

**11<sup>th</sup> INTERNATIONAL CONFERENCE  
ON ENVIRONMENTAL  
SCIENCE AND TECHNOLOGY**

**CEST2009**

**PROGRAMME OF THE CONFERENCE**

**3-5 September 2009  
Chania, Crete, Greece**



**UNIVERSITY OF THE AEGEAN**  
DEPARTMENTS OF:  
▶ ENVIRONMENTAL STUDIES  
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ACTUARIAL-FINANCIAL MATHEMATICS



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## 11<sup>th</sup> INTERNATIONAL CONFERENCE ON ENVIRONMENTAL SCIENCE AND TECHNOLOGY (CEST2009)

The eleventh International biennial Conference on **Environmental Science and Technology** continues the well established tradition of a successful series of CEST Conferences dating back to 1989. Like the previous conferences this conference maintains and upgrades the synthetic and integrated approach towards protection and restoration of the environment, by bringing together engineers, scientists, students, managers and other professionals from different countries, involved in various aspects of environmental science and technology.

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### Venue

The Conference will take place in Platanias, Chania, Crete, Greece, at the *Conference Centre of Minoan Palace Hotel*, between 3 - 5 September 2009.

### Conference topics

- Water Resources Management
- Water Treatment and Analysis
- Marine Pollution
- Wastewater Treatment
- Solid Waste Management
- Soil Contamination and Remediation
- Air Pollution
- Indoor Pollution
- Air Treatment
- Meteorology
- Global Environmental Change
- Ecology
- Environmental Management and Sustainability
- Health & the environment

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The official conference language is English.

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350 € (before 15<sup>th</sup> of July 2009)

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- 19:00 – 19:15 **Russo L. and Belgiorno V.**  
Combined chemical and biological treatment of polycyclic aromatic hydrocarbons contaminated soil
- 19:15 – 19:30 **Kastanek P., Kastanek F., Hajek M., Sobek J. and Solcova O.**  
Dechlorination of polychlorinated biphenyls (PCB) in contaminated soils and oils by nucleophile reactants at the presence of ionic liquids and under application of microwaves
- 19:30 – 19:45 **Chrysochoou M. and Dermatas D.**  
Investigation of Cr(VI) speciation and reduction in chromite ore processing residue (COPR) using micro-XANES, -XRF and -XRD
- 19:45 – 20:00 **Manousaki E. and Kalogerakis N.**  
Physiological and antioxidative changes induced by cadmium, lead and salt stress in a triplex halimus l.
- 20:00 – 20:15 **Putthividhya A. and Manajit K.**  
Geostatistical and reverse modeling assessment of DNAPL source zone architecture using downgradient mass flux-based estimation
- 20:15 – 20:30 **Discussion**

### Session 18

#### WASTEWATER TREATMENT (5)

*Saturday 5 September 2009 – morning*

*ROOM "IMPERIAL 1"*

*Chairs: D. Dermatas, D. Mamais*

- 9:00 – 9:15 **Karageorgos P., Mpasiakos C., Chalarakis E., Dimitrakakis E., Daskalakis C., Psillakis E. and Kalogerakis N.**  
Characterization and control of odours at a piggery facility in Rethymno-Crete
- 9:15 – 9:30 **Kyzas G.Z. and Lazaridis N.K.**  
Dyes removal from simulated textile effluents by chitosan sorbents
- 9:30 – 9:45 **Luptakova A., Balintova M., Macingova E., Jencarova J. and Prascakova M.**  
Remediation of acid mine drainage in the deposit smolnik by physical-chemical and biological-chemical methods
- 9:45 – 10:00 **Lofrano G., Meric S., Inglese M., Nikolaou A.D. and Belgiorno V.**  
Degradation and detoxification of tanning agents by fenton oxidation processes
- 10:00 – 10:15 **Vlyssides A., Barampouti E.M., Mai S. and Tsimas E.**  
Anaerobic digestion of chemically pretreated wastewater from a cheese making factory
- 10:15 – 10:30 **Lee Y.W., Lee J., Choi Y. and Chung J.**  
Reuse of electronic wastewater using combined membrane bioreactor and reverse osmosis
- 10:30 – 10:45 **Sonthiphand P. and Limpiyakorn T.**  
Distribution of ammonia-oxidizing bacteria and archaea in full-scale industrial wastewater treatment plants in Thailand
- 10:45 – 11:00 **Discussion**
- 11:00 – 11:30 *Coffee break*
- 11:30 – 11:45 **Melidis P. and Tseles D.**  
Nitrogen removal from landfill leachate by addition of biodiesel glycerol waste as external carbon source

## DYES REMOVAL FROM SIMULATED TEXTILE EFFLUENTS BY CHITOSAN SORBENTS

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### EXTENDED ABSTRACT

The aim of the current study is to remove reactive dyes (Reactive Red, RR; Reactive Blue, RB; Reactive Yellow, RY) from simulated textile effluents with cross-linked and amino-grafted chitosan beads (amination through grafting reactions either with acrylamide or poly(ethylene imine)), which will present higher sorption capacities than any other cited and studied sorbent (either polysaccharide or activated carbon). To overcome the high swelling degree of chitosan sorbents, beads of chitosan were prepared and not powder. To determine the reuse of sorbents, sequential cycles of sorption-desorption were carried out. Three types of chitosan derivatives were prepared: (i) Cross-linked chitosan beads (*Ch*) [1], which were used as reference in all experiments; (ii) Cross-linked and grafted with acrylamide chitosan beads (*Ch-g-Aam*) [1]; (iii) Cross-linked and grafted with poly(ethylene imine) chitosan beads (*Ch-g-PEI*) [2]. To examine whether our prepared sorbents will be usable in packed bed columns in future studies, some swelling experiments were carried out, where the water uptake was measured gravimetrically. FT-IR spectra of pure chitosan, dye-loaded and non-loaded sorbents were obtained.

Experiments for the effect of pH on sorption of simulated dye mixture were performed by mixing 0.05 g of sorbent with 50 mL of the aqueous simulated dye mixture having the same dye concentrations as measured from a real industrial effluent (197 mg/L of RR, 223 mg/L of RY, and 280 mg/L of RB), and keeping constant the pH of the solution. The solutions were agitated at 160 rpm in a temperature controlled shaker at 25 °C (Julabo SW-21C) for 24 h (contact time). Although the higher sorption of reactive dyes onto chitosan is in acidic pHs, the industrial dyebaths (derived from the dyeing mill) are alkaline (pH ~ 10). Therefore, to simulate the conditions occurred in real dyebaths, the sorption experiments were realized in alkaline conditions.

Kinetic experiments were performed by mixing 0.05 g of sorbent with 50 mL of real dye effluent. The mixture was shaken at 160 rpm for 24 h at 25 °C. Samples were collected at fixed intervals (5, 10, 20, 30 min, 1, 2, 3, 4, 5, 6, 12, 24 h). The pseudo-second order equation was used successfully to fit the experimental kinetic data [3]:

Furthermore, to determine the effect of sorbent's mass on sorption of dyes from dye mixture, a series of experiments were carried out, varying the sorbent's dosage (1 g/L – 10 g/L). The other parameters of sorption were kept constant (pH adjusted to 10; 25 °C; 160 rpm; 24 h). The Langmuir-Freundlich (LF) isotherm, which is essentially a Freundlich isotherm approaching an adsorption maximum  $Q_{max}$  (mg/g) at high concentrations, was used to fit the experimental data.

After sorption experiments, the samples were collected and filtered. The desorption experiments were realized by mixing the collected amount of loaded chitosan with aqueous solutions of 50 mL over a pH range between 2 and 12, at 25 °C for 24 h. This procedure was realized to determine the optimum desorption pH value of the dye-loaded sorbents. In order to determine the reusability of the prepared chitosan sorbents, consecutive sorption-desorption cycles were repeated, following the experimental procedures described above and using the same sorbents.

**KEYWORDS:** Simulated textile effluent, Decolorisation, Sorption, Chitosan sorbents; Isotherms; Kinetics; Reuse.

## 1. INTRODUCTION

Wastewater discharged from dyeing process can be one of the biggest contributors to aquatic pollution and especially to textile effluent, which comprises mainly residual dyes and auxiliary chemicals. In general, dyes are classified as: (i) anionic (reactive, acid, direct), (ii) cationic (basic), and (iii) non-ionic (disperse) [4]. The most studied dye classes in effluent treatment are reactive and basic [5]. The dye loss to the effluent for the main dye-fiber application is 10 – 50% for reactive dyes, while 0 – 5% for basic ones [6]. A study sponsored by American Dye Manufacturers Institute depicts that basic dyes are generally more toxic than acid, reactive and direct [7]. Taking into account that reactive and basic dyes could simultaneously exist in the equalization tank of a dyehouse, it is of fundamental importance to remove both of them [8].

It is known that wastewaters containing dyes are very difficult to treat since the dyes are recalcitrant molecules, resistant to aerobic digestion and stable to oxidicity. Although, activated carbon is the most commonly used method of dye removal by sorption, its cost and regeneration difficulties have impelled researchers to focus on alternative sorbents [9, 10].

Chitosan performs many standards of an excellent biosorbent, such as abundance, non-toxicity, hydrophilicity, biocompatibility, biodegradability, anti-bacterial property, inexpensiveness, and effective sorptive ability for almost all types of dyes, except for basic ones [11,12]. However, raw chitosan presents some major difficulties in sorption process, i.e. (i) unsatisfactory mechanical properties and poor heat resistance, (ii) dissolution in acidic media, (iii) high swelling ratios, which limit its use in columns (hydrodynamic limitations and column fouling), and (iv) limited sorption capacities for basic dyes. To overcome the first three limitations, cross-linking is necessary to improve the stability of sorbents, while for the last limitation a grafting procedure will increase the capacity of sorbents. In general, chitosan can be found as gels, flakes, powders and beads depending upon the preparation procedure. Chitosan beads are preferred as more suitable for operation in a column mode.

## 2. MATERIALS AND METHODS

### 2.1. Materials

High molecular weight chitosan was obtained from Sigma-Aldrich and purified by extraction with acetone in a Soxhlet apparatus for 24 h, followed by drying under vacuum at room temperature. The average molecular weight was estimated at  $3.55 \times 10^5$  g/mol and the degree of deacetylation was 82 wt%. Acrylamide (97% p.a.), isopropyl alcohol ( $\geq 99.7\%$ ), and epichlorohydrin ( $\geq 99\%$ ) were received by Sigma-Aldrich. Poly(ethylene imine) (50% w/v in water) and sodium tripolyphosphate ( $\geq 98\%$ ) were obtained by Fluka, while potassium persulfate (initiator) was obtained from Merck. Glutaraldehyde (50 wt% in water) was received from Sigma-Aldrich and used as reagent grade. All solvents were of analytical grade. The simulated dye effluent was composed of three reactive dyes; Remazol Red 3BS (RR), Remazol Blue RN (RB), and Remazol Yellow Gelb 3RS (RY). The respective commercial dyes, in powder-form, were used as reagents for the preparation of the calibration curves in the analysis of effluents. The purity of dyes has been taken into account for all calculations.

### 2.2. Preparation of chitosan beads

Three types of chitosan derivatives were prepared: (i) cross-linked chitosan beads (*Ch*) [3], which were used as reference in all experiments; (ii) cross-linked and grafted with acrylamide chitosan beads (*Ch-g-Aam*) [3]; (iii) cross-linked and grafted with poly(ethylene imine) chitosan beads (*Ch-g-PEI*) [2]. The exact details of the experimental preparation are described in the already published studies.

### 2.3. Experimental procedure

Experiments for the effect of pH on sorption of simulated effluents were performed by mixing 0.05 g of sorbent with 50 mL of the aqueous simulated dye mixture having the same dye concentrations as measured from a real industrial effluent (197 mg/L of RR, 223 mg/L of RY, and 280 mg/L of RB), and keeping constant the pH of the solution. The solutions were agitated at 160 rpm in a temperature controlled shaker at 25 °C (Julabo SW-21C) for 24 h (contact time).

To determine the effect of sorbent's mass, a series of experiments were carried out, varying the sorbent's dosage (1 g/L – 10 g/L), keeping constant all the other parameters (25 °C; 160 rpm; 24 h). The amount of dye sorbed was expressed as a percentage of the removal, while the amount of total dye uptake at equilibrium  $Q_e$  (mg/g) was calculated using the mass balance equation:

$$Q_e = \frac{(C_o - C_e) \cdot V}{m} \quad (1)$$

where  $m$  (g) is the mass of sorbent;  $V$  (L) the volume of sorbate;  $C_o$  and  $C_e$  (mg/L) are the total initial and equilibrium concentration of each dye, respectively.

The experimental equilibrium data were fitted to the Langmuir–Freundlich isotherm (L-F, Eq. 2), which is essentially a Freundlich isotherm and approaches a maximum at high concentrations [13]:

$$Q_e = \frac{Q_{\max} (K_{LF} C_e)^b}{1 + (K_{LF} C_e)^b} \quad (2)$$

where  $Q_{\max}$  (mg/g) is the total maximum amount of sorption;  $K_{LF}$  (L/mg)<sup>1/b</sup> is the Langmuir–Freundlich constant;  $b$  (-) is the Langmuir–Freundlich heterogeneity constant.

Kinetic experiments were performed by mixing 0.05 g of sorbent with 50 mL of the effluent. The mixture was shaken at 160 rpm for 24 h at 25 °C. Samples were collected at fixed intervals (5, 10, 20, 30 min, 1, 2, 3, 4, 5, 6, 12, 24 h) and then were analyzed. The pseudo-second order equation (Eq. 3) was used to fit the experimental data [1]:

$$C_t = C_o - (C_o - C_e) \left( 1 - \frac{1}{1 + k_2 t} \right) \quad (3)$$

where  $k_2$  (min<sup>-1</sup>) is the rate constant for the pseudo-second order sorption model, and  $C_t$  (mg/L) is the total transient concentration of each dye.

After sorption experiments, the samples were collected and filtered. Desorption experiments were realized by mixing the collected amount of loaded chitosan with aqueous solutions of 50 mL over a pH range between 2 and 12, at 25 °C for 24 h. This procedure was realized to determine the optimum desorption pH value of the dye-loaded sorbents. To determine the reusability of the prepared chitosan sorbents, ten sequential sorption-desorption cycles were repeated, following the experimental procedures described above and using the same sorbents.

### 2.4. Analysis

The residual concentration of dyes was calculated spectrophotometrically (UV-Vis, model U-2000, Hitachi). In the case of dye mixtures, the absorbance  $A$  (-) was measured at the three wavelengths of maximum absorbance of dyes ( $\lambda_{\max,RR} = 541$ ;  $\lambda_{\max,RB} = 588$ ;  $\lambda_{\max,RY} = 419$ ). The molar absorptivity/extinction coefficients  $E$  (L mol<sup>-1</sup> cm<sup>-1</sup>) for the three dyes was calculated from the Lambert – Beer law [14]:

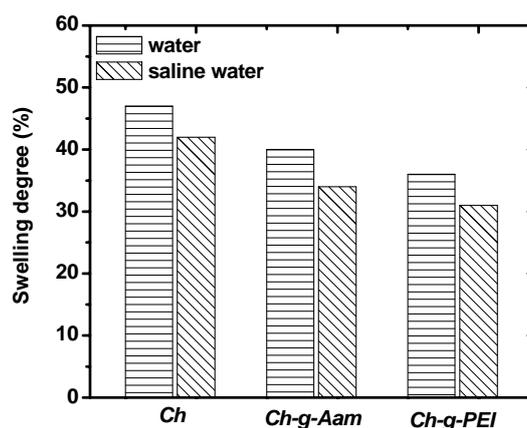
$$A = E \cdot Z \cdot C \quad (4)$$

where  $Z$  the path length (cm). Solving the resulting 3x3 equation system, the concentration of each dye in the dye mixture (effluent) was calculated. The effect of pH and the effect of the auxiliaries used in dyeing process (which still occurred in the sample originated from the dyeing mill) over both the calibration curves and the determined  $\lambda_{\max}$

wavelength of each dye were studied, but no significant deviation was observed (data non shown).

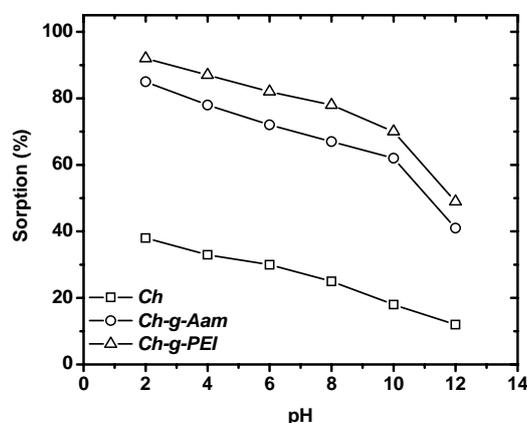
### 3. RESULTS AND DISCUSSION

The prepared sorbents presented low swelling degrees (*Ch*, 47%; *Ch-g-Aam*, 40%; *Ch-g-PEI*, 36%) in deionized water at pH 10. The diffusion of water molecules towards the interior of the macromolecular network is limited by the grafting of additional groups (amido or imino). Furthermore, the swelling degrees at saline water (presence of NaCl) were reduced for all the sorbents (*Ch*, 42%; *Ch-g-Aam*, 34%; *Ch-g-PEI*, 31%). In the presence of NaCl, the osmotic pressure inducing the penetration of water molecules inside the structural chitosan network decreases leading to reduced swelling [15].



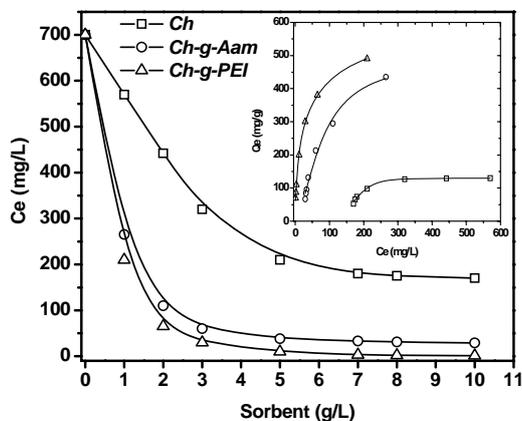
**Figure 1.** Swelling degrees of the prepared chitosan sorbents measured at pH 10 both in deionized and in saline water

The maximum removal was presented at pH 2 for all the materials, while increasing the adjusted pH of the solution, a decrease was observed. The main interaction presented is the electrostatic attraction between protonated amino groups of chitosan-based sorbents and sulfonate groups of reactive dye molecules [16]. For the whole pH range the sorptive behavior of the prepared sorbents followed the order: *Ch-g-PEI* > *Ch-g-Aam* > *Ch*. This could be attributed to the higher basicity of imino groups of *Ch-g-PEI* versus amido groups of *Ch-g-Aam*. At pH 10 the removal of dyes from the simulated mixture was maintained in high levels (*Ch*, 28%; *Ch-g-Aam*, 72%; *Ch-g-PEI*, 77%).



**Figure 2.** Effect of pH on the sorption of simulated effluent onto chitosan sorbents

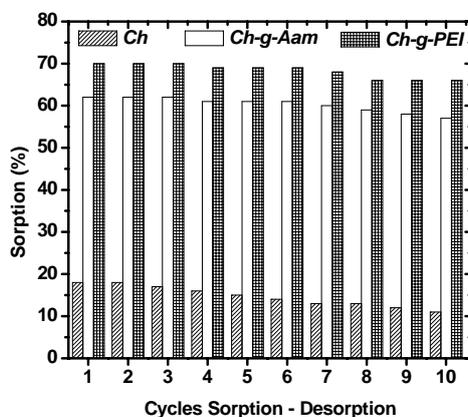
Increasing the mass of sorbent, a higher sorption is achieved (lower residual dye concentrations). Using 10 g/L of the *Ch-g-PEI*, the residual total dye concentration in effluent reaches the lowest value of 1 mg/L, while the respective concentrations for *Ch-g-Aam* and *Ch* were 25 and 162 mg/L, respectively.



**Figure 3.** Effect of sorbent's mass on sorption of dye from simulated dyeing effluents onto chitosan sorbents

A sharp decreasing trend was observed with a steep descent at the beginning of sorption (within 120 min) being succeeded by a more gradual decay (120-360 min) reaching equilibrium into 360 min. The experimental data were successfully fitted to the pseudo-second order equation presenting high correlation coefficients ( $R^2 > 0.998$ ). Chitosan modifications had an effect on the sorption rate; the sorption rate for *Ch-g-PEI* ( $k_2 = 0.061 \text{ min}^{-1}$ ) was faster than that of *Ch-g-Aam* ( $k_2 = 0.057 \text{ min}^{-1}$ ) and *Ch* ( $k_2 = 0.044 \text{ min}^{-1}$ ), which could be attributed to the reasons previously mentioned for the effect of pH (the more basic imines react faster with the active sites of dye molecules).

Strongly alkaline (pH 12) conditions were observed to be necessary for the desorption of loaded reactive dyes by chitosan, showing very high desorptive percentages for all the prepared sorbents (*Ch*, 91%; *Ch-g-Aam*, 95%; *Ch-g-PEI*, 98%). Therefore, aqueous solutions adjusted to pH 12 were used as eluants. Ten sorption-desorption cycles were carried out to reveal the regeneration ability of the prepared sorbents. The reduction in sorption percentages from the 1<sup>st</sup> to 10<sup>th</sup> cycle was 6% for *Ch*, 4% for *Ch-g-Aam*, and 3% for *Ch-g-PEI*. Therefore all the materials can be used repeatedly without any significant loss of their sorptive ability.



**Figure 4.** Sorption-desorption cycles for the prepared sorbents (pH 10 both for sorption and desorption)

#### 4. CONCLUSIONS

In this study, three cross-linked chitosan derivatives (beads) were used as sorbents for the decolorization of simulated effluents: (i) *Ch*, without grafting; (ii) *Ch-g-Aam*, grafted with poly(acrylamide), and (iii) *Ch-g-PEI*, grafted with poly(ethylene imine). The experimental observations are summarized below:

- Although chitosan derivatives present maximum sorption behavior at pH 2, their sorption capacity remains high at alkaline pH.
- Sorption kinetics were successfully fitted to the pseudo-second order kinetic model.
- Sorption-desorption experiments were realized at original pH 10 in ten cycles without significant loss of the sorption capacity of the material, and presenting low-swelling percentages (~35%).
- Only *Ch-g-PEI* could satisfactorily reduce the dye concentration of the effluent below the limit of 1 mg/L (according to legislation), when employing a dosage of sorbent higher of 4 g/L.
- All the previous suggest that *Ch-g-PEI* is a sorbent, which can be effectively used in the technology of the wastewater treatment.

#### REFERENCES

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