázquez, M. Calero, A novel methodology to characterize and to valorize a waste by a fractionation technology, *Process Safety and Environmental Protection*, Volume 109, July 2017, Pages 140-150, ISSN 0957-5820, <https://doi.org/10.1016/j.psep.2017.03.037>.

Abstract: Abstract

This work presents a solution of a problematic waste generated by a local industry. It provides a novelty fractionation methodology for the transformation of a worthless waste into higher value fractions. Besides, this methodology can be applied to other agricultural and forest wastes for an efficient management and use of resources. The waste is composed by a mix of different agroindustrial waste and due to its high organic character it cannot be field deposited. Therefore, a detailed characterization of the waste by fractionation in simpler fractions have been performed with the aim to optimize its use and to propose different application for them. The suggest uses of each fraction increase the added value of the waste and display significant environmental impact improvements of the waste. For example, the fraction obtained from acid hydrolysis (around 30%) present a high calorific value, conferring good properties to be used as fuel.

- **Keywords:** Agroindustrial waste; Breaking-up; Renewable agrowaste; Resource; Thermogravimetric analysis; Valorization

**Demet Gündogan Kalat, Ahmet Yüceer. *Anaerobic mesophilic and thermophilic treatability of vegetable oil refining wastewater. Pages 151-157.***

Two anaerobic filter reactors, one mesophilic (35 °C) and one thermophilic (55 °C), were operated with a vegetable oil refining wastewater at varying organic loadings. The organic loading rates (OLR) applied were in between 0.98–9.96 kg COD/m<sup>3</sup>/d with a constant hydraulic retention time (HRT) of 24 h for each filter reactor. The maximum chemical oxygen demand (COD) removal rates were 97% and methane yield 0.39 ± 0.02 L CH<sub>4</sub>/g CODremoved for each filter reactor. The volatile fatty acids (VFA) concentration in the effluents of mesophilic and thermophilic filter reactors also increased proportionally with the loading rate. The results show that both reactors gave the similar COD removal and methane yield. The data obtained for both mesophilic and thermophilic reactors were then applied to the Stover–Kincannon model and U<sub>max</sub> and K<sub>B</sub> values were determined as 40 g/L day, 44.09 g/L day and 111.11 g/L day, 122.78 g/L day, respectively.

- **Keywords:** Anaerobic digestion; Oil; Grease; Modeling; Half saturation coefficient; Organic loading

**Rekha Krishnan G., R. Radhika, T. Jayalatha, Salu Jacob, R. Rajeev, Benny K. George, B.R. Anjali. *Removal of perchlorate from drinking water using granular activated carbon modified by acidic functional group: Adsorption kinetics and equilibrium studies. Pages 158-171.***

Granular activated carbon was treated with different types of acids in order to improve its capability for the removal of perchlorate from drinking water. The characteristics of acid treated granular activated carbons were examined by SEM, XRD, Raman spectrum and FTIR spectroscopic analysis. The effect of various adsorption parameters such as contact time, initial perchlorate concentration, pH of the solution, temperature and presence of co-existing anions on the efficiency were studied. Maximum adsorption capacities were observed as 20.1, 37.5 and 44.0 mg g<sup>-1</sup> for GAC, GAC-AA and GAC-PH respectively at 303 K. Equilibrium adsorption isotherms and kinetics for the process were investigated and found that the process follows Langmuir adsorption isotherm. The adsorption of perchlorate could be well described by pseudo-second-order kinetic model. Thermodynamic parameters,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  were also evaluated.

- **Keywords:** Perchlorate; Activated carbon; Adsorption; Kinetics; Langmuir isotherm; Sticking probability

**M. Zendehtdel, B. Shoshtari-Yeganeh, H. Khanmohamadi, G. Cruciani. Removal of fluoride from aqueous solution by adsorption on NaP:HAp nanocomposite using response surface methodology. Pages 172-191.**

The new nanocomposite of NaP-Hydroxyapatite (NaP:HAp) has been developed for removal of fluoride from aqueous solution. NaP:HAp nanocomposite has been characterized by using different method such as: X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), Energy Dispersive X-ray analysis (EDAX), surface area (BET) and thermal gravimetric analysis (TGA). Box–Behnken design with three-level and four-factor has been employed for determination of effective process parameters such as solution pH (4–11), temperature (25–55° C), initial adsorbent dose (1–3 g) and initial fluoride concentration (5–25 mg/L) on removal of fluoride from aqueous solution. After 29 batch runs, Quadratic model was established by regression analysis of the experimental data obtained from 29 batch runs. Quantity uptake of fluoride was evaluated using the Langmuir, Freundlich and Dubinin–Radushkevich (DR) models. The rate of adsorption was rapid and followed pseudo-second-order kinetics for this adsorbent. Moreover, thermodynamic parameters ( $\Delta H^\circ$ ,  $\Delta G^\circ$ ,  $\Delta S^\circ$ ) for fluoride sorption on NaP:HAp nanocomposite was also studied from the temperature dependence. The significant novelty of this work is the simple preparation of a new nanocomposite from Hydroxyapatite and zeolite that increased stability of HAp in different pH and temperature. Also, this nanocomposite shows high capacity for adsorption of fluoride related of other sorbent and reusable for several times that makes this method nearly green and friendly environmentally.

- **Keyword:** NaP:Hydroxyapatite; Fluoride removal; Box–Behnken design; Response surface technique; Thermodynamic parameters; Kinetic; Isotherm parameters

**Mahmoud A.A. Aslani, Fatih Celik, Sabriye Yusan, Ceren Kutahyali Aslani. Assessment of the adsorption of thorium onto styrene–divinylbenzene-based resin: Optimization using central composite design and thermodynamic parameters. Pages 192-202.**

Adsorption of thorium on styrene–divinylbenzene-based resin was investigated to obtain the optimum adsorption conditions by using the central composite design (CCD) method. This study was performed in 30 runs of experiments as a function of pH, thorium concentration, contact time and temperature. Adsorption performance of styrene–divinylbenzene-based resin was higher than 98%. The optimum adsorption of thorium using styrene–divinylbenzene-based resin can be successfully predicted statistically by the CCD method. In addition, sorption isotherm models such as Langmuir, Freundlich and Dubinin–Radushkevich were applied, and adsorption of Th(IV) was described most precisely by the Langmuir isotherm, which has the highest R<sup>2</sup> (0.99) value. Thermodynamic parameters showed that the adsorption is an exothermic and spontaneous physical process. The results of this study reveal that this type of synthetic resin can be used as an effective sorbent material for the removal of Th(IV) ions from weakly aqueous solutions in remediation and nuclear wastewater treatment.

- **Keywords:** Adsorption; RSM; CCD; Lewatit S1468; Th<sup>4+</sup>; Thermodynamic

**Nouha Bakaraki Turan, Hanife Sari Erkan, Güleda Onkal Engin. The investigation of shale gas wastewater treatment by electro-Fenton process: Statistical optimization of operational parameters. Pages 203-213.**

Shale gas is an alternative natural source of energy resulting from the anaerobic degradation of organics within shale formations. However, shale gas exploration is

accompanied by shale gas wastewater production constituting a new source of pollution threatening the environment. Electro-Fenton process (EF) is used for the first time in this study as a new method for shale gas wastewater treatment where the optimum operating parameters of the the responses including COD, color, total phenol removal efficiencies and waste sludge volume were determined using a response surface methodology (RSM). Based on the analysis of variance (ANOVA), the coefficient of determination ( $R^2$ ) was calculated and found to be above 0.94 for all the responses. The maximum removal efficiencies were found to be around 87.35%, 89.15%, and 91.75% for COD, color, and total phenol removal under the optimum conditions, respectively. The operational cost of the EF process applied to shale gas wastewater for COD removal at optimum conditions was determined to be 4.13 €/m<sup>3</sup>. The results indicated that the electro-Fenton seems to be an efficient treatment method for shale gas wastewater.

- **Keywords:** Shale gas wastewater; Electro-Fenton process; Response surface methodology; Optimum operating parameters

**Lidia Bandura, Dorota Kołodyńska, Wojciech Franus. *Adsorption of BTX from aqueous solutions by Na-P1 zeolite obtained from fly ash.* Pages 214-223.**

The adsorption of BTX (benzene, toluene, o- and p-xylene) from aqueous solution by synthetic zeolite Na-P1 obtained from fly ash was examined. The adsorbent was characterized by scanning electron microscope (SEM-EDS) and X-ray diffraction (XRD). Surface area and pore volume distribution were determined using a nitrogen adsorption/desorption isotherm. BTX adsorption tests, including the influence of contact time, sorption isotherms and the influence of initial concentration, were performed in a batch multicomponent system. The sorption capacity followed the order xylenes > toluene > benzene, and the removal efficiency decreased with an increase in initial BTX concentration. The process kinetics was evaluated using pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The adsorption equilibrium was reached within 24 h and followed pseudo-second-order kinetics. The Langmuir, Freundlich and Temkin models were used to evaluate the adsorption capacity of Na-P1. The Langmuir model was found to be the most suitable for all BTX sorption from a multicomponent system. The calculated maximum adsorption capacities of Na-P1 ( $q_{max}$ ) for benzene, toluene, o- and p-xylene were 0.032, 0.050, 0.147 and 0.129 respectively.

- **Keywords:** Synthetic zeolites; Zeolite Na-P1; BTX removal; Adsorption kinetics; Adsorption isotherms; Water treatment

**Vladas Vekteris, Ina Tetsman, Vadim Mokshin. *Investigation of the efficiency of the lateral exhaust hood enhanced by aeroacoustic air flow.* Pages 224-232.**

This paper presents a novel concept of local push-pull ventilation system used to remove aerosol particles from open surface tanks. Sound waves generated by aerodynamic sound generator are introduced into the push air flow of lateral exhaust hood and used to agglomerate aerosol particles. Results of calculation of parameters of sound generator and aeroacoustic air flow are presented. It is established that 5–10  $\mu\text{m}$  aerosol particles are aggregated better at frequencies below the ultrasonic range (1–5 kHz) and aerosols with a particle size of less than 5  $\mu\text{m}$  are more effectively aggregated at ultrasonic frequencies. It was experimentally established that the relative air humidity measured above open surface tank is decreased up to 1.6 times in presence of acoustic field as compared with humidity obtained for conventional push-pull air removal system. It is also obtained that increase of the temperature of the liquid increases the aerosol removal efficiency of lateral exhaust hood enhanced by aeroacoustic air flow.

- **Keywords:** Open surface tank; Lateral exhaust hood; Acoustic field; Aerosol particles; Air humidity; Removal efficiency

**Rita Gusain, Surindra Suthar. *Potential of aquatic weeds (Lemna gibba, Lemna minor, Pistia stratiotes and Eichhornia sp.) in biofuel production. Pages 233-241.***

The aim of this study was to assess the biofuel production efficiency of aquatic weeds *Lemna gibba*, *Lemna minor*, *Pistia stratiotes* and *Eichhornia sp.* In order to see the thermos-chemical properties of the weed biomass, the proximate, elemental (C, H, N and, O) and, biochemical (carbohydrate, starch and lipids) characteristics of biomass were determined. The lipids from plant biomass was also extracted and then analyzed for preparing the fatty acid profiling (FAME). The results revealed the content of volatile matter, fixed carbon, ash, C, H, N and, O in the ranges of 44.6–59, 18.8–26.3, 18.7–24.9, 32.03–38.02, 4.39–4.87, 2.54–5.31 and, 51.81–59.99%, respectively in dried weed biomass. The Fourier transform infrared spectroscopy (FTIR) analysis suggested the presence of high energy molecules in weed biomass. The content of starch in weed biomass was comparable with other industrial crops being used for bioethanol production. The GC-FID analysis of lipids (FAME analysis) indicated the presence of C16:0, C18:0, C18:1, C18:2 and C18:3 as dominant fatty acids (FAs), which found commonly in biodiesel. The bioethanol production efficiency of weed biomass was also investigated using a microreactor-based trial. Results thus showed a yield of 0.218, 0.197, 0.215 and, 0.189 g ethanol in g<sup>-1</sup> dry biomass of *L. minor*, *L. gibba*, *P. stratiotes* and, *Eichhornia sp.*, respectively. Our results conferred that the biomass of aquatic weeds can be utilized as potential feedstock for production of ethanol, butanol, biodiesel, etc. under the clean energy initiatives.

- **Keywords:** Bioenergy; Lipid profiling; FAME; CHNS; Sugar content; FTIR; Biodiesel

**Amirali Rezazadeh, Laobing Zhang, Genserik Reniers, Nima Khakzad, Valerio Cozzani. *Optimal patrol scheduling of hazardous pipelines using game theory. Pages 242-256.***

An approach based on game theory is proposed to schedule security patrolling for a pipeline system. The method proposes numbers of patrolling paths according to the risk of security incidents on the pipeline system, in order to allow the patrolling team to covering high-risk segments more than low-risk segments. Patrolling of the pipeline system was modeled mathematically, based on time and distance discretization. The overall approach also examines the presence of security countermeasures on a pipeline system, and their effects on the patrolling schedule. The application of the method is explained by an illustrative case study.

- **Keywords:** Security; Risk assessment; Game theory; Patrolling; Pipeline system; Mathematical modeling

**Manal Ali, Amal Danial, Ahmed Tawfik. *Self-dark fermentation of lipids rich wastewater for 2-biofuels (H<sub>2</sub> and Et-OH) production. Pages 257-267.***

Food processing industry produces huge quantities of lipids rich wastewater which affect negatively on the environment. However, wastewater represents an attractive and sustainable source for biofuels production via robust anaerobic digestion process. Hydrogen (H<sub>2</sub>) and ethanol (Et-OH) production from lipids rich wastewater via up-flow anaerobic staged reactor (UASR) was investigated at different hydraulic retention times (HRTs) and organic loading rates (OLRs). H<sub>2</sub> and Et-OH production significantly (p <

0.01) increased from  $44.6 \pm 20.9$  to  $80.3 \pm 19.9$  L/day and from  $107.6 \pm 25.8$  to  $195.2 \pm 22.2$  mg/L at decreasing the HRT from 22 to 12 h, respectively. Likely, the production of H<sub>2</sub> and Et-OH was largely deteriorated at reducing the OLR from 45 to 12.7 gCOD/L/day. H<sub>2</sub> production amounted to 26.2 and 120 L/day at OLRs of 12.7 and 45 gCOD/L/day, respectively. The palmitate, stearate, and oleate were substantially increased from 100 to 1249 mg/L, from 122 to 1213 mg/L and from 67 to 1187 mg/L at increasing the initial lipids concentration from 2 to 10 g/L, respectively. Two different Clostridium sp. namely EBR-02E-0045, and EBR-02E-0046 were detected and identified in the reactor. Based on these results, it is recommended to apply the UASR for the treatment of lipids rich wastewater simultaneously with 2-biofuels production at OLR not exceeding 45 gCOD/L/day and HRT of 12 h.

- **Keywords:** Up-flow anaerobic staged reactor; Lipids; Hydrogen; HRT; OLR; Microbial community

**Sina Khakzad, Faisal Khan, Rouzbeh Abbassi, Nima Khakzad. *Accident risk-based life cycle assessment methodology for green and safe fuel selection. Pages 268-287.***

Using the emissions produced during the entire life-cycle of a fuel or a product, Life-cycle assessment (LCA) is an effective technique widely used to estimate environmental impacts. However, most of the conventional LCA methods consider the impacts of voluntary releases such as discharged toxic substances and overlook involuntary risks such as risk of accidents associated with exploration, production, storage, process and transportation. Involuntary risk of hazardous materials such as fuels could be quite significant and if ignored may result in inaccurate LCA. The present study aims to develop a methodology for accident risk-based life cycle assessment (ARBLCA) of fossil fuels by considering both the voluntary and involuntary risks. The application of the developed methodology is demonstrated for liquefied natural gas (LNG) and heavy fuel oil (HFO) as fuels of a hypothetical power plant. Adopting a Bayesian network approach, the comparative analysis of the fuels helps an analyst not only overcome data uncertainty but also to identify holistically greener and safer fuel options.

- **Keywords:** Risk analysis; Life cycle analysis; Risk-based LCA; Accident analysis; Product selection

**Haibibu Xiyili, Seda Çetintaş, Deniz Bingöl. *Removal of some heavy metals onto mechanically activated fly ash: Modeling approach for optimization, isotherms, kinetics and thermodynamics. Pages 288-300.***

This study was recommended for the purpose of showing that mechanically activated fly ashes can be firstly used as an adsorbent for the removal of some heavy metals such as Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II) from aqueous solutions. And with the idea that the adsorption capacity of fly ash can be modified by increasing the surface activity with mechanical activation, adsorption properties of activated fly ash samples were examined. Adsorption experiments were conducted on both fly ash samples. The optimizing of process parameters was evaluated employing response surface method (RSM) and adsorption mechanism can be explained by the quadratic model. The activated fly ash showed higher removal percentage (96% (w/w)) of all metals than the raw fly ash under the same experimental conditions. A pseudo-second order kinetic model fitted the adsorption data well. Moreover, the adsorptions of heavy metal ions on raw and activated fly ashes fit the Langmuir isotherm very well. Thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) were showed that the adsorption process is suitable, spontaneous and endothermic. The adsorption/desorption behavior of a multi-metal mixture on raw and activated fly ashes was firstly investigated. The adsorption/desorption percentages of Cu(II) and Pb(II) ions were higher than other ions. Mechanical activation results in decrease in particle size, increase in surface roughness and agglomerated particles as evident by

characterization using XRD and SEM techniques. The results indicated that the heavy metal pollutants of aqueous solutions could be reduced using activated fly ash as a low-cost, available and waste adsorbent.

- **Keywords:** Adsorption; Ball milling; Fly ash; Heavy metals; Mechanical activation; RSM

**Gaurav Sharma, Mu. Naushad, Amit Kumar, Shailja Rana, Shweta Sharma, Amit Bhatnagar, Florian J. Stadler, Ayman A. Ghfar, Mohammad Rizwan Khan. *Efficient removal of coomassie brilliant blue R-250 dye using starch/poly(alginic acid-cl-acrylamide) nanohydrogel. Pages 301-310.***

In this study, we have synthesized a starch/poly(alginic acid-cl-acrylamide) nanohydrogel (ST/PL(AA-cl-AAm) NHG) by co-polymerization method which was used as an effective adsorbent for the removal of coomassie brilliant (CB) blue R-250 dye from the aqueous solution. The synthesized nanohydrogel was characterized by FTIR, SEM and TEM techniques. The effect of initial dye concentration, temperature, and agitation time on the adsorption ability of the nanohydrogel was studied comprehensively. The experimental outcomes exhibited that the prepared nanohydrogel had high adsorption tendency to remove the CB from the aqueous solution. The regression coefficient values for Langmuir (0.99), Freundlich (0.93) and Tempkin (0.98) recommended that adsorption process fit to langmuir isotherm. The pseudo-second-order equation showed the better adsorption kinetics of the adsorption process. The feasibility of CB adsorption onto ST/PL(AA-cl-AAm) NHG was also studied thermodynamically and the results indicated that the adsorption was spontaneous and chemical in nature.

- **Keywords:** Starch/Poly(alginic acid-cl-acrylamide); Nanohydrogel; Coomassie brilliant blue; Adsorption; Thermodynamics; Kinetics

**Valeria Villa, Genserik L.L. Reniers, Nicola Paltrinieri, Valerio Cozzani. *Development of an economic model for the allocation of preventive security measures against environmental and ecological terrorism in chemical facilities. Pages 311-339.***

Several recent events raised the attention toward possible major accidents triggered by external acts of interference in industrial facilities. In particular, a growing concern is present with respect to the intentional release of dangerous substances resulting in environmental and eco-terroristic attacks. Therefore, optimal selection and allocation of preventive security measures is becoming more important for decision-makers. Despite the existence of economic models supporting the decision-making process, their applications within the chemical industry security context are relatively limited. This study describes a specific model for economic analysis and selection of physical security measures, with respect to potential environmental and eco-terroristic attacks in chemical facilities. An example of application to a relevant case study is presented to show the model capabilities. Site-specific analysis of the baseline physical security system performance allows comparing the costs of different security upgrades with the benefits related to either prospective or retrospective losses, meanwhile accounting the uncertainties related to the threat probability. Selection of the most profitable security measures within budget constraints and definition of economic indicators are the main outputs of the model, in order to support decision-making processes for allocation of security barriers.

- **Keywords:** Security cost-benefit analysis; Security cost-effectiveness analysis; Physical security measures; Security decision-making; Chemical industry; Environmental accident

**Marzieh Talebi, Saeed Abbasizadeh, Ali Reza Keshtkar. *Evaluation of single and simultaneous thorium and uranium sorption from water systems by an electrospun PVA/SA/PEO/HZSM5 nanofiber. Pages 340-356.***

The performance of poly vinyl alcohol/sodium alginate/poly(ethylene oxide)/HZSM5 (PVA/SA/PEO/HZSM5) nanofiber adsorbent synthesized by electrospinning method for sorption of Th(IV) and U(VI) ions from aqueous systems was investigated in a batch system. The predicted optimum sorption conditions were determined as HZSM5 content of 10 wt%, adsorbent dosage of 1 g/L and initial pH 5.5 by response surface methodology (RSM). The results of experimental confirmation test showed that the predicted model agreed reasonably well with the experimental data. The prepared nanofiber adsorbents were characterized by SEM, FTIR, TGA, BET and BJH analyses. Also, the effects of contact time, initial concentration and temperature were evaluated. The kinetic data of metal ions were well described by the double-exponential model. The maximum sorption capacity of Th(IV) and U(VI) ions were estimated to be 274.6 and 144.7 mg/g, respectively in the single system. Thermodynamic modeling indicated that the nature of both Th(IV) and U(VI) sorption was endothermic and spontaneous and was favored at higher temperature. In binary system, the sorption capacity decreased with increasing another metal ion concentration. The combined effect of metal ions onto the nanofiber was found to be antagonistic. The selectivity order of metal ions sorption onto the adsorbent was Th(IV) > U(VI).

- **Keywords:** PVA/SA/PEO/HZSM5 nanofiber; Sorption; RSM; Swelling; Isotherm; Binary system

**Jianlong Li, Fubao Zhou, Shihang Li. *Experimental study on the dust filtration performance with participation of water mist. Pages 357-364.***

To study the influence of water mist on the dust filtration performance, a lab-scale experimental dust collector system was built and tested for dust laden air filtration pressure drop and dust emission concentration during the collector operation with a water mist spraying rate of 0–3200 mL/h. Next, filtration performance was evaluated and the morphology of dust deposition on the filter was analyzed. Moderate water mist was found to be beneficial in decreasing pressure drop, prolonging the filtration cycle, reducing the dust emission and improving the filtration performance. Conversely, an excess water mist accelerated the pressure drop increasing rate, raised the filter cleaning frequency and decreased the filtration performance. Additionally, the influence of water mist on the filtration performance was found to be mainly due to the changing of filtration pressure drop. The dust deposition morphology analysis showed that a moderate water mist brought a more open dust cake, and thereby led to the decrease of pressure drop; whereas an excess water mist gave rise to the liquid bridge in the cake, leading to the increase of pressure drop.

- **Keywords:** Coal dust; Dry-type filtration; Water mist; Liquid bridge; Dust cake structure; Deposition morphology

**Rex T.L. Ng, Mimi H. Hassim, Markku Hurme. *A hybrid approach for estimating fugitive emission rates in process development and design under incomplete knowledge. Pages 365-373.***

Fugitive emissions are one of the most notable contributors to atmospheric releases in chemical process industries affecting not only the economy but also both the environment and workers' health. In order to reduce fugitive emissions released in this process, the assessment of fugitive emissions should be conducted at the early stage of chemical process design when the cost of making changes is the lowest. This is however

impeded by the limited knowledge on the leak sources, since the process is still under design. The paper presents a hybrid approach for estimating fugitive emission rates early in the design phase. The method combines a pre-calculated emission database of standard process module based approach with estimation by using generic piping and instrumentation diagrams if a suitable module is not available from the database. Also, both working and breathing emissions are included in the assessment. The emissions' assessment from a case study of hydrodealkylation distillation and storage systems is presented to demonstrate the proposed approach.

- **Keywords:** Fugitive emission; Volatile organic compounds; Greenhouse gases; Health risk; Process design; Process development

**Mohammed J. Ajrash, Jafar Zanganeh, Behdad Moghtaderi. *Deflagration of premixed methane-air in a large scale detonation tube. Pages 374-386.***

Methane explosion hazards in pipes are of pivotal concern in chemical plants. Accurate knowledge of flame deflagration and its behaviours are required to reduce the consequences of accidental fires and explosions. Considering a lack of experimental work exists in large scale methane-air deflagration systems, a detonation tube (30 m long) was facilitated at the University of Newcastle to cover the knowledge gap in terms of boosting flame deflagration of low methane concentrations and also examining flame deflagration characteristics with different reactive lengths (3, 6, 12 and 25 m). The feature of injecting methane at varied reactive sections (RS) was achieved using a balloon isolation system, a 50 mJ chemical ignitor used to ignite the initial explosion section. The results revealed that stagnation pressure gradually increased, from 2.03 bar to 3.77 bar then 4.57 bar, with increasing RS length from 3 m to 6 m then 12 m, respectively. There was no significant influence of 1.25% or 2.5% methane concentrations on dynamic or stagnation pressures, however, they extended the travelling flame distance by about 3 m for RS lengths of 12 m and 25 m. At 9.5% methane concentration and for a RS of 12 m a state of fast deflagration was observed, associated with 5 bar pressure rise. The pressure wave up to 6.5 m was only a few milliseconds (about 15 ms) ahead of the flame for almost the full methane concentration range, however, after this point the gap between the pressure wave and the flame significantly varied in accordance to the methane concentration, where the data analysis at 15 m indicated that for 9% methane concentration the flame was only 21 ms behind the pressure wave, and for 5% and 15% methane concentration the flame was behind the pressure wave in the range of 55–93 ms. Due to the limited length of the DT compared with the large volume of methane injected, there was no significant influence on the flame deflagration properties when extending the RS length from 12 m to 25 m, as the mixture initially located after 12 m pushed out through the open end.

- **Keywords:** Methane deflagration; Detonation tube; Flame velocity; Dynamic pressure; Pressure wave; Flame intensity; Damage level

**Soraya Hosseini, Farahnaz Eghbali Babadi, Salman Masoudi Soltani, Mohamed Kheireddine Aroua, Shervan Babamohammadi, Asefe Mousavi Moghadam. *Carbon dioxide adsorption on nitrogen-enriched gel beads from calcined eggshell/sodium alginate natural composite. Pages 387-399.***

Bio-degradable calcined egg-shell/sodium alginate (CES/SA) beads were prepared and functionalized using aqueous ammonia (33%). The tailor-made beads were then used as adsorbent for CO<sub>2</sub> capture in a fixed-bed reactor. The performance of the prepared beads was evaluated under various experimental conditions (i.e. 1 &lt; P &lt; 2.5 bar, 30 &lt; T &lt; 50 °C, 50 &lt; flow rate &lt; 90 ml/min and an inlet CO<sub>2</sub> concentration between 20 to

45 vol%). Modification with ammonia could successfully introduce additional functional groups containing nitrogen onto the surface of the CES/SA (up to 10.56 wt%). The results showed an increase in CO<sub>2</sub> adsorption with ammonia-impregnated CES/SA, compared to the non-impregnated CES/SA. A maximum CO<sub>2</sub> adsorption capacity of 0.2380 mmol/g was obtained for the gel beads with 45% CO<sub>2</sub> concentration at 1 bar and 30 °C. The adsorption capacity decreased with an increase in temperature and increased with an elevation in the inlet CO<sub>2</sub> concentration, pressure and flow rate. Among the investigated isotherm models (i.e. Sips, Freundlich and Toth), the Toth isotherm model best described the adsorption data. The thermodynamic properties using the adsorption isotherm data revealed the entropy change ( $\Delta S > 0$ ) reflected the affinity of the adsorbent with the CO<sub>2</sub> molecules. The CO<sub>2</sub> adsorption/desorption process indicated a drop in the CO<sub>2</sub> adsorption capacity of the gel beads in the second cycle; however, this almost remained constant in the subsequent cycles. This observation pointed out to a chemisorption process for the fresh adsorbent and a physical adsorption mechanism for the subsequent adsorption cycles.

- **Keywords:** Ammonia; Bio-degradable adsorbent; CO<sub>2</sub> adsorption; Egg shells; Gel bead; Sodium alginate

**M. Sheikhalishahi, L. Pintelon, A. Azadeh. *An integrated approach for maintenance planning by considering human factors: Application to a petrochemical plant.* Pages 400-409.**

In this paper a novel approach is presented for maintenance planning by considering grouping strategy and human factors. The proposed approach describes various steps from system configuration to maintenance plan review. In previous studies, it has been shown that grouping maintenance activities would reduce total maintenance cost by saving set-up costs. In order to model a more realistic situation, work complexity is incorporated to the model. Also, a special attention is paid to human factors during maintenance planning to investigate whether human error would be increased by performing various activities at the same period. It is shown fatigue and time pressure have impact on the preferred maintenance plan. Consecutive maintenance grouping approach is compared with two well-known meta-heuristic algorithms including genetic algorithm and simulated annealing. In order to show the applicability of the proposed approach a petrochemical plant in Iran is selected as a case study. According to the results of the case study, however from theoretical point of view, consecutive maintenance grouping is not capable of handling variable setup cost and work complexity, it could be used for generating initial solution for meta-heuristic algorithms to improve the quality of final solution.

- **Keywords:** Maintenance planning; Human factors; Dynamic grouping strategy; Multi-component system; Genetic algorithm; Simulated annealing

**Wei-Hsiang Chen, Sian-Jhang Lin, Feng-Chi Lee, Mei-Hsia Chen, T.Y. Yeh, C.M. Kao. *Comparing volatile organic compound emissions during equalization in wastewater treatment between the flux-chamber and mass-transfer methods.* Pages 410-419.**

The emission of volatile organic compounds (VOCs) during equalization in wastewater treatment plants (WWTPs) is a particular source of concern. In this study, VOC emissions during equalization in three industrial WWTPs were analyzed by two different approaches. The flux-chamber method is a standard method used in many countries including Taiwan, as the theory behind the mass-transfer method is well-established. The objective was to investigate whether different outcomes were generated between two estimation methods and to determine potential overestimation of VOC, chemical oxygen demand (COD), or total organic carbon (TOC) removals in the WWTPs due to VOC emission during

equalization. In the results, the estimated VOC fluxes during equalization were similar between two approaches. Recognizable amounts of VOCs were emitted during equalization (up to 28.2%, 13.6%, and 7.6% in three WWTPs). Their impacts on the COD (e.g., less than 0.1% in three WWTPs) or TOC removals (e.g., less than 11.4% in three WWTPs) were rather limited. Through the correlation analysis, the estimated VOC emission flux was not dependent upon individual but on co-influence of the compound's physicochemical characteristics, water quality, and operation during equalization. Although two approaches generated similar outcomes, the results by the flux-chamber method seemed to be more relevant to the operation during equalization, while the water quality were more important to the results by the mass-transfer method. Both methods were effective to quantify VOC emission during wastewater equalization, as the flux-chamber method is possibly a preferable option given their applicability and economic comparison.

- **Keywords:** Volatile organic compound; Industrial wastewater treatment; Equalization; Emission flux; Flux chamber; Mass transfer

**L. Bilińska, M. Gmurek, S. Ledakowicz. *Textile wastewater treatment by AOPs for brine reuse. Pages 420-428.***

The most contaminated textile wastewater stream, dyeing discharge with a high residual salt content, was selected to undergo dedicated treatment by advanced oxidation processes (AOPs). A simulated mixture, based on an industrial recipe and containing Reactive Yellow 145 (RY145), Reactive Red 195 (RR195), and Reactive Blue 221 (RB221), was investigated. These dyes are used together in the trichromatic technique in industrial dyeing, and they occur together in wastewater. In this study, for the first time, several ozone-based AOPs (O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/UV and O<sub>3</sub>/UV/H<sub>2</sub>O<sub>2</sub>) were tested under comparable conditions and assessed. Moreover, the roles of hydrogen peroxide and UV during the AOPs were determined. The influence of textile auxiliaries on the AOPs was also investigated. Due to the usage of multiple dyes in the same mixture, colour was evaluated based on whole UV-vis spectra by recalculating them as integrals. Extremely fast decolourization of the textile wastewater was observed during ozonation. Only 10% colour remained after 10 min of treatment, and satisfactory mineralization was also achieved. During the AOP experiments, it was found that ozonation is the best treatment method for implementation in the industry. Textile wastewater treated by AOPs could be reused as a source of 'ready to use' brine for the next textile dyeing operation.

- **Keywords:** Ozone-based AOPs; Simulated textile wastewater; Mixture of the dyes; Scavenging effect; Brine recycling

**Jin Anotai, Piyawat Tanvanit, Sergi Garcia-Segura, Ming-Chun Lu. *Electro-assisted Fenton treatment of ammunition wastewater containing nitramine explosives. Pages 429-436.***

The treatment of an actual wastewater from ammunition manufacturing process containing highly hazardous nitramine explosives has been studied by different water treatment technologies based on Fenton's chemistry. The in-situ production of hydroxyl radical as highly oxidizing agent conducted to the overall degradation of the nitramine explosives contained in the effluent samples. The kinetic abatement of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) followed the crescent order Fenton = photo-Fenton > electro-assisted Fenton process. The greater performance of the electro-assisted process is justified by the faster regeneration of Fe<sup>2+</sup> from the electrochemical reduction and the oxidation contribution of the heterogeneous hydroxyl radical electrogenerated on the dimensional stable anode surface. On the other hand, similar DOC abatements of ca. 60% were attained after 2 h of treatment for all the technologies, being slightly superior for the photo-Fenton process due to the photodecarboxylation of carboxylate-iron complexes. The evaluation of the

BOD5 and COD allowed considering the effluent biodegradability enhancement after Fenton's technologies treatment, being feasible their application prior to a biological treatment. From the by-products identification, degradative pathways of the main nitramine pollutants contained in the actual effluent have been proposed.

- **Keywords:** Photo-Fenton; Anodic oxidation; RuO<sub>2</sub>/IrO<sub>2</sub> dimensional stable anodes (DSA); Water treatment technologies; Actual effluent; electro-Fenton

**Santiago Ortiz-Monsalve, Juliana Dornelles, Eduardo Poll, Mauricio Ramirez-Castrillón, Patricia Valente, Mariliz Gutterres. *Biodecolourisation and biodegradation of leather dyes by a native isolate of *Trametes villosa*. Pages 437-451.***

Dyeing is an important step in the leather manufacture process. Effluent from this stage contains some types of synthetic dye that may be a threat to the environment and human health. Biological treatment of dye-containing wastewaters by microorganisms has been presented as a cost effective and promising environmentally friendly alternative. In the present work, the potential of Brazilian native white-rot fungi strains, collected and screened to produce extracellular ligninolytic enzymes, was evaluated for the biodecolourisation and biodegradation of different azo tannery dyes. The strain SCS-10 showed high activity of ligninolytic enzymes and allowed the colour removal of dyes in solid media. This isolate was characterised morphologically and identified as *Trametes villosa*, based on a molecular analysis of the internal transcribed spacer (ITS) region sequences. *T. villosa* SCS-10 showed high biodecolourisation efficiency for the dyes assessed, achieving  $95.71 \pm 1.29$ ,  $92.76 \pm 0.99$  and  $96.84 \pm 1.39\%$  for Acid Red 357, Acid Black 210 and Acid Blue 161, respectively, at 100 mg L<sup>-1</sup>, 30 °C, pH 5.5 and 150 rpm, within 168 h of treatment. Remarkable peaks of laccase activity (1150–1550 U L<sup>-1</sup>) were observed during specific periods in the biodecolourisation process. The complete inhibition of Lac activity by sodium azide (NaN<sub>3</sub>, 0.1 mM) led to biodecolourisation values of  $13.29 \pm 0.93$ ,  $12.30 \pm 0.46$  and  $20.05 \pm 2.08\%$  for AR357, AB210 and AB161, respectively. These results confirmed the main role of laccase in colour removal, although biosorption also had a minor involvement in biodecolourisation. In vitro assays also showed the efficiency of decolourisation of the leather dyes. The enzymatic crude extract produced by *T. villosa* allowed  $85.45 \pm 3.43$  (AR357),  $76.96 \pm 1.39$  (AB210) and  $90.17 \pm 0.97\%$  (AB161) of biodecolourisation when enhanced by the use of the redox mediator 1-hydroxybenzotriazol (HBT, 1 mM). UV-vis and FTIR spectral analyses confirmed the occurrence of enzymatic biodegradation as the mechanism responsible for colour removal. *T. villosa* SCS-10 was able to tolerate high concentrations of the dyes (200–1000 mg L<sup>-1</sup>) and a wide range of pH (4.0–8.0) during biodecolourisation. The native isolate *T. villosa* SCS-10 is considered a suitable candidate for the treatment of dye-polluted wastewater from the leather industry due to the mechanisms of enzymatic biodegradation and biosorption.

- **Keywords:** Biodecolourisation; Biodegradation; Biosorption; Azo tannery dyes; Leather; White-rot fungi; *Trametes villosa*

**Hamid Jahanian. *Optimization, a rational approach to SIL determination. Pages 452-464.***

In process industry, SIL determination is a risk assessment process through which target Safety Integrity Levels (SIL) are allocated to Safety Instrumented Functions (SIF). A target SIL represents the significance of the hazard against which the SIF protects the plant. This paper introduces new SIL determination methods by taking an optimization approach. Unlike the conventional methods, which are generally focused on calculating the gap between the existing and tolerable levels of risk, the methods introduced in this paper are aimed at optimizing the marginal cost or the benefit-cost ratio. By incorporating the cost factor into the SIL determination process, these methods deliver

the most reasonably practicable solutions that can minimize the risk while taking into account the cost of solution. The new methods are formulated for corporate risk and the risk to community (i.e. ALARP). Both methods are derived for demand and continuous modes of SIF operation. Furthermore, a new Safety Index is introduced to combine the SIL and the average Probability of Failure on Demand (PFD) or Frequency of Failure per Hour (PFH). The application of the mathematical models is demonstrated through a practical example from power industry.

- **Keywords:** SIL determination; PFDavg; PFH; Cost benefit analysis; ALARP; Expected utility

**Hadi Baseri, Saeed Tizro. *Treatment of nickel ions from contaminated water by magnetite based nanocomposite adsorbents: Effects of thermodynamic and kinetic parameters and modeling with Langmuir and Freundlich isotherms.* Pages 465-477.**

Co-precipitation procedure was applied in order to obtain different kinds of magnetic nanocomposite adsorbents for the removal of Ni(II) ions from aqueous solution. Prepared nanoadsorbents were characterized by using Fourier transform infrared spectroscopy, X-ray diffractometer, field emission scanning electron microscopy, transmission electron microscopy and the thermogravimetric analysis. The average sizes of nanoparticles were found to be  $60 \pm 10$  nm. Adsorption studies of heavy metal ions were carried out by batch experiments. Several factors effecting the adsorption of Ni(II) ions on the surface of magnetic nanoadsorbents such as pH (2–12), temperature (293–333 K), contact time (10–60 min), adsorbent dose (0.04–0.24 g), shaking rate (100–750 rpm) and initial concentration of analyte (10–100 mg L<sup>-1</sup>) were studied. The maximum adsorptive removal percentage of Ni(II) ions onto magnetite–citric acid was found to be about 96% at pH 8, temperature 313 K, contact time 50 min, adsorbent dose 0.2 g, shaking rate 500 rpm and initial Ni(II) ions concentration 25 mg L<sup>-1</sup>. The maximum adsorption capacity for Ni(II) ions was obtained 46.513 mg g<sup>-1</sup> by using citric acid–magnetite as the best nanoadsorbent. The equilibrium adsorption data were well fitted to Langmuir and Freundlich isotherm models, with a better fitting to the Langmuir model for magnetite–citric acid adsorbent. A positive value (39.754 kJ mol<sup>-1</sup>) of enthalpy change ( $\Delta H_0$ ) suggests that the adsorption process was endothermic. Negative values of Gibbs free energy ( $\Delta G_0$ ) reveal the feasibility and spontaneity nature of the adsorption process and the adsorption kinetics of Ni<sup>2+</sup> was found to follow a pseudo-second-order kinetic model. Obtained results clearly showed that magnetite based nanoadsorbents could be efficient, cost-effective and safe adsorbents for the removal of Ni(II) ions from aqueous solution.

- **Keywords:** Co-precipitation; Ni(II) ions; Magnetic nanocomposite adsorbents; Kinetics; Thermodynamic parameters; Adsorption isotherms

**D. Perondi, P. Poletto, D. Restelatto, C. Manera, J.P. Silva, J. Junges, G.C. Collazzo, A. Dettmer, M. Godinho, A.C.F. Vilela. *Steam gasification of poultry litter biochar for bio-syngas production.* Pages 478-488.**

Poultry litter, the major waste generated by poultry farming, has its main use in soil as a fertilizer. However, the uncontrolled use of poultry litter for this purpose can result in environmental impacts such as the emission of methane, a greenhouse gas. Therefore, the thermochemical conversion of this waste can be a solution to this problem, since its products can be converted into useful energy. In this work, pyrolysis experiments were conducted in a tubular reactor, using N<sub>2</sub> atmosphere and a final temperature of 800 °C. Furthermore, the steam gasification of poultry litter biochar obtained in the pyrolysis experiments was investigated in a fixed-bed tubular reactor at different temperatures (800, 850 and 900 °C). The maximum hydrogen (H<sub>2</sub>) reaction rates were observed in

the first 15 min of the reaction, and there was a change in the maximum reaction rate towards lower reaction times with increased temperature. The elevated H<sub>2</sub> yield may be associated with metals present in the biochar, especially potassium (K). Bio-syngas (H<sub>2</sub> + CO) obtained from steam gasification of poultry litter biochar presented high potential to reduce iron ore by indirect reduction (IR) in blast furnaces (BF), or in direct reduced iron (DRI) processes.

- **Keywords:** Bio-syngas production; Steam gasification; Poultry litter biochar; Pyrolysis; Renewable energy; Fixed-bed reactor

**Jingde Li, Francisco Hernandez, Hong Hao, Qin Fang, Hengbo Xiang, Zhan Li, Xihong Zhang, Li Chen. *Vented Methane-air Explosion Overpressure Calculation—A simplified approach based on CFD. Pages 489-508.***

This paper presents new correlations developed through numerical simulations to estimate peak overpressures for vented methane-air explosions in cylindrical enclosures. A series of experimental tests are carried out first and the results are used to validate the numerical models developed with the commercial CFD software FLACS. More than 350 simulations consisting of 16 enclosure scales, 12 vent area to enclosure roof area ratios, 8 gas equivalence ratios and 9 vent activation pressures are then carried out to develop the Vented Methane-air Explosion Overpressure Calculation (VMEOC) correlations. Parameters associated with burning velocity and turbulence generation, oscillatory combustion and flame instabilities in vented gas explosion are taken into account in the development of new correlations. Comparing to CFD simulations, the VMEOC correlations provide a faster way to estimate the peak overpressure of a vented explosion. Additionally, it is proved in this study that the VMEOC correlations are easier to use and more accurate than the equations given in the up-to-date industrial standard- NFPA-68 2013 edition.

- **Keywords:** Vented gas explosion; Methane-air explosion; Vent area; Vent activation; Peak overpressure

**Saba Yavari, Amirhossein Malakahmad, Nasiman B. Sapari, Sara Yavari. *Sorption properties optimization of agricultural wastes-derived biochars using response surface methodology. Pages 509-519.***

Pyrolysis of biomass into biochar and application of a carbon-rich product to water and soil media have been demonstrated to be effective in sequestering of contaminants. Fundamentally, biochar characteristics are controlled by feedstock and pyrolysis variables. The present study investigated the effects of synthesis variables (highest treatment temperature, heating rate and residence time) on biochar sorption properties. Oil palm empty fruit bunch (EFB) and rice husk (RH) biomasses were compared as initial feedstock. The variables were optimized using response surface methodology (RSM) to optimize the values of responses including biochars organic carbon content, cation exchange capacity (CEC), surface area and pores volume. Sorption performances of the optimized biochars were further investigated in removal of a polar imidazolinone herbicide from soil. Based on the results, pyrolysis temperature was the most effective variable on the responses followed by residence time and heating rate. Optimum conditions to maximize the biochars sorption properties were pyrolysis temperature of 493.44 °C and 700 °C and residence time of 1 h and 3 h for EFB and RH biochars, respectively. The best heating rate was 3 °C/min for both biochars. Optimized EFB biochar showed higher affinity for the herbicide due to its higher CEC and functionality, effective in sorption of polar compounds.

- **Keywords:** Oil palm empty fruit bunches; Rice husk; Pyrolysis temperature; Heating rate; Residence time; Response surface methodology (RSM)

**Kamyar Yaghmaeian, Gholamreza Moussavi, Ali Mashayekh-Salehi, Anoshiravan Mohseni-Bandpei, Mohammad Satari. *Oxidation of acetaminophen in the ozonation process catalyzed with modified MgO nanoparticles: Effect of operational variables and cytotoxicity assessment.* Pages 520-528.**

The oxidation of acetaminophen (ACT) was investigated in the catalytic ozonation process (COPs) an ozonation process with modified MgO (m-MgO) nanoparticles as catalyst. The effect of main operational variables including solution pH and concentration of m-MgO, ACT and ozone concentration was investigated on ACT degradation in the COP. The complete degradation and 94% mineralization of 50 mg/L ACT obtained at the solution pH around 5, MgO concentration of 2 g/L and ozone concentration of 1.8 mgO<sub>3</sub>/min, within a reaction time of 30 min. The cytotoxicity fresh and COP-treated ACT solution was assessed using the human embryonic kidney (HEK) cultured cells. The results indicated that treating ACT solution in the m-MgO/O<sub>3</sub> process under optimum experimental conditions as compared to the fresh (untreated) ACT solution considerably increased the viability of HEK cells. Therefore, the COP with m-MgO nanoparticle as the catalyst is a promising and efficient process for the oxidation and detoxification of ACT as a model of emerging contaminants in the contaminated water.

- **Keywords:** Advanced oxidation process; Emerging contaminants; Catalytic ozonation; Metal oxide; MgO; Cytotoxicity

**Valeria Casson Moreno, Vincenzo Russo, Riccardo Tesser, Martino Di Serio, Ernesto Salzano. *Thermal risk in semi-batch reactors: The epoxidation of soybean oil.* Pages 529-537.**

The interest in the epoxidation of vegetable oils is constantly growing in the chemical industry. The most common process is based on the oxidation of the unsaturated bonds by peroxyacids generated in situ, in the water phase, using concentrated hydrogen peroxide and the corresponding organic acid in presence of a mineral acid as catalyst. The overall epoxidation reaction is highly exothermic, hence operating conditions should be always addressed by safety considerations related to the possibility of runaway reactions. In this paper, best operating conditions and safety considerations have been defined for a complex reaction network for the epoxidation of soybean oil, which includes the decomposition reactions of the performic acid generated during the epoxidation. Furthermore, sensitivity-based reactor stability criteria have been applied and compared, for the design of an adequate Early Warning Detection System for the process.

- **Keywords:** Soybean oil; Epoxidation; Runaway reaction; Thermal risk; Early Warning Detection System; Reactor stability

**Saeid Ahmadzadeh, Ali Asadipour, Mostafa Pournamdari, Behzad Behnam, Hamid Reza Rahimi, Maryam Dolatabadi. *Removal of ciprofloxacin from hospital wastewater using electrocoagulation technique by aluminum electrode: Optimization and modelling through response surface methodology.* Pages 538-547.**

Pharmaceuticals as severe contaminants of surface and ground water around the manufacturing communities and residential zones received growing attention recently. Since, there is no report on ciprofloxacin (CIP) removal using electrocoagulation (EC) process by aluminum electrodes, the present work deals with efficient removal of CIP from hospital wastewater using mentioned method. Response surface methodology (RSM) was used to evaluate the main effects of parameters, their simultaneous interactions and quadratic effect to achieve the optimum condition for EC process. According to the obtained results from regression analysis, it was found that the

experimental data are best fitted to the second-order polynomial model with coefficient of determination ( $R^2$ ) value of 0.9086, adjusted correlation coefficient (Adj.  $R^2$ ) value of 0.8796 and predicted correlation coefficient (pred.  $R^2$ ) value of 0.7834. EC process was applied successfully with removal efficiency of 88.57% under optimal operating condition of pH 7.78, inter-electrode distance 1 cm, reaction time 20 min, current density 12.5 mA  $\text{cm}^{-2}$  and electrolyte dose of 0.07 M NaCl with the initial CIP concentration of 32.5 mg  $\text{L}^{-1}$ . The experimental efficiency was in satisfactory agreement with the predicted efficiency of 90.34%. The obtained results revealed that, sweep flocculation as a determinant mechanism controlled the adsorption of CIP molecules on aluminum hydroxide precipitates. Electrode consumption and electrical energy consumption were found to be 66.80 g  $\text{m}^{-3}$  and 0.613 kWh  $\text{m}^{-3}$ , respectively. The obtained results from real sample analysis revealed that the initial CIP concentration of  $154 \pm 6 \mu\text{g L}^{-1}$  of hospital wastewater were found to reach zero after applying optimal condition of EC process.

- **Keywords:** Hospital wastewater treatment; Electrocoagulation process; Al electrode; Ciprofloxacin; Response surface methodology; Electrical energy consumption

**Tahira Mahmood, Rahmat Ali, Abdul Naeem, Muhammad Hamayun, Madeeha Aslam.** *Potential of used Camellia sinensis leaves as precursor for activated carbon preparation by chemical activation with  $\text{H}_3\text{PO}_4$ ; optimization using response surface methodology.* Pages 548-563.

In this study, an attempt was made to produce a low cost activated carbon (AC) from a cheap precursor material, used tea leaves (UTLs) by chemical activation with  $\text{H}_3\text{PO}_4$ . The operating variables of the preparation process were optimized by central composite design (CCD), a subset of response surface methodology (RSM). The conditions optimized were activation temperature, chemical impregnation ratio (IR) and activation time with % age yield, iodine (I<sub>2</sub>) and methylene blue (MB) number as the targeted responses. The optimization was carried out to maximize yield, I<sub>2</sub> and MB number values. The optimal preparation conditions were determined as: activation temperature of 600 °C, IR of 1.30 and activation time of 130 min, under which a carbon yield 33.55%, I<sub>2</sub> and MB uptake of 1051 mg  $\text{g}^{-1}$  and 321 mg  $\text{g}^{-1}$  respectively, could be achieved. The surface properties of optimized AC were characterized by various physico-chemical techniques including scanning electron microscope imaging (SEM), FTIR analysis, surface area and X-rays diffraction analysis, Boehm's titration, point of zero charge (pHPZC) and proximate-ultimate analysis. The results showed that the surface of AC was highly porous with many channels and cracks and has acidic nature, have large amount of acidic functional groups and low ash content.

- **Keywords:** Activated carbon; Used tea; CCD; Optimization; Yield; Iodine number

**Lalatendu Muduli, Prasanta K. Jana, Devi Prasad Mishra.** *A novel wireless sensor network deployment scheme for environmental monitoring in longwall coal mines.* Pages 564-576.

Longwall mining is extensively practiced worldwide for the safe extraction of coal from underground coal mines. In this paper, we analyzed several sensor node deployment schemes and proposed a novel wireless sensor network (WSN) deployment scheme for environmental monitoring in longwall coal mines. The proposed scheme is based on the probabilistic event detection approach for complete coverage of the monitoring regions in longwall coal mines. The virtual force method is applied to minimize the redundant overlapping regions of the sensor nodes by preserving connectivity of the network. Moreover, the funneling effect that causes energy hole problem in a linear wireless sensor network is resolved. The performance of the WSN is evaluated through

simulations. The simulation results showed that the proposed scheme provides best area coverage as compared to the existing node deployment strategies and is very cost effective.

- **Keywords:** Node deployment; Wireless sensor networks; Mine environment monitoring; Longwall coal mine; Gate roads

**Niall Ramsden, Khalid A.M. Abusaieda. *A study of water cooling using different water application techniques to protect storage tank walls against thermal radiation.* Pages 577-598.**

Amongst the hazards associated with storage tanks is the effect of the thermal radiation that results from an adjacent tank fire and its consequences for the mechanical strength of the metal and the tank contents at elevated temperatures, which may lead ultimately to the failure of the tank. A series of tests were undertaken to study the generation of dry spots and the effectiveness of the use of water cooling in reducing the hazards of fire for adjacent tanks. The research involved an extensive programme of experiments studying the effectiveness of different water cooling techniques on mitigating tank and pool fires. The work was conducted at Asturias, Spain, by the LASTFIRE Project. This report gives a description and the findings of the work performed, which involved evaluating the effectiveness of water cooling in reducing the heat loading on an adjacent tank impacted by a pool fire. The results demonstrate that water cooling and the liquid in the adjacent tank can significantly reduce heat loading, as the wall temperature is maintained below that at which catastrophic failure might occur, or such that the rate of temperature rise is reduced to a level that provides time for emergency response teams to control the fire incident.

- **Keywords:** Storage tank; Cooling system; Pool fire; Dry spots

**Chunyu Wen, He Sheng, Liming Ren, Yang Dong, Jun Dong. *Study on the removal of hexavalent chromium from contaminated groundwater using emulsified vegetable oil.* Pages 599-608.**

Emulsified vegetable oil (EVO) is an oil-in-water emulsion that could serve as a slowly released electron donor. In this work, column experiments were conducted to elucidate feasibility of EVO for removing hexavalent chromium from groundwater, and to investigate the influences of adding acetate and  $Mg(OH)_2$  as amendment. Results showed that a one-time EVO injection stimulated a depletion of terminal electron acceptors, such as  $O_2$ ,  $Fe(III)$ , and released aqueous  $Fe(II)$ , generating reducing conditions and resulting in a drastic decrease in  $Cr(VI)$  concentration. EVO and amended EVO is feasible to remove  $Cr(VI)$  from groundwater. EVO added columns (EVO, EVO + acetate, EVO +  $Mg(OH)_2$ ) retained and removed  $Cr(VI)$  contamination in simulated groundwater for 177, 191 and more than 240 days, respectively.  $Cr(VI)$  was completely removed from simulated groundwater and XPS characterization confirmed that it was stably immobilized in sediments as  $Cr(III)$  compounds. In addition, the amendment of EVO with acetate and  $Mg(OH)_2$  facilitated EVO performance on  $Cr(VI)$  removal by enhancing the bioreduction of  $Fe(III)$ . Microbial community structure analysis revealed that EVO injection cause decline in microbial community richness and diversity while induced accumulation of microbes related to organic fermentation and iron reduction, showing potential for further  $Cr(VI)$  removal.

- **Keywords:** Emulsified vegetable oil; Chromium; In-situ biostimulation; Immobilization; Microbial community

**Inmaculada González, Antonio Serrano, Juan García-Olmo, M. Carmen Gutiérrez, Arturo F. Chica, M. Ángeles Martín. *Assessment of the***

***treatment, production and characteristics of WWTP sludge in Andalusia by multivariate analysis. Pages 609-620.***

Agricultural recovery is the primary option for the final destination of sewage sludge, which must be properly treated, stabilized and sanitized. However, these processes are occasionally eliminated or not carried out properly for economic reasons or due to the design and size of the treatment plant. In this study, 62 samples of sewage sludge (21 and 41 samples from Seville and from Huelva, respectively) were characterized. Variable annual sludge production and equivalent inhabitants are virtually proportional (related by a potential power function of 0.9134). The results were evaluated through multivariate statistical analysis in order to assess the operability status of the WWTPs and the final quality of the sludge generated in the processes. Principal components analysis provided information on two separate groups for the bulk of waste water treatment plant (WWTPs) analyzed: (1) a nickel group, where the samples showed outliers above 50 mg/kg with respect to other WWTPs; and (2) the group where total nitrogen, organic matter and total potassium (K<sub>2</sub>O) showed abnormally high values. Linear discriminant analysis models allowed the detection of WWTPs that used inadequate treatments but where geographical area and number of equivalent inhabitants were not significant.

- **Keywords:** Sludge; Heavy metals; PCA; Discriminant analysis; Stabilization; Dewatering

***H. Bakraouy, S. Souabi, K. Digua, O. Dkhissi, M. Sabar, M. Fadil. Optimization of the treatment of an anaerobic pretreated landfill leachate by a coagulation-flocculation process using experimental design methodology. Pages 621-630.***

Nowadays, landfill leachates are one of the most critical environmental issues faced by countries around the world. They result from the percolation of rain water through layers of solid waste, to which is added water from biochemical processes in waste's cells and water that comes from wastes themselves. They are therefore highly charged with organic and mineral matter, which requires treatment before discharge to the receiving environment. In recent years, many techniques have been developed for leachate treatment. In this study, landfill leachate selected comes from Rabat city's landfill. Landfill leachate is treated by anaerobic combined with coagulation flocculation (CF) process, using ferric chloride as coagulant and a cationic polymer as flocculant. The leachate is characterized by high COD and BOD<sub>5</sub>. The BOD<sub>5</sub>/COD ratio is equal to  $0.58 \pm 0.01$ , revealing that it is a young leachate with a very important biodegradability. The leachate was also loaded with phenolic compounds whose concentration reached  $341.6 \pm 21.3$  mg/L. The optimization of the doses of coagulant and flocculant was performed using factorial design of experiments. Optimal dosages obtained were: 4.4 g/L of coagulant and 9.9 mL/L of flocculant. Removal efficiencies reached:  $89 \pm 6$ ,  $69 \pm 4.8$ ,  $94 \pm 1.3$ ,  $80 \pm 8.7$  and  $89 \pm 1.2\%$  for phenol, turbidity, color, COD and absorbance at 254 nm (Abs 254 nm) respectively.

- **Keywords:** Landfill leachate; Anaerobic pretreated; Coagulation flocculation; Factorial design of experiments; Optimization; Dosages

***Qun Zhou, Botao Qin, Dong Ma, Ning Jiang. Novel technology for synergetic dust suppression using surfactant-magnetized water in underground coal mines. Pages 631-638.***

Coal dust is an increasingly serious problem in underground coal mines. This research developed and tested a novel dust prevention technology of surfactant-magnetized water that utilizes the synergy between magnetization and surfactants to markedly improve the wettability of water, resulting in better dust suppression than water sprays alone. The

technology was systematically studied in laboratory and field conditions. A compound surfactant was developed as part of the new technology and was effective at low dosage (0.03 wt%, approximately one-sixth that of conventional alternatives). The new surfactant exhibited excellent synergetic effects with magnetization, with reduced surface tension (28.07 mN m<sup>-1</sup>, 7.2% lower than that of the original solution). A new type of magnetic apparatus was designed and formed the core of the novel dust suppression technology. The magnetic device produces a powerful and consistent magnetic field (300–350 mT) to achieve effective magnetization of water flow. In field tests, the new technology increased respirable dust and total dust suppression efficiencies by 44.94% and 31.79%, respectively, compared to that of water spray. And the new technology effectively improves the atmosphere in mechanized underground coal mines, contributing to a safer and healthier working environment.

- **Keywords:** Dust control; Surfactant-magnetized water; Surfactant; Dust suppression efficiency; Magnetic apparatus

**Bouamama Abbar, Abdellah Alem, Stéphane Marcotte, Anne Pantet, Nasre-Dine Ahfir, Laurent Bizet, Davy Duriatti. *Experimental investigation on removal of heavy metals (Cu<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup>) from aqueous solution by flax fibres. Pages 639-647.***

This study was carried out to examine the adsorption capacity of the flax fibres tows (FFT) adsorbent for the removal of heavy metals from aqueous solution using batch-adsorption techniques. The influence of contact time, pH, initial concentration and adsorbent quantity on the adsorption process was studied. Results revealed that adsorption rate increased rapidly, and the optimal removal efficiency was reached within 60 min. The adsorption isotherms could well be fitted by the Langmuir model. The RL value in the present investigation was less than one, indicating that the adsorption of the metal ions onto FFT is favourable. After treatment of the aqueous solution with FFT, the levels of heavy metals were observed to decrease with 97.4% for lead, 79% for copper, and 73.28% for zinc. These results indicate that the FFT can be used without specific treatment and are economically viable for the removal of metal ions. We are currently investigating the use of FFT as a bio-based material for the treatment of runoff water in urban zone.

- **Keywords:** Biomass; Heavy metals; Adsorption; Flax fibre; Runoff; Filtration

**Daniela Cadar, Nicoleta Liliana Olteanu, Elena Adina Rogozea, Adina Roxana Petcu, Aurelia Meghea, Maria Mihaly. *Recovery of targeted hydrophilic compounds from simulated wastewaters using nonionic microemulsion systems. Pages 648-658.***

The efficiency of a new eco-friendly microemulsion system based on Polyoxyethylene (4) Lauryl ether/Butyl acetate/Water was compared to that of Polyoxyethylene (4) Lauryl ether/Ethyl acetate/Water. The two systems were analyzed with respects to the recovery of monocomponent or multicomponent targeted hydrophilic compounds (Crystal Violet dye and Co<sup>2+</sup> ions) from polluted liquid media. In order to determine the optimal recovery conditions, the influence of surfactant and dye concentrations on the volumetric ratio of aqueous phase to microemulsion (F) was studied. Furthermore, heavy metal concentrations and distribution coefficients were analyzed using the ternary and pseudo-ternary phase diagrams. The results showed that the Polyoxyethylene (4) Lauryl ether/Butyl acetate/Water system was more efficient compared to the Polyoxyethylene (4) Lauryl ether/Ethyl acetate/Water system in the recovery of hydrophilic compounds for both monocomponent (Crystal Violet dye or Co<sup>2+</sup>) and multicomponent (Crystal Violet dye and Co<sup>2+</sup>) systems. A recovery efficiency of 90.6% for dye and heavy metal ions

was obtained using the Polyoxyethylene (4) Lauryl ether/Butyl acetate/Water microemulsion system.

- **Keywords:** Polyoxyethylene (4) lauryl ether; Microemulsion; Recovery; Distribution coefficient; Dye; Heavy metal

**Faiz Miran, Muhammad Waseem Mumtaz, Hamid Mukhtar, Muhammad Danish. *Value-added use of residual glycerol from biodiesel production process via the optimized synthesis of alkyd resins. Pages 659-669.***

Current research work describes the value-added use of residual glycerol from biodiesel production process via the optimized synthesis of alkyd resins. Response surface methodology based on central composite response surface design was used for the optimization of alkyd resins synthesis. Various reaction parameters including phthalic anhydride to oil molar ratio, catalyst concentration, reaction temperature, reaction time and rate of stirring were optimized to obtain the optimum yield of alkyd resin by using alcoholysis–polyesterification method. The optimized reaction parameters to obtain the highest alkyd resin yield (84%) were depicted to be 0.4:1 molar ratio (phthalic anhydride to oil), 0.6% catalyst concentration, 250 °C reaction temperature, 7.5 h reaction time and 650 rpm rate of stirring. Elucidation of the chemical structure of alkyd resin was done through FT-IR analysis which confirmed the presence of ester links and aromatic CC which resulted from polymerization reaction. Physico-chemical properties, chemical resistance and adhesive properties of synthesized alkyd resins were also evaluated which depicted that the resin films were highly resistant to brine, water and acid. These results ascertained technical compatibility of the synthesized alkyd resin for potential uses comparable to standard alkyd resins with additional eco-friendly benefits due to its biodegradability and biocompatible nature.

- **Keywords:** Biodiesel; Glycerol; Response surface methodology; optimization; FT-IR; Reaction parameters; Sunflower oil; Central composite response surface design

**D.C. Viana, J.F. Pires, R.A. Braga. *Biospeckle laser technique applied for estimating disinfection accomplishment of wastewaters subjected to chlorination. Pages 670-676.***

Despite the undesirable effects of its byproducts, such as the formation of trihalomethanes, chlorination is the most widely used method of disinfection in the Wastewater Treatment Plants (WWTPs) worldwide. Therefore, besides reducing the labor cost of this treatment stage, the automatic product dosage as calcium hypochlorite may increase its efficiency, avoiding wastage and reducing its unwanted effects. To accomplish it, a digital controller needs to be constantly fed with information that allows it to estimate the disinfection potential of the process, which traditionally occurs by means of gauges that concomitantly appraise the Oxidation–Reduction Potential (ORP) and the pH of the water in analysis. In this work, the technique known as biospeckle laser was investigated as an alternative to support the measurements required for an automatic chlorination system, performing the correlation between the biological activity level and the presence/inactivation of pathogenic microorganisms in samples of water collected after the biological treatment stage of a WWTP. Five treatment groups were analyzed by 16 replications and the responses were consistent when compared with those obtained using standard methods for this sort of analysis, demonstrating that the investigated technique is feasible for the desired purpose, indicating if the disinfection is being satisfactory or not.

- **Keywords:** Biospeckle; Wastewater treatment; Chlorination; Disinfection; Laser; Automation

**Tongqiang Xia, Fubao Zhou, Xinxin Wang, Jianhong Kang, Zhejun Pan. *Safety evaluation of combustion-prone longwall mining gobs induced by gas extraction: A simulation study.* Pages 677-687.**

Underground methane-rich and combustion-prone longwall mining gobs are usually subjected to the symbiotic threat of spontaneous coal combustion and gas explosion, resulting in significantly economic and environmental impacts. Inappropriate methods or control parameters of gas extraction in combustion-prone longwall mining gobs may trigger a series of secondary accidents, such as the formation of excessive carbon monoxide, and even a gas explosion. Although gob coal-gas interactions induced by gas extraction have been comprehensively investigated previously, few studies are able to quantitatively predict how the symbiotic hazard of gas explosion and spontaneous coal combustion is formed, and guide how to change the design or control parameters for safety and efficiency. In this work, the formation criteria of the coal combustion-gas explosion hazard and a new index of gas extraction safety are proposed to make up for these knowledge gaps. Furthermore, gob gas migration, coal self-heating and their symbiotic risk evolution induced by gas extraction under the different gas control, face mining and ventilation parameters were investigated. The results show that although gas extraction can significantly reduce gob gas emission into the workplace, it simultaneously exerts great influence on coal self-ignition and gob safety.

- **Keywords:** Coal-gas symbiotic disaster; Spontaneous combustion; Gas explosion; Gas extraction; Safety degree; Longwall mining gob

**Hamidreza Pourzamani, Saeed Parastar, Majid Hashemi. *The elimination of xylene from aqueous solutions using single wall carbon nanotube and magnetic nanoparticle hybrid adsorbent.* Pages 688-696.**

Hybrid adsorbent of single wall carbon nanotubes- magnetic nanoparticle (SWCNT-MN) has been used for the elimination of a variety of pollutants. The aim of the present study was to eliminate xylene from aqueous solutions using this hybrid adsorbent. The xylene solution was made in a synthetic manner with 10, 30, 70, and 100 mg/l concentrations. In different pHs (2-11), nanoparticles of magnetic iron were added to the solution in different concentrations namely 500, 1000, 1500, and 2000 g/l and the efficiency of xylene elimination was determined by SWCNT-MN nanoadsorbents after 2-20 min. Xylene was measured using GC/MS device. The data were analyzed by Design Expert software using Taghuchi OA method. Also, ISOFIT software was used to investigate the isotherm of xylene adsorption. The optimal conditions of xylene elimination was obtained in primary concentration of 100 mg/l, adsorbent dosage of 2000 mg/l, contact time of 20 min, and pH 8. In the created optimal conditions, 99.2% of xylene was eliminated by SWCNT-MN nanoadsorbents and the adsorption capacity of SWCNT-MN nanoadsorbents for xylene was 50 mg/g. The effect of main factors and important interaction obtained by the software in designing the experiment showed that Prob > F was less than 0.05 for all main factors and the interaction between xylene's primary concentration and SWCNT-MN nanoadsorbents dosage. Among the main factors, the contact time had the highest effect (34%). The investigation of isotherm of xylene adsorption by SWCNT-MN nanoadsorbents indicated that GLF isotherm is the most appropriate adsorption isotherm.

- **Keywords:** Xylene; Single-wall carbon nanotubes; Iron nanoparticle; Adsorption; Isotherm; Hybrid adsorbent

**Xiyuan Xiao, Zhichao Jiang, Zhaohui Guo, Mingwei Wang, Huiwen Zhu, Xiaoqing Han. *Effect of simulated acid rain on leaching and transformation of vanadium in paddy soils from stone coal smelting area.* Pages 697-703.**

The agricultural soil contaminated with vanadium (V) has been attracting attention due to its adverse effect on human health and ecosystems. In this study, the leaching risk and transformation characteristics of V in contaminated paddy soils collected from the vicinity of stone coal smelting area were evaluated by a column leaching experiment with simulated acid rain (SAR). The results showed that the amount of soluble V leached was slight and only accounted for 0.04–0.06% of the total V, however, the concentrations of V in leachates after leaching with 10 years of rainfall precipitation using SAR at pH 4.5, pH 5.6 and neutral pH 7.0 were found to be 49.0, 71.3 and 61.1 µg/l, respectively, which were higher than or near to the V threshold limit of Chinese Environmental Quality Standards for Surface Water (50 µg/l) (GB 3838-2002). The percentages of V in both the reducible and oxidizable fractions of the soils increased by 2.10–3.50%, whilst that in residual fraction decreased by 4.52–6.07% after leaching. The results suggest that the mobility of V in polluted paddy soil is increased by long-term rainfall leaching and poses a potential risk of V pollution in surrounding water.

- **Keywords:** Vanadium; Leaching behavior; SAR; Paddy soil; Stone coal smelting area

**Nicolas Cuervo, Olivier Dufaud, Laurent Perrin. *Determination of the burning velocity of gas/dust hybrid mixtures.* Pages 704-715.**

The laminar flame speed is an essential input for Computational Fluid Dynamics simulation programs aiming to predict the effects of explosions. In this study, an approach to assess fundamental flame propagation properties from the analysis of the flame velocity as a function of its stretching and hydrodynamic instabilities was developed. A numerical tool was developed to analyse videos of propagating flames in order to estimate their unstretched burning velocities. Markstein's theory, developed for gases and assuming a linear relation between the flame stretch and its speed, was then extended to dust clouds and hybrid mixtures of starch and methane. At first, the approach was validated with pure methane and was extended to pure starch and hybrid mixtures of both compounds. Finally, it appears that hybrid mixtures, especially when the gas concentration is greater than the lower explosive limit, can present a synergetic effect enabling faster flame propagation with regard to pure gas flames. Indeed, the stretching of a gas flame is strongly influenced by the addition of dusts. Nevertheless, for lower gas concentrations and larger dust concentrations called 'dust-driven regime', the presence of powders tends to limit the flame velocity to that of the less reactive compound, i.e. the dust.

- **Keywords:** Dust explosion; Burning velocity; Hybrid mixtures; Turbulence; Flame propagation; Flame stretching

**Wen Nie, Yanghao Liu, Hao Wang, Wenle Wei, Huitian Peng, Peng Cai, Yun Hua, Hu Jin. *The development and testing of a novel external-spraying injection dedusting device for the heading machine in a fully-mechanized excavation face.* Pages 716-731.**

This paper discusses the development of a novel external-spraying injection dedusting device, which has the potential to reduce substantially the amount of dust produced by a heading machine during the cutting process in a fully-mechanized coal face. Firstly, the migration rules of the inner wind flow field are analyzed using numerical simulations, and then the atomization function of the spraying nozzle is optimized. Consequently, the nozzle exhibited the highest airborne dust reduction rate at a spraying pressure of 4 MPa. The proposed device's functionality was also tested by experiments, with the results indicating that as the spraying pressure increased from 2 MPa to 8 MPa, the gas-liquid ratio increased at first and then decreased, reaching a maximum of 1.269 at a spraying pressure of 4 MPa, which was subsequently once again selected as the optimal spraying pressure. Finally, field experiments were conducted on the developed dedusting device,

with the results showing that, compared with the original spraying dust reduction method, when the developed external-spraying injection dedusting device was opened, using the dust reduction method (d), the average dust reduction rates of the total coal and respirable dust are enhanced by 17.0% and 18.3% respectively; moreover, using the dust reduction method (c), the average dust reduction rates of total coal and respirable dust are enhanced by 11.6% and 12.0% respectively. Therefore, it can be calculated that by using the injection dedusting method, the average reduction rates are enhanced by 5.4% and 6.3% respectively. In particular, the use of one of the proposed dust removal methods at the measuring point where the machine's driver is located, led to the average concentrations of total dust and respirable dust decreasing from 305.1 mg/m<sup>3</sup> and 129.5 mg/m<sup>3</sup> to 88.2 mg/m<sup>3</sup> and 38.3 mg/m<sup>3</sup> respectively.

- **Keywords:** Coal dust; Heading machine; Nozzle; External-spraying; Injection dedusting; Dust reduction rate

**Athanassios Nikolakopoulos, Antonis Kokossis. *A problem decomposition approach for developing total water networks in lignocellulosic biorefineries*. Pages 732-752.**

Water streams in lignocellulosic biorefineries deviate from the dilute waters streams encountered in conventional chemical processes. Moreover, thermal and chemical interactions between components restrict the use of linear approximations for the mass transfer models. This paper proposes a new targeting and design method for the integration of water into lignocellulosic biorefineries. The focus is on the large deviations from the typical assumptions on constant flows and dilute mixtures. New transshipment models for fixed load, fixed flowrate and hybrid systems are developed that reflect on the non-ideal aspects of the water streams. The methodology assesses targets further reducing the solution space defined by the flowrates of the water streams and the inlet concentrations. It involves a preliminary stage where the set of a surrogate model constraints required by the augmented transshipment models are built using a detailed simulation of the process. The optimization procedure produces targets for water consumption and further determines a superstructure of reduced size for the total water network. The methodology is tested on a real biorefinery pilot plant, where there is also available an option for regeneration of water. Results for the background process show that 85.5% savings can be achieved by exploiting an optimal combination of the reuse, regeneration and recycle options.

- **Keywords:** Water integration; Mathematical modelling; Biorefinery; Superstructure; Transshipment model