Under the Auspices:



In cooperation with:



IWA Regional Conference on Wastewater Purification & Reuse



Conference Program

Organized by









DECENTRALISED ADMINISTRATION OF CRITE







REGION OF CRETE





Host Organisation

The Municipal Enterprise for Water and Wastewater of the City of Heraklion is the project promoter of the EL0030 project titled "Agricultural Utilization of Tertiary Treated Wastewater as an Alternative Water



Resource". The project is funded by the European Economic Areas Grants and the Greek Ministry of Decentralized Development and Competitiveness. Aim of the project is to create and operate the largest wastewater purification and reuse distribution network in

Greece, providing more than 1,500,000 m³ per year of high quality alternative water, mainly for irrigation purposes.

The Municipal Enterprise for Water and Wastewater of the City of Heraklion, is one of the largest relevant organisations in the country. It operates a number of water and wastewater treatment plants, with the largest one found in the area of Phinikia, treating more than 35,000 m³ of wastewater per day.

Host City

Heraklion is one of the oldest cities in Europe, with a history dating back more than 3,500 years and a population that exceeds 250,000 people.

Here you will find the world renowned ruins of the city of Knossos, one of the most visited Archaeological sites in Europe and a social life, only found in the heart of the Mediterranean region.



In the past six years, starting

with the Athens 2004 Olympic Games (Heraklion was hosting in a brand new stadium a number of football games), the city was reshaped, reinventing the most important element in the island, the sea. A new seafront has been created, starting from the old port (with the fortress of Coule), to the Pangrition Stadium. Among other things, an 8,000 m foot and bicycles path, exactly by the sea, was constructed.

Important Dates

- Deadline for Abstracts Submissions
- CONTINUES EVALUATION PROCESS
- Full Paper Submission:
- Early Registration Deadline:

30th of September, 2011 WITHIN 15 DAYS 30th of November, 2011 31st of December, 2011

Organising Committee

- Mr Ioannis Vitsaksakis, General Director, Municipal Enterprise for Water and Wastewater of Heraklion, Co-Chair
- Dr Thrassyvoulos Manios, Associate Professor, Technological Educational Institute of Crete, Co-chair
- Professor Nikolaos Kalogerakis, Technical University of Crete, Co-Chair
- Mr Charilaos Papamattheakis, Technical Director, Municipal Enterprise for Water and Wastewater of Heraklion. Co-Chair
- Mr Emmanouil Mavrakis, Decentralised Administration of Crete
- Dr Daniel Mamais, Assistant Professor, National Technical University of Athens
- Mr Charalambos Papadogiannis, Municipal Enterprise for Water and Wastewater of Heraklion

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With the support of:





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IWA Regional Conference on Wastewater Purification & Reuse



28th, 29th and 30th of March, 2012 Heraklion, Crete, Greece

Organized by



MUNICIPAL ENTERPRISE FOR WATER AND WASTEWATER OF HERAKLION





TECHNOLOGICAL EDUCATIONAL INSTITUTE OF CRETE



TECHNICAL UNIVERSITY OF CRETE

Welcome to WWPR2012

Whoever works with water knows that wastewater can both be a helping tool as well as a possible threat. It can be utilized as an alternative water resource and help save millions of cubic meters of fresh



water, or it can contaminate even larger amounts, if disposed improperly, threatening the lives of millions. In a world that water demand is



increasing, the importance of that simple statement is significant, especially for arid and semi-arid regions as in the Mediterranean basin.

The Wastewater Purification and Reuse Regional Conference aims to gather all of you that your research, your business or your daily activity is related to the purification of the wastewater and its reuse, independently of the region that takes place and the purpose. We also believe that through the current technical and scientific achievements, as well as the exchange of experiences

among partners, we will be able to increase the water reuse parameter as a tool and reduce the threat of the wastewater implementation.

We also believe that one of the most important ways to achieve that goal is through personal communication and interaction.

For all the above reasons we do hope that you will respond to our invitation.



Conference Themes

- Wastewater purification and water reuse legislation
- Water reuse history
- Wastewater purification: membranes and other physical methodologies
- Wastewater purification: chemical methods
- Wastewater disinfection
- Pollutants in the final effluent
- Pathogens in the final effluent
- Pathogens: qualitatively and quantitatively monitoring
- Pathogens re-generation after disinfection
- Public health risks and issues
- Public perspective towards water reuse
- Effect of water reuse on soils and cultivations
- Water reuse as part of a water management scheme
- Wastewater purification economics
- Water reuse economics
- Water reuse in non-agricultural related activities
- Reuse of non municipal wastewaters
- Designing and implementing a water reuse scheme
- · Case studies of water reuse schemes: opportunities, problems and solutions

Also during WWPR2012 two workshops will take place, entitled:

- «Sewage Sludge Management: Problems and Solutions». Aim is to present state of the art solutions in sewage sludge management.
- «Desalination: New Trends and Technological Advances» Aim is as suggested by the title – to present best options in desalination, mainly for potable water production.

Abstracts can be also submitted for these two workshops, which will be included in the conference proceedings.

Selected papers will be published in Water Science & Technology.



Conference Fees

Early Registration by 31st of December, 2011

Full delegate	300€
IWA Member	200€
Union of the Greek Municipal Enterprises for	
Water and Wastewater	200€
Students	150€

Late Registration, after the 1st of January 2012	
Full delegate	400€
• IWA Member	300€
Union of the Greek Municipal Enterprises for	
Water and Wastewater	300€
• Students	200€

Official conference languages: English, Greek









Conference Program

IWA Regional Conference on Wastewater Purification & Reuse 2012

28th, 29th & 30th of March Heraklion, Crete, Greece

EDITED BY

Dr Thrassyvoulos Manios Associate Professor, Technological Educational Institute of Crete, Co-chair

> Professor Nikolaos Kalogerakis Technical University of Crete, Co-Chair

Mr Charilaos Papamattheakis Technical Director, Municipal Enterprise for Water and Wastewater of Heraklion, Co-Chair

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- Dr Thrassyvoulos Manios, Associate Professor, Technological Educational Institute of Crete, Co-chair
- Professor Nikolaos Kalogerakis, Technical University of Crete, Co-Chair
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- Mr Emmanouil Mavrakis, Decentralised Administration of Crete
- Dr Daniel Mamais, Assistant Professor, National Technical University of Athens
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- Mrs Anna Troulinou, Region of Crete.

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- Prof Edward Stentiford, Leeds University, U.K.
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- Dr Nikos Tzortzakis, Technological Educational Institute of Crete, Greece.
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POSTER'S LIST

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0020	M. Kampourakis, M. Theodorakopoulou, I. Petousi, M. Fountoulakis	USING ALOE VERA EXTRACTION FOR WASTEWATER PATHOGENS SUPPRESSION
0063	Ali Tahir Hassan	CONSTRUCTED WETLANDS FOR WASTEWATER REUSE IN AGRICULTURE – A FEASIBILITY STUDY OF THE CITY OF AN NAJAF, IRAO.
0070	Dr George Z. Kyzas Dimitrios N. Bikiaris Nikolaos K. Lazaridis	DECOLORIZATION OF INDUSTRIAL EFFLUENTS WITH POLYMERIC ADSORBENTS – AN APPROACH WITHOUT THE EQUALIZATION STEP
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0100	Kanghoon Lee, JuHyun Kim, Nguyen Hai, Sudheer Kumar Shukla, I.T. Yeom,	EFFECT OF NORMAL EXTRA CARBON SOURCE ON 1,4-DIOXANE BIODEGRADATION WITH MIXED CONSORTIUM OF BACTERIA
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0153	D. Traksel, F.I.H.M. Oesterholt,	CASE STUDIES APPLIED COOLING WATER RESEARCH FOR CHEMICAL INDUSTRIES
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0174	J.Y. Park, J.W. Nam J.H. Kim, W.W. jeong E.J. Lee, Y.S. Lee A. Jang, Prof. H.S. Kim	EVALUATION OF CHEMICAL CLEANING PURSUANT TO CHEMICALS OF BWRO PROCESS FOR REUSED SEWAGE

DECOLORIZATION OF INDUSTRIAL EFFLUENTS WITH POLYMERIC ADSORBENTS – AN APPROACH WITHOUT THE EQUALIZATION STEP

George Z. Kyzas, Dimitrios N. Bikiaris, and Nikolaos K. Lazaridis

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EXECUTIVE SUMMARY – SHORT PAPER

The dyeing process of cotton textiles using mainly reactive dyes involves unit operations such as (i) desizing, (ii) scouring, (iii) bleaching, (iv) dyeing, and (v) finishing. The waste streams from each individual sub-operation are collected to an "equalization tank", where they are mixed and homogenized. In particular, the wastewater produced by the dyeing bath-reactor contains hydrolyzed reactive dyes, dyeing auxiliaries, and electrolytes. The latter are responsible for the high saline content of the wastewater, which exhibits high pH values (10-11). So, the large volume of colorized effluents after the dyeing process has to be treated.

A typical effluent treatment is broadly classified into preliminary (equalization and neutralization), primary (screening, sedimentation, flotation, and flocculation), secondary (reduces the organic load and facilitate the physical/chemical separation), and tertiary stages (decolorization). In the latter, adsorption has been applied either in a single mode, mainly for dyes removal from simulated/synthetic wastewaters, or in a combinational mode for total cleaning of real wastewaters. The novelty of this study is the processing (decolorization) of effluent originated directly from the dyeing bath before entering the equalization tank. In this way, only a small fraction (~ 10%) of the entire discharge volume will be treated, which means saving money and energy. Thus, it was investigated the feasibility of removing dyes from the dyeing reactor of a Greek dyeing industry by adsorption onto various polymeric adsorbents (chitosan).

To accomplish this endeavour chitosan was suitably modified by amido and vinyl-imido groups. Three types of cross-linked chitosan adsorbents were synthesized: (i) non-grafted chitosan beads (Ch), which were used as reference in all experiments; (ii) chitosan beads grafted with acrylamide (Ch-g-Aam), and (iii) chitosan beads grafted with vinyl-imidazol (Ch-g-VID).

The maximum removal was presented at pH=2 for all the materials in the case of simulated effluents (Ch, 43%; Ch-g-Aam, 90%; Ch-g-VID, 97%). Similar trend was observed for the real effluents (Ch, 38%; Ch-g-Aam, 85%; Ch-g-VID, 92%), but with lower adsorption percentages, due to the presence of dyeing auxiliaries. Increasing the pH of the solution, a decrease of adsorption was observed. The explanation for this behaviour is that under acidic conditions hydrogen atoms (H⁺) protonate the amine groups rendering



them into the cationic form (-NH3⁺). On the other hand, the reactive dyes in aqueous solutions are dissolved and the sulfonate groups are dissociated and converted to anions. Thus, the adsorption mechanism proceeds via electrostatic interaction between the two counterions. The maximum removal was observed at pH=2, where the protonation is the highest, while increasing pH the removal reduces due to the deprotonation of amino sites. In fact, for the whole pH range the adsorption behaviour of the prepared adsorbents follows the order: Ch-g-VID>Ch-g-Aam>Ch. This is attributed to the higher basicity (electropositivity) of vinyl-imido groups (Ch-g-VID) versus amido groups (Ch-g-Aam). Thus, more positively charged groups occur on VID-grafted derivative than on amido-grafted, rendering the electrostatic reaction between chitosan and dye molecules stronger. The pKa (10.5) of VID is higher than that of Aam (7.9) and Ch (6.5), and the higher the pKa value of the ligand grafted onto the adsorbent; the wider is the effective pH range for anionic dye adsorption.

However, the chitosan derivatives presented significant removal percentages also in the alkaline region at pH 10 (simulated effluent: Ch, 31%; Ch-g-Aam, 68%; Ch-g-VID, 82%, real effluent: Ch, 18%; Ch-g-Aam, 62%; Ch-g-VID, 70%), which could be attributed to a combination of decreased electrostatic and other interactions, as van der Waals forces, hydrogen bonding and pi-pi interactions.

Another important parameter in the adsorption mechanism is the presence of high ionic strength (approx. 1 mol/L NaCl) in simulated and real effluent. It is known that, in the acidic pH range the salt content screens the opposite charges of chitosan surface and the dye molecules and has a negative effect in the sorption of anionic dyes. However, in the highly alkaline pH=10 the presence of electrolytes suppresses the negative charge build-up at the chitosan surface and promotes increased dye-uptake:

Chitosan -
$$CH_2OH + OH^T \iff Chitosan - CH_2O^T + H_2O$$
 (1)

In this case, the resulted dissociated groups can react covalently with the dye molecules as in the dyeing process of textiles:

Chitosan -
$$CH_2O^- + Dye - Cl \rightarrow Chitosan - CH_2 - O - Dye + Cl^-$$
 (2)

The above reaction (with the formation of ether bond) takes place in the interaction of RR and RY dyes, which contains the chloride atom in their reactive group (1,3,5-triazinyl group). In the case of RB, the interaction occurs through another covalent bond as follows:

$$Dye - SO2 - CH2 - CH2 - OSO3Na \rightarrow Dye - SO2 - CH = CH2 + NaHSO4$$
(3)

Chitosan -
$$CH_2O^{-} + H_3O^{+} + Dye - SO_2 - CH = CH_2 \rightarrow Dye - SO_2 - CH_2 - CH_2 - Chitosan + H_2O$$
 (4)

As far as the covalent adsorption mechanism, FTIR spectra of the prepared adsorbents were obtained before and after decolorization. The presence of new peaks for the loaded adsorbents Ch, Ch-g-Aam, Ch-g-VID (1094, 1148, 1137 cm⁻¹) originated from the formation of ether bond -CH₂-O- (Eqs. 2, 4) confirm the proposed additional mechanism of adsorption in alkaline conditions.

For the rest of our study the experiments were realized at pH=10, which was dictated by the following reasons: (i) pH=10 is the original alkalinity of textile effluents, (ii) avoidance of additional cost due to the pH



regulation, (iii) dye removal at this pH still remains high in acceptable levels, presenting only 20% decrease with respect to pH 2.

Three series of equilibrium experiments were realized: (i) with simulated single-dye solutions by varying the initial concentration of adsorbate and (ii) with simulated mixtures and real effluents by varying the initial concentration of adsorbent. So, the ratio between the concentration of the compound remaining in solution and adsorbed on the solid decreases when the solute concentration increases; providing a concave curve. The results clearly indicate a progressive saturation of the solid and the data were fitted to the Langmuir-Freundlich (L-F) isotherm model. The values of correlation coefficient (R²), which is a measure of the goodness of fitting, confirm that the L-F model results in an excellent prediction of the experimental data. The VID-adsorbent (Ch-g-VID) showed the maximum adsorption capacity for all the dyes (RR, 1412 mg/L; RY, 1392 mg/L; RB, 1329 mg/L). The capacity of chitosan derivatives followed the order: Ch-g-VID>Ch-g-Aam>Ch.

In the case of data from simulated mixtures and real effluents by varying the initial concentration of adsorbent (pH~10), the residual dye content was expressed in concentration (mg/L) and ADMI units. Typical adsorption isotherms were observed for all materials. One may discern the reduction of the total residual dye content, increasing the mass of adsorbents. The adsorption behavior of the adsorbents followed the same order as in the case of pH edges. VID-derivative was superior than amido- derivative. So, it has been showed that 10 g/L of the adsorbents decreases the residual total dye concentration to 1, 29, 171 mg/L for Ch-g-VID, Ch-g-Aam and Ch, respectively. The VID-derivative succeeded to decrease the dye content to 145 ADMI Units, with 5 g/L dosage. It should be stressed that, according to the US Pollutant Discharge System the permitted level is 300 ADMI units.

Then, the possibility of desorption was studied. The adsorption, realized with real effluents (pH~10), followed by desorption of the dye-loaded chitosan derivatives over the whole pH range. Increasing the pH an increase in desorption percentage were observed, reaching maximum in the highly alkaline region 10-12. It is generally surprising to get a good adsorption and desorption at the same pH. However, there was a significant difference between the two processes with respect to the ionic strength. Adsorption was realized in the presence of 1 mol/L NaCl, while desorption in its absence. The high electrolyte content generates high osmotic pressure in the bulk and causes more sodium ion penetration into chitosan matrix, which eventually helps/favours dye molecule uptake. In the contrary, the absence of electrolyte reverses the mass transfer from the solid phase to the bulk.

To investigate the possibility of reuse of chitosan adsorbents, sequential adsorption-desorption experiments in batch mode were conducted for ten cycles. The reduction in adsorption percentages from the 1st to 10th cycle was: 7% for Ch, 5% for Ch-g-Aam, and 4% for Ch-g-VID. The decrease in the adsorption efficiency can be attributed to several reasons as: (i) a progressive saturation of the reactive groups of the adsorbent by dye molecules; (ii) a degradation of material due to extreme pH and salinity conditions and (iii) a progressive blocking of the reactive groups of the adsorbent by dye impurities and dyeing auxiliary



reagents. Therefore all the materials could be used repeatedly without any significant loss of their adsorptive ability.

Remazol Brilliant Red 3BS (RR)

Remazol Brilliant Blue RN (RB)

Remazol Yellow Gelb 3RS (RY)

Fig. 1. Reactive dyes used.

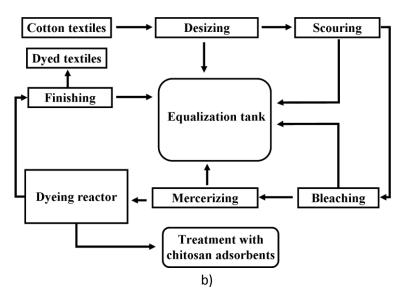


Fig. 2. Proposed treatment of dyeing effluents.



Decolorization of industrial effluents with polymeric adsorbents - An approach without the equalization step

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Problem

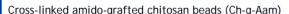
- The dyeing process of cotton textiles using reactive dyes (cotton fibers makes up about half of the worldwide consumption of fibers) involves unit operations such as (i) desizing, (ii) scouring, (iii) bleaching, (iv) dyeing, and (v) finishing.
- The waste streams from each individual sub-operation are collected to an "equalization tank", where they are mixed and homogenized.
- •The wastewater produced by the dyeing bath-reactor contains hydrolyzed reactive dyes, dyeing auxiliaries, electrolytes (-60-100 g/L of NaCl and Na₂CO₃). The latter are responsible for the high saline content of the wastewater, which exhibits high pH values (10-11).
- •In a typical dyeing procedure with reactive dyes, for 1 kg of cotton are required 0.6-0.8 kg of NaCl, 30-60 g of dyestuff, and 70-150 L of water.
- •The large volume of colorized effluents after the dyeing process has to be treated in some manner.

Objective

The processing (decolorization) of effluents originated directly from the dyeing bath before entering the equalization tank. In this way, only a small fraction (~10%) of the entire discharge volume will be treated, which means saving money and energy. Thus, it was investigated the feasibility of removing dyes from the dyeing reactor of a Greek dyeing industry by adsorption onto various polymeric adsorbents (chitosan).

Adsorbents

Cross-linked non-grafted chitosan beads (Ch)





Cross-linked N-vinylamido-grafted chitosan beads (Ch-g-VID)

Cotton textiles Desizing Washing Equalization tank Scouring Mercerizing Dyeing reactor Dyeing partners (-10) Partners (-10) Dyeing bath

Experimental Procedure

Effect of dosage

UV-Vis analysis

1-10 g/L adsorbent 50 mL dye solution (700 mg/L) pH=free(~10) 24 h contact, T=25 °C, 160 rpm

Reuse

Optimum adsorption conditions with pH=free Optimum desorption conditions with pH=10

Kinetic studies

1 g/L sorbent 50 mL dye solution (700 mg/L) pH=free(~10), T=25 °C,160 rpm 5-30 min and 1-24 h contact Fixed time samples collection UV-Vis analysis

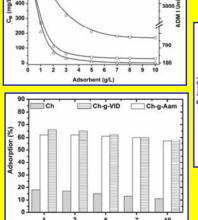
Effect of pH on desorption

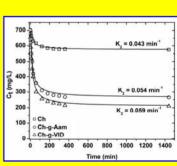
~1 g/L adsorbent

50 mL eluant solution pH=2-12 24 h contact, T=25 °C, 160 rpm UV-Vis analysis

Results and Discussion

Ch-q-VID





Conclusions

Cycles Adsorption - Desorption

- •Although the maximum adsorption behavior was at pH=2, adsorption capacity remains high at the original pH (-10) of the effluent.
- Adsorption-desorption experiments were realized at natural pH=10 in 10 cycles without significant loss of the adsorption capacity of the material, and presenting low-swelling percentages (~35%).
- •Only Ch-g-VID could satisfactorily reduce the dye concentration of the effluent below the limit of 300 ADMI units, when employing a dosage of adsorbent higher of 5 g/L.
- •All the previous suggest that Ch-g-VID is an adsorbent, which can be effectively used in the technology of the wastewater treatment.

CERTIFICATE OF ATTENDANCE

We certify that Dr. George Z. Kyzos has participated in the

IWA REGIONAL CONFERENCE ON "Wastewater Purification & Reuse"

which has taken place in Greece, in Heraklion of Crete from 28th to 30th of March 2012,

.....

Mr C. Papamattheakis

Municipal Enterprise for Water and Wastewater of Heraklion Dr T. Manios

Technological Educational Institute of

Prof. N. Kalogerakis

Technical University of Crete

Organised by:



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