

# Process Safety and Environmental Protection

Rok 2015, Volume 95

May 2015



**W. Dastyar, T. Amani, Sh. Elyasi. *Investigation of affecting parameters on treating high-strength compost leachate in a hybrid EGSB and fixed-bed reactor followed by electrocoagulation–flotation proces.***

In this research, treatability of high-load compost leachate in a hybrid expanded granular sludge bed (EGSB) and fixed-bed (FB) bioreactor followed by electrocoagulation–flotation (ECF) system was examined. The operational factors in EGSB–FB were influent chemical oxygen demand (COD), hydraulic retention time (HRT) and COD/nitrogen ratio (COD/N). And, their interactive effects on the efficiency of COD removal and biogas production rate (BPR) as responses were analyzed and correlated by response surface methodology (RSM). The optimum conditions of the hybrid EGSB–FB reactor were acquired at COD=7800 mg/L, HRT=35 h, COD/N=70, in which COD removal efficiency was 83% and BPR 94 mL/h. The amount of confidence interval was 95%. COD (relevant coefficient=9.8) and HRT (relevant coefficient=-24) were resulted respectively as the most effective parameters on COD removal and BPR. Yet, COD/N parameter imposed negative effect on COD removal and BPR in values less than about 100. The outcomes indicated that operated ECF as post-treatment in constant conditions (electrolysis time=75 min, electrodes distance=3 cm, voltage=20 V) successfully satisfied discharge criteria in the most part of experimental domains.

- **Keywords:** Anaerobic digestion; Compost leachate; Hybrid EGSB–FB; ECF process; Response surface methodology (RSM); Wastewater treatment

**Majid Bagheri, Sayed Ahmad Mirbagheri, Zahra Bagheri, Ali Morad Kamarkhani. *Modeling and optimization of activated sludge bulking for a real wastewater treatment plant using hybrid artificial neural networks-genetic algorithm approach.***

Prediction of sludge bulking is a matter of growing importance around the world. Sludge volume index (SVI) should be monitored to predict sludge bulking for a wastewater treatment plant. This study was an effort to develop hybrid artificial neural network-genetic algorithm models (MLPANN-GA and RBFANN-GA) to accurately predict SVI. Operating parameters, including MLVSS, pH, DO, temperature, TSS, COD and total nitrogen were the inputs of neural networks. Genetic algorithm was utilized in order to optimize weights and thresholds of the MLPANN and RFBANN models. Training procedures for SVI estimation were successful for both the MLPANN-GA and RBFANN-GA

models. The training and validation models showed an almost perfect match between experimental and predicted values of SVI. The results indicated that with low experimental values of input data to train ANNs, the MLPANN-GA compared with the RBFANN-GA is more accurate due to higher coefficient of determination (R<sup>2</sup>) and lower root mean squared error (RMSE) values. The values of RMSE and R<sup>2</sup> for the optimal models approached 0 and 1, respectively. The mean average error for the ANN models did not exceed 3% of the input values of the measured SVI. The GA increased the accuracy of all the MLPANN and RBFANN models.

- **Keywords:** Activated sludge bulking; Sludge volume index; Artificial neural networks; Multi-layer perceptron; Radial basis function; Genetic algorithm

**Leila Yosefi, Mohammad Haghghi, Somaiyeh Allahyari, Saeid Ashkriz. *Effect of ultrasound irradiation and Ni-loading on properties and performance of CeO<sub>2</sub>-doped Ni/clinoptilolite nanocatalyst used in polluted air treatment.***

In this research nanocatalysts containing 5, 10 and 15 wt.% of Ni, dispersed by sonication over CeO<sub>2</sub>-clinoptilolite composite support were compared toward total oxidation of toluene. Their catalytic performance at different temperatures between 150 and 350 °C was studied based on the oxidative destruction of toluene. The results indicated that the activity of Ni/CeO<sub>2</sub>-clinoptilolite nanocatalyst for toluene oxidation increased from 33 to 44% at 250 °C by employing sonochemical method in synthesis of catalyst. Meanwhile, the catalytic activity was also improved when Ni content was increased from 5 to 10 and 15 wt.%. With the aid of several characterization techniques like XRD, FESEM, PSD, EDX, BET and FTIR, the correlation between nanocatalyst structure and its activity was addressed. It is indicated that sonochemical method can lift the catalytic activity due to the better dispersion of catalyst active components and also higher surface area. Among sonicated samples, 15 wt.% Ni nanocatalyst showed the highest toluene oxidation due to the better dispersion of catalyst active components and hence to more effective catalytic sites.

- **Keywords:** Natural zeolite; Clinoptilolite; Ni/CeO<sub>2</sub>-clinoptilolite; Toluene; Total oxidation; Ultrasound

**S.M. Al-Salem. *Carbon dioxide (CO<sub>2</sub>) estimation from Kuwait's petroleum refineries.***

A detailed study of carbon dioxide (CO<sub>2</sub>) sources from petroleum refineries in Kuwait was conducted. The aim was to estimate the amount of CO<sub>2</sub> being emitted and determine the influencing factors on physical and chemical process in refineries. Three refineries were considered in this work, processing around 900 Mbpd of crude oil. Process heaters stacks constituted 62–75% of the CO<sub>2</sub> emissions, ranking at the top of the sources. Hydrogen production (HP) units via steam-methane reforming ranked seconded in the final assessment, ranging from 12% to 25% in the studied refineries. The configuration of the refinery was determined to be a critical factor in such work. The properties of the processed oil, in terms of density, sulfur content and API were essential in comparing results obtained in this work to other refineries specific rates. Carbon capture and storage (CCS) presents itself as a viable solution for the reduction of the carbon footprint of Kuwait downstream sector, especially when considering the purity of the HP units product gas. The work presented in this paper can be considered as the cornerstone of future carbon mitigation plans in the country.

- **Keywords:** Carbon dioxide (CO<sub>2</sub>); Petroleum; Refinery; Heaters; Hydrogen production; API; Reforming

**Jordi Lladó, Conxita Lao-Luque, B. Ruiz, E. Fuente, Montserrat Solé-Sardans, Antonio David Dorado. *Role of activated carbon properties in atrazine and paracetamol adsorption equilibrium and kinetics.***

Adsorption of two widespread emerging water contaminants (atrazine and paracetamol) onto three different activated carbons was investigated. The carbons were characterized and the influence of their physicochemical properties on the adsorption performance of atrazine and paracetamol was evaluated. The adsorption equilibrium data were fitted to different adsorption isotherm models (Langmuir, Freundlich, and Dubinin–Radushkevich) while the adsorption rates were described using three different kinetic models (pseudo second order, intraparticle diffusion and a new approach based on diffusion-reaction models). The results indicated that hydrophobic character of the compounds does not affect the sorption capacity of the tested carbons but does influence the uptake rate. The model proposed, based on mass balances, lead to interpret and compare the kinetic of different adsorbents in contrast to classical empirical models. The model is a simple and powerful tool able to satisfactorily estimate the sorption capacities and kinetics of the carbons under different operation conditions by means of only two parameters with physical meaning. All the carbons studied adsorbed paracetamol more effectively than atrazine, possibly due to the fact that sorption takes place by H-bonding interactions.

- **Keywords:** Adsorption; Paracetamol; Atrazine; Kinetics; Diffusion model; Sludge activated carbon

**K. Thirugnanasambandham, V. Sivakumar. *Optimization of treatment of grey wastewater using Electro-Fenton technique – Modeling and validation.***

In this present study, grey wastewater was treated using Electro-Fenton (E-Fenton) process. The aim of this research was to optimize the operating parameters in E-Fenton process such as current density, H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> molar ratio, electrode distance and initial pH for the removal of chemical oxygen demand (COD) and total suspended solids (TSS) from grey wastewater using response surface methodology (RSM). Four factors three levels Box–Behnken response surface design (BBD) was used for the optimization of process parameters. Mathematical models were developed with high coefficient determination values and the numerical optimization method was used for optimization. Under the optimum conditions such as current density of 10 mA/cm<sup>2</sup>, H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> molar ratio of 0.70, treatment time of 14 min and pH of 4 shows 90% of COD removal and 85% of TSS removal.

- **Keywords:** Grey wastewater; Electro-Fenton process; COD removal; TSS removal; Optimization; Validation

**Guibin Lu, Caixing Zhang, Liping Chen, Wanghua Chen, Ting Yang, Yishan Zhou. *Kinetic analysis and self-accelerating decomposition temperature (SADT) of β-nitroso-α-naphthol.***

To study the thermal hazard of β-nitroso-α-naphthol, both dynamic and isothermal tests were performed with a differential scanning calorimeter (DSC). The dynamic tests indicated that the initial decomposition temperature of β-nitroso-α-naphthol ranged from 153 °C to 173 °C. The interrupt-rescanning method verified the autocatalytic characteristic of β-nitroso-α-naphthol decomposition. DSC curves obtained at five constant temperatures confirmed that the decomposition of β-nitroso-α-naphthol was an autocatalytic reaction. Activation energy  $E$  was 149 ± 8 kJ/mol calculated by Kissinger method.  $E$  values calculated by induction period method and isothermal method were in line with that obtained by Friedman method. On the basis of the kinetic analysis, the safety parameter

SADT of  $\beta$ -nitroso- $\alpha$ -naphthol in 50 kg standard packaging was 81 °C based on Semenov model and 67 °C based on Frank-Kamenetskii model.

- **Keywords:**  $\beta$ -Nitroso- $\alpha$ -naphthol; Differential scanning calorimeter; Interrupt-rescanning method; Kinetic analysis; Thermal hazard; SADT

**Tarek G. Ammari, Ibrahim Al-Labadi, Alaedeen Tahboub, Ayoup Ghrair. *Assessment of unmodified wetland bio-waste: Shoots of *Cyperus laevigatus*, for cadmium adsorption from aqueous solutions.***

*Cyperus laevigatus* grows in natural and constructed wetland ecosystems built for domestic effluents treatment. The use of unmodified shoots of *C. laevigatus* as a wetland bio-waste for cadmium (Cd) removal from aqueous solutions was assessed. Batch adsorption experiments were conducted to investigate effects of pH, contact time, adsorbent dose, and Cd concentration at an ionic strength of 0.01 mol/l NaNO<sub>3</sub> on adsorption efficiency and capacity. Adsorption is strongly affected by solution pH, and the optimum pH is 5.5. The equilibrium was established within a maximum of 120 min. Cd removal increased to 65.4% with decreasing the adsorbent dose from 30 to 5 g/l. Equilibrium adsorption capacity increased from 0.70 to 4.73 mg/g as initial Cd concentration increased from 5 to 50 mg/l whereas Cd removal decreased from 70% to 47.3%, respectively. Freundlich isotherm best described the equilibrium data compared to the Langmuir isotherm (R<sup>2</sup> 0.997 and 0.892, respectively). The monolayer adsorption capacity was 7.49 mg/g. Cd adsorption kinetic onto *C. laevigatus* obeyed the pseudo-second-order kinetic model indicating that chemisorption is the rate-limiting step. Unmodified shoots of *C. laevigatus*, as a costless bio-waste and environmentally friendly biosorbent, could be used for treating Cd-contaminated water systems.

- **Keywords:** Adsorption; Adsorption isotherms; Cadmium; Raw *Cyperus laevigatus* shoots; Pseudo-second order kinetic model; Constructed wetlands

**J. Laaffat, N. Ouazzani, L. Mandi. *The evaluation of potential purification of a horizontal subsurface flow constructed wetland treating greywater in semi-arid environment.***

The potential purification of an horizontal subsurface flow constructed wetlands (HSSFCW) treating greywater in a Moroccan primary school was investigated according to the monitoring of water quality parameters over a period of 100 days through two simultaneous stages: first, an internal three dimensional grid of sampling ports; secondly, an entry and exit. The calibration of the relaxed TIS concentration model based on tank in series hydraulic assumption with experimental data gave the frequency distribution profiles of K-rate constant values for the three parameters: BOD<sub>5</sub>, COD and TN, whose maximum values are respectively 50 m/yr, 70 m/yr, and 42 m/yr. The HSSFCW system has higher K-rate coefficient for all the three parameters at the bottom layer compared with the surface layer, with increasing K-rates over length. The analysis of bacteriological and chemical results has shown that the HSSFCW could not completely remove all pollutants (especially TN and TP), but it could be used successfully to upgrade the quality of greywater to an acceptable level. However, we predict that there will be an increase in removal efficiencies with time bearing in mind that the system is newly implemented.

- **Keywords:** Greywater; Horizontal subsurface flow constructed wetland; Removal potential; Modeling; Relaxed TIS concentration model; Semi-arid environment

**Liming Yuan, Alex C. Smith. *Numerical modeling of water spray suppression of conveyor belt fires in a large-scale tunnel.***

Conveyor belt fires in an underground mine pose a serious life threat to miners. Water sprinkler systems are usually used to extinguish underground conveyor belt fires, but because of the complex interaction between conveyor belt fires and mine ventilation airflow, more effective engineering designs are needed for the installation of water sprinkler systems. A computational fluid dynamics (CFD) model was developed to simulate the interaction between the ventilation airflow, the belt flame spread, and the water spray system in a mine entry. The CFD model was calibrated using test results from a large-scale conveyor belt fire suppression experiment. Simulations were conducted using the calibrated CFD model to investigate the effects of sprinkler location, water flow rate, and sprinkler activation temperature on the suppression of conveyor belt fires. The sprinkler location and the activation temperature were found to have a major effect on the suppression of the belt fire, while the water flow rate had a minor effect.

- **Keywords:** Conveyor belt fires; Computational fluid dynamics; Water sprinkler systems; Flame spread; Ventilation

**Jie Cheng, Yong Pan, Xiaoya Song, Juncheng Jiang, Gaoyan Li, Li Ding, Hehe Chang. *A new method for the prediction of flash points for ternary miscible mixtures.***

The flash point is one of the most important physicochemical parameters used to characterize the fire and explosion hazard for flammable liquids. The flash points of ternary miscible mixtures with different components and compositions were measured in this study. Four model input parameters, being normal boiling point, the standard enthalpy of vaporization, the average number of carbon atoms and the stoichiometric concentration of the gas phase for mixtures, were employed and calculated based on the theory of vapor–liquid equilibrium. Both multiple linear regression (MLR) and multiple nonlinear regression (MNR) methods were applied to develop prediction models for the flash points of ternary miscible mixtures. The developed predictive models were validated using data measured experimentally as well as taking data on flash points of ternary mixtures from the literature. Results showed that the obtained average absolute error of both the MLR and the MNR model for all the datasets were within the range of experimental error of flash point measurements. It is shown that the presented models can be effectively used to predict the flash points of ternary mixtures with only some common physicochemical parameters.

- **Keywords:** Ternary miscible mixtures; Flash point; Multiple linear regression; Multiple nonlinear regressions; Prediction; Physicochemical parameters

**Javad Saien, Amir Azizi. *Simultaneous photocatalytic treatment of Cr(VI), Ni(II) and SDBS in aqueous solutions: Evaluation of removal efficiency and energy consumption.***

Simultaneous photocatalytic reduction of poisonous Cr(VI) and Ni(II) ions, coupled with photocatalytic oxidation of sodium dodecyl benzene sulfonate (SDBS) were studied with a trace amount of commercial titania nanoparticles and by means of a direct-photo-irradiation reactor. The co-presence of metal ions and SDBS causes metal ions reduction as well as SDBS oxidation to enhance and energy efficiency to improve. XRD, XPS and FTIR analysis were used to characterize TiO<sub>2</sub> particles before and after usage with the aim of evaluating the mechanism of reactions. The effect of major operating parameters, pH and temperature, was investigated. Under conditions of [Cr(VI)]<sub>0</sub> = 5 mg/L, [Ni(II)]<sub>0</sub> = 5 mg/L, [SDBS]<sub>0</sub> = 10 mg/L, [TiO<sub>2</sub>] = 40 mg/L, pH 6 and T = 35 °C; the removal efficiencies of 55.4%, 71.2% and 57.2% were obtained, respectively, for Cr(VI) and Ni(II) reduction, as well as for SDBS oxidation, after 110 min operation. The relevant kinetic model jointed with the Arrhenius equation was introduced. Pseudo-first-order reactions are relevant. Energy

consumption (electrical and thermal) evaluations revealed that operations at higher temperatures provide significant cost reduction. Meantime, a criterion was proposed for a consistent assessment of this kind of processes.

- **Keywords:** Photocatalytic process; Hexavalent chromium; Divalent nickel; SDBS; Energy consumption; Titania

**Kok Leong Theam, Aminul Islam, Hwei Voon Lee, Yun Hin Taufiq-Yap. *Sucrose-derived catalytic biodiesel synthesis from low cost palm fatty acid distillate.***

The current homogeneous acid catalyst for biodiesel product however, would lead to formation of many undesirable by-products that make the post treatment of the biodiesel to be difficult and costly. Thus, sucrose-derived solid acid catalyst was developed in the present study which aims to improve the esterification process and reduce the generation of waste. The physicochemical properties of the synthesized catalysts were studied by various techniques such as, BET surface area, X-ray diffraction (XRD), temperature programmed desorption of NH<sub>3</sub> (TPD-NH<sub>3</sub>), scanning electron microscopy (SEM). Response surface methodology (RSM) with central composite design (CCD) is used to determine the optimum parameters for the catalytic reaction. The experimental results showed that the catalyst exhibited good catalytic activity in the transesterification of PFAD, providing maximum biodiesel yield of 94% at optimum parameters. The better catalytic activity of the aforementioned catalyst in the biodiesel reaction could be attributed to the presence of optimal number of catalytically active acid site density on its surface.

- **Keywords:** Biodiesel; Palm fatty acid distillate; Solid acid carbon; TPD-NH<sub>3</sub>; Response surface methodology; Ball milling

**Edmund C. Jong, Yiming Peng, William T. Bradley, Kray D. Luxbacher, Zach Agioutantis, Harold M. McNair. *Development of a perfluoromethylcyclohexane (PMCH) permeation plug release vessel (PPRV) for tracer gas studies in underground mines.***

Perfluoromethylcyclohexane (PMCH) is a member of the perfluorocarbon tracer (PFT) group of compounds. PMCH has been widely used in various tracer gas studies to characterize ventilation systems, atmospheric transport patterns, and pollution distribution schemes. PMCH exists as a volatile liquid at room temperature and pressure, a characteristic that prevents PMCH from being deployed using traditional means. This paper presents a design for a permeation plug release vessel (PPRV) for PMCH. The PPRV is designed to passively deploy PMCH vapor at constant rate as a function of temperature and plug thickness for quantitative tracer gas studies. Details regarding the development process and the release rate analysis are included.

- **Keywords:** Tracer gas; Perfluoromethylcyclohexane; Ventilation; Flow characterization; Underground mines; Perfluorocarbon tracers

**Lokeshkumar P. Ramteke, Parag R. Gogate. *Removal of ethylbenzene and p-nitrophenol using combined approach of advanced oxidation with biological oxidation based on the use of novel modified prepared activated sludge.***

The treatment of a synthetically prepared wastewater containing ethylbenzene and p-nitrophenol has been investigated using combined treatment schemes based on the advanced oxidation process followed by the conventional aerobic oxidation process (using primary activated sludge (PAS), modified prepared activated sludge (MPAS) based on the

use of combined sludge from different treatment sources and activated sludge (AS)). The operating conditions for the pretreatment scheme have been optimized and it has been observed that initial pH of 3–3.5, a  $\text{Fe}^{2+}$  dosage of  $2.0 \text{ g L}^{-1}$  and a  $\text{H}_2\text{O}_2$  dosage of  $1.5 \text{ g L}^{-1}$  in combination with ultrasound gives the best performance. Approximately, 55–70% reduction in the chemical oxygen demand (COD) was obtained at optimum conditions after pretreatment from initial conditions of COD as 3642 and  $3417 \text{ mg L}^{-1}$  and BOD as 881 and  $533 \text{ mg L}^{-1}$  for the wastewater containing ethylbenzene and p-nitrophenol respectively. From an initial BOD5/COD (BI) value of around 0.15–0.2, the ratio was found to increase to about 0.30–0.35 after pretreatment, which is considered good for the aerobic treatment. In the case of aerobic oxidation, promising results were obtained for the modified prepared activated sludge giving better conversion ability of intermediates into solid residue and higher biomass yield that could be separated by simple filtration as compared to the primary activated or the activated sludge treatment. The best treatment approach as established in the work was ultrasound assisted Fenton process as the pretreatment followed by biological oxidation using MPAS.

- **Keywords:** Biodegradation; Advanced oxidation process; Modified prepared activated sludge; Fenton oxidation; Ultrasound; Biodegradability index; Combined processes

**D. Laboureur, A.M. Birk, J.M. Buchlin, P. Rambaud, L. Aprin, F. Heymes, A. Osmont. *A closer look at BLEVE overpressure.***

The overpressure produced by the boiling liquid expanding vapor explosion (BLEVE) is still not well understood. Various methods have been published on the overpressure modeling in the far field. They mostly differ by the modeling of the expansion energy, used to scale the distance to the source where the overpressure needs to be calculated. But these methods usually include a experimentally fitted reduction factor, and are mostly overestimating the overpressures. Today there is a growing interest in modeling the BLEVE overpressure in the near field, for studying the blast effect on critical infrastructure such as bridges and buildings. This requires a much better understanding of the BLEVE blast. This paper goes deeper in the understanding of the physical phenomenon leading to the BLEVE blast wave generation and propagation. First, mid-scale BLEVE experiments in addition to new experimental data for near field blast from a small scale supercritical BLEVE are analyzed. And second, an analysis method of the shocks observed in the experiments is presented based on fundamental gas dynamics, and allows the elaboration of a new modeling approach for BLEVE overpressure, based on the calculation of the initial overpressure and radius of the blast.

- **Keywords:** BLEVE; Blast wave; Overpressure; Modeling; Moving shock; Stationary shock

**Grzegorz Poplewski. *A new methodology for the synthesis of an optimum flexible water networks.***

This paper presents a new optimization model for the synthesis of direct reuse/recycle water networks with data uncertainties. In this case, data uncertainties were originated from the varying parameters of the water sources and sinks, which fluctuate within a given range of values. The aim of the method is to design an optimum flexible water network (FWN) that ensures minimum fresh water consumption and yet fulfilling all process constraints and uncertain parameters. The resulting FWN also features the minimum number of pipelines, which will ease process operation and control. Due to the complexity of the problem, multistep solving method based on theorem of corner points has been developed. The FWN obtained using the proposed method also includes information on the maximum flow rate in the pipelines, which is essential for detailed network design stage. The resulting model is a mixed integer linear problem (MILP),

which may be solved to obtain global optimum solution. Two case studies were used to elucidate the newly proposed method.

- **Keywords:** Flexibility; Data uncertainty; Water network integration; Source-sink matching; Optimization; Process integration

**Xueling Liu, Qi Zhang, Yue Wang. *Influence of particle size on the explosion parameters in two-phase vapor–liquid n-hexane/air mixtures.***

A number of explosions believed to be two-phase in nature have occurred within process industries, which emphasizes the need for investigations regarding the underlying mechanisms that contribute to mist explosions. This study provides new experimental data regarding the influences of the particle size of liquid-phase n-hexane on the explosion parameters in two-phase vapor–liquid n-hexane/air mixtures. A series of experiments was conducted as follows. First, a set of two-phase vapor–liquid n-hexane/air mixtures of various concentrations was obtained with a Sauter mean diameter SMD of  $18.51\ \mu\text{m}$ . In this case, the ignition energy ( $CU_2/2$ ) was constant at  $28\ \text{J}$ . The concentration was varied and the explosion pressure and explosion temperature were measured in order to determine the influence of the concentration on the explosion pressure and temperature, and the lower flammability limits were analyzed. Finally, a series of experiments was conducted on n-hexane/air mixtures with various concentrations and at various ignition energies. The minimum ignition energies of the heterogeneous n-hexane/air mixtures were determined and are discussed here. Particularly, we clarify a comparison with our previous experimental analyses. The maximum rate of pressure rise  $[dP/dt]_{\text{max}}$  of the two-phase vapor–liquid n-hexane/air mixtures indirectly proved that a range of particle size at which a significant burning velocity enhancement occurs (i.e., transition range).

- **Keywords:** Vapor–liquid two-phase n-hexane/air mixtures; Particle size distribution; Explosion parameters; Lower flammability limit; Minimum ignition energy; Spray and turbulence

**Bianca Mella, Ana Cláudia Glanert, Mariliz Gutterres. *Removal of chromium from tanning wastewater and its reuse.***

The chromium (Cr) used in the manufacture of leather from hides has well-known adverse effects when inappropriately disposed in the environment. The tanneries use large quantities of water for processing hides. The recovery of Cr from the wastewater produced in the tanning step is an environmentally friendly and economically viable alternative avoiding the disposal of large amount of Cr-containing sludge in industrial hazardous waste landfills. This work aims at studying the removal of the Cr from the tanning wastewater through chemical precipitation (CP) and electrocoagulation (EC) techniques and its reuse in tanning process. In the CP experiments, efficient Cr removal from wastewater samples was achieved, with up to 99.74% removal efficiencies. In the EC experiments, three different electrode materials, Al, Cu, and Fe were tested. The highest removal efficiency of 97.76% was obtained with Al electrodes by conducting electrolysis at  $3.0\ \text{V}$  for  $110\ \text{min}$ . This was followed by Fe electrodes and Cu electrodes, which showed removal efficiencies of 90.27% (at  $2.5\ \text{V}$ ) and 69.91% (at  $2.0\ \text{V}$ ), respectively, for an electrolysis of  $100\ \text{min}$ . The recovered Cr was reused as a tanning agent in leather processing, where good crossing of Cr was reached in leathers tanned with the liquors prepared from the sludge, and the pH and ash content values were measured. While the hides tanned with the Cr-containing liquor recovered by CP and by EC with Cu electrodes showed good hydrothermal stability and Cr content above 2.5%  $\text{Cr}_2\text{O}_3$ , the hides tanned with Cr-containing liquors recovered by chemical precipitation and by EC conducted with Fe and Cu electrodes showed contents of Cr according to technical specifications. However, the Cr samples obtained with the iron electrode showed a dark coloration due to oxidation of the iron. It can be concluded

that the tanning process with Cr recovered by CP and by EC with Cu electrodes showed the best results.

- **Keywords:** Chrome; Wastewater; Reuse; Chemical precipitation; Electrocoagulation; Cost comparison

**R.P. Cleaver, A.R. Halford. *A model for the initial stages following the rupture of a natural gas transmission pipeline.***

Experience shows that, despite the best efforts of the pipeline industry worldwide, pipelines do fail and release their contents to the atmosphere. In the case of below-ground pipelines transmitting natural gas, there is a chance that the release will be ignited, posing a significant hazard to any people in the vicinity. Mindful of this hazard, an international group of gas companies have collaborated over a period of many years on research projects aimed at developing an understanding of how these releases may arise (failure causes), how often they might occur (failure frequency), what type of releases might be produced (failure modes) and what type of behaviour might be produced for each of these modes of release (consequence analysis). This paper has been prepared to describe the mathematical models that have been developed on behalf of this group to assess the initial transient period following the rupture of a buried natural gas transmission pipeline assuming the release ignites immediately. It gives details of the equations used by the different models and it refers to some of the experimental data that has been used in the development of the models. A comparison of the model with the experimental data is provided. This demonstrates that the early stages could have a significant impact when evaluating the harm that could be caused. This provides a justification for developing the models rather than using a simpler alternative that does not take the initial highly transient period into account.

- **Keywords:** Consequence assessment; Pipeline ruptures; Mathematical modelling; Natural gas fires; Impulsively started flows; Risk assessment

**T.S. Anirudhan, M. Ramachandran. *Adsorptive removal of basic dyes from aqueous solutions by surfactant modified bentonite clay (organoclay): Kinetic and competitive adsorption isotherm.***

Cationic surfactant (Hexadecyltrimethylammonium chloride) modified bentonite clay was prepared and systematically studied for its adsorption behavior as an efficient adsorbent for the removal of basic dyes such as methylene blue (MB), crystal violet (CV) and Rhodamine B (RB) from aqueous phase. Organo modified clay shows better capacity for the removal of three dyes. The adsorption process was found to be dependent on pH and initial dye concentration. The maximum dye sorption was found to be at a pH of 9.0 (99.99% for MB, 95.0% for CV and 83.0% for RB). The adsorption capacity for the dyes was found to be 399.74, 365.11 and 324.36  $\mu\text{mol/g}$  for MB, CV and RB, respectively at 30  $^{\circ}\text{C}$ . The equilibrium uptake was attained within 240  $\text{min}$ . The kinetic studies were revealed that sorption follows a pseudo-second-order kinetic model which indicates chemisorption between adsorbent and adsorbate molecules. Adsorption isotherm indicates non-energetically adsorption sites which fit with Freundlich isotherm model. The fitness of kinetics and isotherm models was evaluated by using HYBRID error analysis function. Competitive adsorptions of dyes were studied by using binary component systems.

- **Keywords:** Bentonite; Organoclay; Adsorption isotherm; Adsorption kinetics; Competitive adsorption isotherm; Basic dyes

**Mohammad Foroughi-dahr, Hossein Abolghasemi, Mohamad Esmaili, Ghadir Nazari, Bettina Rasem. *Experimental study on the adsorptive behavior of Congo red in cationic surfactant-modified tea waste.***

The adsorption of Congo red (CR), an anionic dye, from aqueous solution by a cationic surfactant-modified tea waste (TW) was studied in batch experiments. Cetyl trimethyl ammonium bromide (CTAB) and cetyl pyridinium bromide (CPB) was used for the modification of TW and ground TW. CTAB-modified TW exhibited the highest adsorption capacity with respect to the other prepared adsorbents. The adsorption of CR on CTAB-TW as a function of adsorbent dosage, pH of the solution, contact time, and initial dye concentration was investigated. The optimum amount of CTAB-TW was found to be 0.2 g. The equilibrium CR adsorption data on CTAB-TW were best described by the Langmuir isotherm model. The adsorption capacity of CR on CTAB-TW was found to be 106.4 mg/g which is relatively high with respect to the other adsorbents. The adsorption kinetics of CR on CTAB-TW followed a pseudo-second-order model. Moreover, the intraparticle diffusion model was used to describe the kinetic data. It was found that diffusion is not the only rate controlling step. The adsorbent was characterized by the Brunauer–Emmett–Teller (BET) analysis, Fourier-transform-infrared (FTIR) spectroscopy, and scanning-electron-microscopy (SEM). The mechanism for the adsorption of CR on the surfactant modified TW may include hydrophobic interaction, van der Waals interaction,  $\pi$ - $\pi$  stacking and electrostatic interaction.

- **Keywords:** Adsorption; Anionic dye; Surfactant; CTAB; CPB; Modified tea waste

**Leyla Benammar, Taha Menasria, Ammar Ayachi, Messaoud Benounis. *Phosphate removal using aerobic bacterial consortium and pure cultures isolated from activated sludge.***

In the present study, an attempt is made to evaluate the kinetics of biological phosphate removal using a bacterial consortium of activated sludge, as well as screening for dominant polyphosphates accumulating bacteria. The results showed an efficient phosphate uptake ( $P < 0.001$ ) of the consortium, with rates related to the initial concentration of both phosphate and carbon sources. Short chain volatile fatty acids presented the suitable substrates for enhanced biological phosphorus removal, of which maximum yield reached 99.23% and 78.51% in basal salt medium supplemented with 0.5% of sodium acetate and lactate respectively. Fifteen phosphate-accumulating bacteria were isolated from the activated sludge and only four isolates were selected and characterized as *Pseudomonas aeruginosa* AS1, *Moraxella lacunata* AS2, *Acinetobacter junii* AS3 and *Alcaligenes denitrificans* AS4. The highest efficiency of phosphate uptake using pure culture was achieved with *Ac. junii* AS3 (83.36) followed by *P. aeruginosa* AS1 (81.78%), *Al. denitrificans* AS4 (76.72%), and *M. lacunata* AS2 with 50.6%.

- **Keywords:** Phosphate removal; Polyphosphate-accumulating bacteria; Activated sludge; Bacterial consortium; Batch culture

**Shimaa M. Abdel Moniem, Mohamed E.M. Ali, Tarek A. Gad-Allah, Ahmed S.G. Khalil, Mathias Ulbricht, M.F. El-Shahat, Azza M. Ashmawy, Hanan S. Ibrahim. *Detoxification of hexavalent chromium in wastewater containing organic substances using simonkolleite-TiO<sub>2</sub> photocatalyst.***

Innovative simple method for the preparation of simonkolleite-TiO<sub>2</sub> photocatalyst with different Zn contents was achieved. The prepared photocatalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), FT-IR, Raman and diffuse reflectance spectroscopy techniques. The photocatalytic activities of the materials were evaluated for the simultaneous detoxification of hexavalent chromium (Cr(VI)) and oxidation of organic compounds commonly present in wastewater under simulated solar

light. The best photoreduction efficiency of Cr(VI) has been achieved at 1000 ppm simonkolleite-TiO<sub>2</sub> photocatalyst of 5% Zn/TiO<sub>2</sub> weight ratio, and pH value of 2.5 to enhance the adsorption onto catalyst surface. Photoreduction was significantly improved by using formic acid as holes scavenger owing to its chemical adsorption on the catalyst surface. Finally, 100% photoreduction of Cr(VI) could be achieved using formic/simonkolleite-TiO<sub>2</sub> systems under sunlight.

- **Keywords:** Simonkolleite; TiO<sub>2</sub>; Cr(VI); Detoxification; Photoreduction; Organic oxidation

**A. Azizi, M.R. Alavi Moghaddam, R. Maknoon, E. Kowsari. *Innovative combined technique for high concentration of azo dye AR18 wastewater treatment using modified SBR and enhanced Fenton process as post treatment.***

The purpose of this research was to evaluate the performance of combined biological/advanced oxidation process (AOP) system for treatment of wastewater containing high concentration (500 mg/L) of azo dye Acid Red 18 (AR18). Two alternating anaerobic-aerobic sequencing batch reactors (SBR1 and SBR2 without and with external feeding at the beginning of aeration cycle, respectively) were operated. The effluent of the SBRs was then post treated through enhanced Fenton process (using zero-valent iron combined with ultrasonic irradiation). More than 90% and 97% of COD was removed in the combined SBR/AOP system without external carbon source (CTS1) and with external feeding (CTS2), respectively. The analysis of dye and its metabolites using UV-vis and HPLC analysis also proved that 99% of the original dye was decolorized and more than 89% of its metabolites were degraded through CST2 which is significantly higher than the reported values in the literature. Besides, more than 87% of phosphorus removal efficiency was obtained in CST2 compared to only 54.5% removal efficiency in CST1. Regarding the findings of this study, the proposed combined treatment system (CTS2) can be suggested as an effective technique for treatment of high azo dye AR18 concentration wastewater.

- **Keywords:** Acid Red 18 decolorization; Alternating anaerobic-aerobic modified SBR; Biodegradation; Enhanced Fenton process; External feeding

**Chao-Yin Kuo, Hung-Min Hsiao. *Preparation of iodine doped titanium dioxide to photodegrade aqueous bisphenol A under visible light.***

Highly photoactive iodine-doped titanium dioxide (I-doped TiO<sub>2</sub>) photocatalysts were synthesized to degrade aqueous bisphenol A (BPA) under irradiation by visible light and sunlight. The band gap energies of TiO<sub>2</sub> and I-doped TiO<sub>2</sub> (I/Ti mole ratio = 0.5%) were 3.01 and 3.04, and the BPA photodegradation rate constants were 1.61, and 5.11 h<sup>-1</sup>, respectively. The most probable reaction mechanism was proposed to involve IO<sub>4</sub><sup>-</sup> and IO<sub>3</sub><sup>-</sup> as electron acceptors that generate an inductive effect, increasing the photocatalytic efficiency of TiO<sub>2</sub>. Results indicated that I-doped TiO<sub>2</sub> not only acted favorably as a photocatalyst, but also exhibited considerable mineralization effects. In addition, a recycling test after ten experiments demonstrated the stability and reusability of the photocatalyst.

- **Keywords:** Iodine doped; Photocatalysis; Sunlight; Bisphenol A