

# 10<sup>th</sup> HELLENIC POLYMER SOCIETY CONFERENCE

with international participation



4 - 6

December 2014  
Patras, Greece



*The conference is dedicated to the memory of  
Prof. **Anastasios Dondos**,  
Prof. **Ioannis Mikroyannidis** and Prof. **Nikos Kalfoglou***

## POSTER SESSION

### Applications of Polymeric Materials

- |     |  |
|-----|--|
| P1  | <b>Zoi Terzopoulou</b> , D. Bikiaris, D. Lampropoulou<br>Department of Chemistry, Aristotle Univ. of Thessaloniki<br><i>Synthesis and evaluation of molecularly imprinted polymeric fibers for the selective separation of abacavir sulfate as pharmaceutical compound</i>   |
| P2  | <b>Vasilis T. Koukountzis</b> <sup>1,2</sup> , G. Ch. Lainioti <sup>1</sup> , G. A. Voyiatzis <sup>2</sup> , J. K. Kallitsis <sup>1,2</sup><br><sup>1</sup> Department of Chemistry, Univ. of Patras, <sup>2</sup> FORTH/ICE-HT, Patras<br><i>Flame-retardant coatings based on magnesium hydroxide and phosphorus compounds for wood applications</i>   |
| P3  | <b>Athanasios Katsouras</b> , C. L. Chochos and A. Avgeropoulos<br>Department of Materials Science Engineering, Univ. of Ioannina<br><i>High band gap indacenodithiophene and indacenodithienothiophene copolymers as electron donors in organic photovoltaics</i>   |
| P4  | D. Druvari, N. D. Koromilas, <b>Georgia Ch. Lainioti</b> , G. Bokias, J. K. Kallitsis<br>Department of Chemistry, Univ. of Patras<br><i>Preparation of PSF blends with polymers bearing biocidal groups</i>  |
| P5  | <b>Dionysia N. Saranti-Karamesini</b> <sup>1,2</sup> , K. D. Papadimitriou <sup>1</sup> , I. Thanasoula <sup>1</sup> , V. Deimede <sup>1</sup> , J. Kallitsis <sup>1,2</sup><br><sup>1</sup> Department of Chemistry, Univ. of Patras, <sup>2</sup> FORTH/ICE-HT, Patras<br><i>Thermal cross-linking of double bond side functionalized aromatic copolymers</i>  |
| P6  | <b>Miltiadis Zamparas</b> <sup>1</sup> , V. Bekiari <sup>1</sup> and G. Bokias <sup>2</sup><br><sup>1</sup> Department of Fisheries and Aquaculture Technology, Technological Educational Institute of Western Greece, <sup>2</sup> Department of Chemistry, Univ. of Patras <i>Ionic hydrogels as potential sorbent materials of inorganic nitrogen nutrients</i>   |
| P7  | <b>Georgios Linardatos</b> <sup>1</sup> , V. Bekiari <sup>1</sup> and G. Bokias <sup>2</sup><br><sup>1</sup> Department of Fisheries and Aquaculture Technology, Technological Educational Institute of Western Greece, <sup>2</sup> Department of Chemistry, Univ. of Patras<br><i>Anionic hydrogels as potential sorbent materials of organic and inorganic positively charged pollutants</i>  |
| P8  | <b>Konstantinos Nikolaou</b> <sup>1</sup> , N. Koromilas <sup>2</sup> , G. Bokias <sup>2</sup> , P. Avramidis <sup>3</sup> , G. Hotos <sup>1</sup> , V. Bekiari <sup>1</sup><br><sup>1</sup> Department of Fisheries and Aquaculture Technology, Technological Educational Institute of Western Greece, <sup>2</sup> Department of Chemistry, Univ. of Patras, <sup>3</sup> Department of Geology, Univ. of Patras<br><i>Monitor the action of biocidal polymers under accelerated biofouling conditions</i>   |
| P9  | A. Plomaritis, M. Kostoglou, J. Lioumbas, <b>T.D. Karapantsios</b> , P. Xidas, K. Triantafyllidis, D. Bikiaris<br>School of Chemistry, Aristotle Univ. of Thessaloniki<br><i>Innovative device for measuring the thermal conductivity of polymeric materials of high heterogeneity and uneven surface</i>  |
| P10 | G. Z. Kyzas <sup>1</sup> , <b>Panoraia I. Siafaka</b> <sup>1</sup> , E. G. Pavlidou <sup>2</sup> , K. J. Chrissafis <sup>2</sup> , D. N. Bikiaris <sup>1</sup><br><sup>1</sup> Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle Univ. of Thessaloniki, <sup>2</sup> Laboratory of Solid State Physics, Department of Physics, Aristotle Univ. of Thessaloniki<br><i>Simultaneous adsorption of basic dye and heavy metal onto succinyl-grafted chitosan from wastewaters</i> |
| P11 | X. Tsilimigkra <sup>1</sup> , A. Baltopoulos <sup>1</sup> , A. Kotrotsos <sup>1</sup> , N. Siakavellas <sup>2</sup> , <b>V. Kostopoulos</b> <sup>1</sup><br><sup>1</sup> Applied Mechanics Lab., <sup>2</sup> Nuclear Technology Lab., <sup>1,2</sup> Department of Mechanical Engineering & Aeronautics, Univ. of Patras<br><i>Strategies and feasibility study on developing vascular networks in structural polymer composites</i>  |
| P12 | <b>Polyxeni Dimoka</b> , D.E.Vlachos, N. Athanasopoulos, A. Kotrotsos, K. Antoniadis, V. Kostopoulos<br>Applied Mechanics Laboratory, Department of Mechanical Engineering and Aeronautics, Univ. of Patras<br><i>Self-heating composite molds for the "green" manufacturing of composite components</i>   |
| P13 | <b>Anastasia Meristoudi</b> <sup>1</sup> , S. Pispas <sup>1</sup> , A. Christopoulos <sup>2</sup> , G. Tsamasphyros <sup>2</sup><br><sup>1</sup> Theoretical and Physical Chemistry Institute, NHRF, <sup>2</sup> Department of Applied Mechanics, Faculty of Applied Mathematics and Physics, National Technical Univ. of Athens<br><i>Self-healing polymer materials based on multifunctional furan and maleimide compounds</i>  |

# Simultaneous adsorption of basic dye and heavy metal onto succinyl-grafted chitosan from wastewaters

George Z. Kyzas<sup>1</sup>, **Panoraia I. Siafaka**<sup>1</sup>, Eleni G. Pavlidou<sup>2</sup>, Konstantinos J. Chrissafis<sup>2</sup>, Dimitrios N. Bikiaris<sup>1</sup>

<sup>1</sup>Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece

<sup>2</sup>Laboratory of Solid State Physics, Department of Physics, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece

psiafaka@chem.auth.gr

## ABSTRACT SUMMARY:

In this work, a grafted (with carboxylic groups) chitosan material was synthesized and the adsorption mechanism of a basic dye (Remarcyl Red TGL denoted as CR) and a heavy metal (zinc ions denoted as Zn) was investigated both in single-component and binary solutions. Succinyl-grafted chitosan (CSUC) was completely characterized using various techniques as SEM, XRD, and TGA, while the variety of adsorption interactions dominated in different pH-conditions (electrostatic forces, hydrogen bonding, chelation, simple diffusion phenomena etc) were confirmed with FTIR spectroscopy.

## INTRODUCTION:

Recent years researchers are focused on investigating the removal of either dyes or heavy metals from industrial effluents. Both of those two pollutants play an important role to the phenomenon known as “environmental pollution”. Many industries (employed with dyestuffs, textile, paper and plastics) use dyes in order to colorize their products and also consume substantial volumes of water generating a considerable amount of colored wastewaters. Although over 100,000 commercially available dyes exist and more than  $7 \times 10^5$  tons are produced annually, the most studied dye classes are reactive and basic ones. The dye loss from the dyeing process to the effluent is estimated 10-50% for reactive dyes and 0-5% for basic ones. However, that small percentage of basic dyes along with their high toxicity and carcinogenesis characterize them as the number one target-for-removal.

Waste streams from metal cleaning and plating facilities, mining, corrosion and electronic device manufactures may contain considerable amount of toxic heavy metals. So, the presence of heavy metal ions in industrial effluents and drinking water resources is also relevant due to its toxicological profile and potential impacts on the human health and environment. Amongst the numerous techniques regarding the removal of

environmental pollutants, adsorption has been found to be a superior technique as compared to other methods of wastewater treatment in terms of cost, simplicity of design and operation, availability, effectiveness, and insensitivity to toxic substances. Adsorption, as one of the most promising techniques, ++be used to remove different types of pollutants and especially dyes and heavy metals.

In recent literature, numerous works have been published studying the removal of dyes or heavy metals from single-component solutions. However, only few of them focus on adsorption of either dyes or metals in multi-component aqueous systems (in each case two or more same-type pollutant). Even smaller number of works has been published regarding the simultaneous removal of both dyes and metals from effluents. The need of the study of simultaneous removal of dyes and ions is obvious given the extended co-existence of both of them in large amounts of wastes (and mainly industrial effluents).

The selection of CSUC material was based on the already experience of our research team with the use of chitosan as adsorbent for environmental pollutants (i.e., dyes, heavy metals, drugs) in line with the extensive bibliographic report for the impressive results of chitosan as adsorbent.

In the present study, the modification of chitosan was achieved by grafting the carboxylic groups of succinic anhydride onto chitosan backbone. The final product is denoted here after as CSUC. As heavy metal ion (target pollutant), Zn(II) was selected because of its widespread existence in aqueous media (effluents etc). Zinc is most often found in plating and galvanizing operations. Material's characterization includes various techniques as SEM, FTIR, XRD, and TGA. Major adsorption factors were investigated as the effect of pH, contact time, and initial pollutant's concentration (dye or metal in single-component solutions and simultaneous existence in binary aqueous mixtures). In order to study the behavior of CSUC in the simultaneous removal of metal and dye (synergetic or antagonistic), selectivity

experiments in binary mixtures were also carried out. The regeneration of adsorbents was investigated with 40 stages of adsorption and desorption (reuse cycles).<sup>1-5</sup>

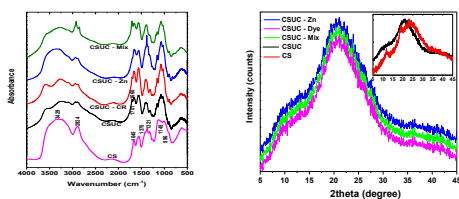
## EXPERIMENTAL METHODS:

**Preparation of adsorbents.** The synthesis of CSUC was mainly based on Hirano and Moriyasu method,<sup>6</sup> but modifying some ratios. Briefly, 3 g of chitosan were dissolved in aqueous acetic acid solution (6% v/v). The solution was diluted with 300 mL of methanol and the mixture was stirred for 1 h. 4 g of succinic anhydride were dissolved in 100 mL of acetone and this solution was added to the chitosan solution prepared above for 30 min at 25°C. Then, the reaction was allowed to continue at room temperature for 18 h. The obtained viscous solution was diluted with 400 mL of deionized water and the pH was adjusted to 10 (using 2M NaOH solution). The product was washed several times with water: acetone mixture (50:50) and the solution was freeze-dried after dialysis for 5 days. The final product obtained (CSUC) seemed like cotton-white material.

The particle size of the prepared CSUC was in the range of 950-1025  $\mu\text{m}$ . Its scheme was like rigid flakes. The final grafting percentage (GP, %) of SUC in CSUC was 47%.

## RESULTS AND DISCUSSION:

The structures of CS and CSUC were confirmed by FTIR spectra (Figure 1a).



**Figure 1.a)** FTIR spectra of CS, CSUC, and CSUC after CR, Zn, and Mix adsorption. **b)** X-ray diffraction (XRD) patterns of CSUC after Zn, CR and Mix adsorption. (Inset: X-ray diffraction (XRD) patterns of CS and CSUC before adsorption).

In the case of CS, a broad band at  $3429\text{ cm}^{-1}$  is attributed to the stretching of  $-\text{OH}$  and  $-\text{NH}_2$  groups. Amino groups should give two characteristic peaks between  $3070\text{--}3300\text{ cm}^{-1}$  but due to the strong absorption of  $-\text{OH}$  groups and the existed water traces, all groups are merged into one broad peak. A band at  $2924\text{ cm}^{-1}$  corresponds to the stretching of  $\text{C-H}$  groups, comparing the spectrum of grafted (CSUC) with

that of neat chitosan (CS), one new peak appears. This peak at  $1701\text{ cm}^{-1}$  (appeared as shoulder) corresponds to the carbonyl group that was attached to chitosan by adding the succinic anhydride. The stronger adsorption of the amide I ( $1660\text{ cm}^{-1}$ ) and amide II peak ( $1568\text{ cm}^{-1}$ ) indicates the successful succinylation of chitosan.

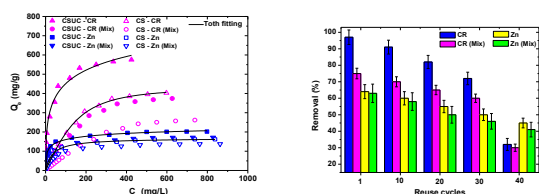
Figure 1b shows the XRD profiles of the materials after CR, Zn, and Mix adsorption, while the inset shows the XRD patterns of CSUC and neat chitosan (CS). The XRD pattern of CS presents two typical peaks at between  $10\text{--}12^\circ$  and  $20.3^\circ$ , which are typical fingerprints of semi-crystalline chitosan. In the case of CSUC, the crystalline peak at  $10\text{--}12^\circ$  is not observed, unlike the peak at  $20.3^\circ$ , which exists in broader limits. Furthermore, all patterns of metal-loaded CSUC (both CSUC-Zn and CSUC-Mix) show amorphous structure. This fact can be attributed to the adsorption mechanisms dominated (chelation, electrostatic interactions etc) between adsorbents and metals.

### Adsorption of pollutants

Isotherms for the adsorption in CS and CSUC are illustrated in Figure 3a. In particular, in the case of CR removal the neat chitosan (CS) presents  $Q_{\text{max}} = 472\text{ mg/g}$ , while after grafting the respective value was  $857\text{ mg/g}$ , which corresponds to  $\sim 82\%$  increase. The latter reveals that the main adsorption interaction is the electrostatic interaction between deprotonated carboxylic groups of chitosan and positively charged groups of CR ( $\equiv \text{N}^+$ ). The grafting of carboxylic groups also affects the Zn removal from single-component solutions, representing an increase of 47% (from  $167\text{ mg/g}$  for CS to  $245\text{ mg/g}$  for CSUC). In the case of binary solution, the conditions are more complex and consequently the effect of grafting is complicated. Similarly, the simultaneous removal of Zn and CR from solutions was larger for CSUC ( $443\text{ mg/g}$  for CR and  $179\text{ mg/g}$  for Zn) compared to that for CS ( $326\text{ mg/g}$  for CR and  $142\text{ mg/g}$  for Zn). The results of reuse ability of CSUC (Fig. 2b), showed a single-component adsorption and desorption in the case of CR, the loss in the removal ability from the 1st cycle to the 10th is 6% (from 97 to 91%), while proceeding to the next stages the loss until the 20th cycle and 30th was 9 and 10%, respectively. From 30th to 40th cycle a sudden reduction (40%) of the removal ability is observed (the CR removal was 32%), implying the saturation of the adsorbent's use. Similar reuse-behavior is observed for CR removal in the simultaneous presence of Zn; On the contrary, the reuse ability of CSUC in the case of Zn adsorption



is different. The reduction was relatively mild (~5%) for all cycles (removal in 1st: 64%; 10th: 60%; 20th: 55%; 30th: 50%; 40th: 45%). Similar behavior (slight reduction of ~8%) is observed when both CR co-exist (removal in 1st: 63%; 10th: 58%; 20th: 50%; 30th: 46%; 40th: 41%). The different in reuse behavior for Zn adsorption/desorption is maybe due to come chelation reactions of zinc ions with CSUC which are milder reactions than the strong ionic electrostatic forces of CSUC-CR system.



**Figure 2.a)** Isotherms (fitting to L-F equation) for the adsorption onto CS and CSUC of CR, Zn, and Mix **b)** Cycles of adsorption-desorption for the reuse of CSUC as super-adsorbent for CR, Zn, and MIX adsorption

#### CONCLUSIONS:

The use of succinyl-grafted chitosan as multi-adsorbent for simultaneous removal of zinc and cationic/basic dye from effluents was investigated. The adsorption experiments showed a strong increase of maximum adsorption capacity of the material after grafting (CSUC) both for

single-component solutions (either CR or Zn) and mixture (Mix). The interesting concluding remark of the nearly constant reuse behavior of the material for 40 cycles demonstrated the reuse potential of this material. The competitive adsorption phenomenon was confirmed both in SEM distribution maps of Zn, where the number of dots (traces of Zn existence) was clearly larger and more intense in the case of CSUC-Zn than in CSUC-Mix. The latter confirmed that in the case of Mix adsorption, the metal ions competed with dye molecules for possibly the same adsorption sites.

#### REFERENCES:

- [1] Zollinger, H., Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments (1987)
- [2] Pearce, C. I.; Lloyd, J. R.; Guthrie, J. T., Dyes Pigments, 58, 179 (2003).
- [3] Blackburn, R. S., Environ. Sci. Technol., 38;4905 (2004).
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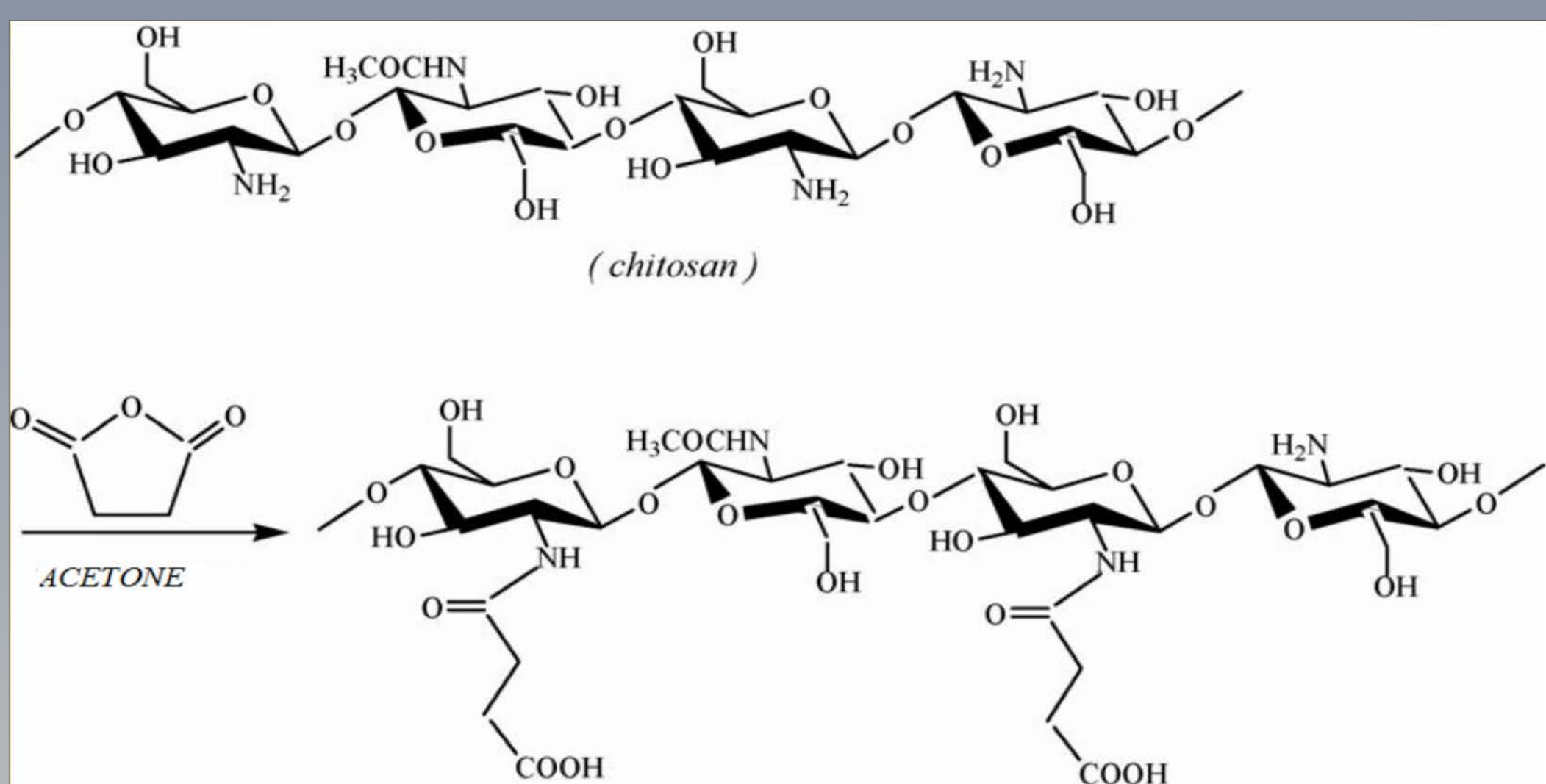
<sup>2</sup>Laboratory of Solid State Physics, Department of Physics, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece

## INTRODUCTION

Recently, researchers are focused on the removal of either dyes or heavy metals from industrial effluents. Both of those two pollutants play an important role to the global phenomenon known as “environmental pollution”.

## EXPERIMENTAL METHODS

### I. Preparation of adsorbents



The synthesis of CSUC was mainly based on Hirano and Moriyasu method, after modifying some ratios. Figure 1 shows the schematic preparation route.

Figure 1. N-succinyl-g-Chitosan

### II. Characterization of adsorbents (FT-IR, XRD studies)

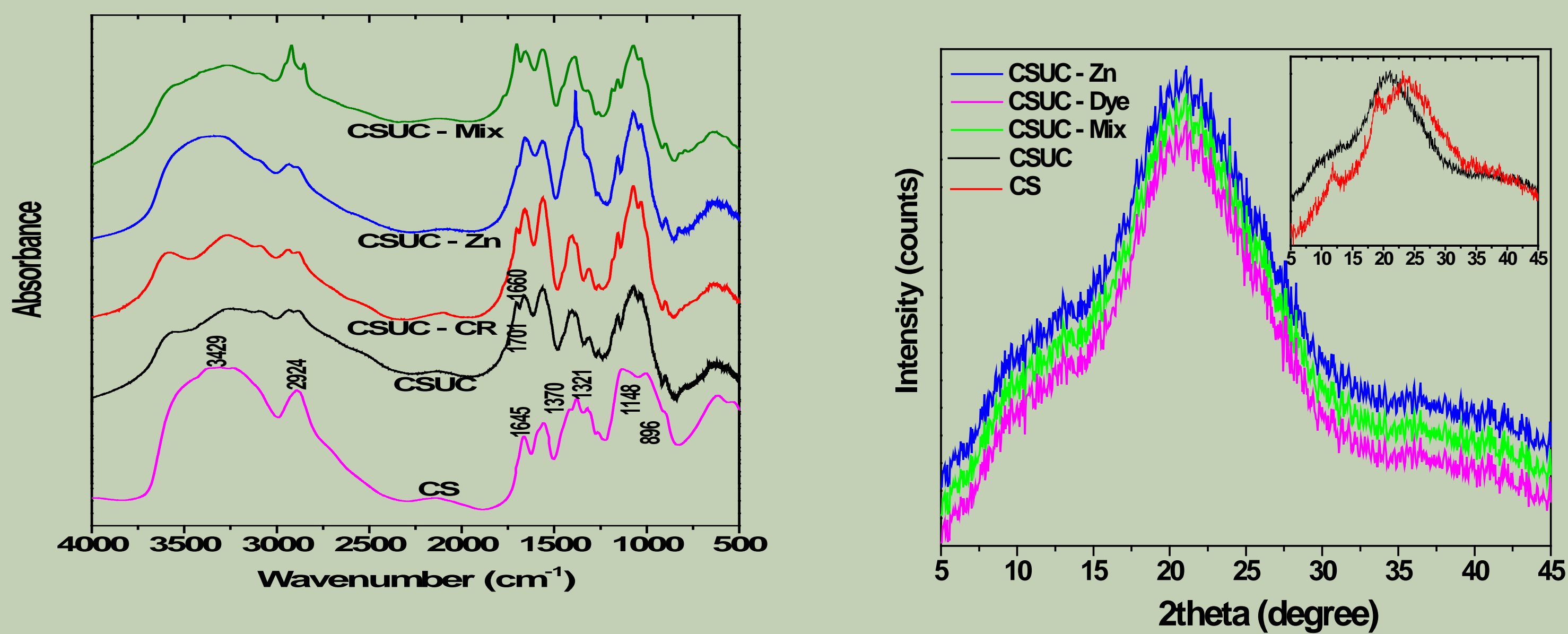


Figure 2.a) FTIR spectra of CS, CSUC, and CSUC after CR, Zn, and Mix adsorption. b) X-ray diffraction (XRD) patterns of CSUC after Zn, CR and Mix adsorption. (Inset: X-ray diffraction (XRD) patterns of CS and CSUC before adsorption).

The structures of CS and CSUC were confirmed by FTIR spectra (Figure 2a). In the case of CS, a broad band at 3429 cm<sup>-1</sup> is attributed to the stretching of -OH and -NH<sub>2</sub> groups. Comparing the spectrum of grafted (CSUC) with that of neat chitosan (CS), one new peak appears. This peak at 1701 cm<sup>-1</sup> (appeared as shoulder) corresponds to the carbonyl group that was attached to chitosan by adding the succinic anhydride. The stronger adsorption of the amide I (1660 cm<sup>-1</sup>) and amide II peak (1568 cm<sup>-1</sup>) indicates the successful succinylation of chitosan.

Figure 1b shows the XRD profiles of the materials after CR, Zn, and Mix adsorption, while the inset shows the XRD patterns of CSUC and neat chitosan (CS). The XRD pattern of CS presents two typical peaks at between 10-12° and 20.3°, which are typical fingerprints of semi-crystalline chitosan. CSUC diffractogram shows broad peak at 20.3°. Furthermore, all patterns of metal-loaded CSUC (both CSUC-Zn and CSUC-Mix) show amorphous structure. This fact can be attributed to the adsorption mechanisms dominated (chelation, electrostatic interactions etc) between adsorbents and metals.

## CONCLUSIONS

The use of succinyl-grafted chitosan as multi-adsorbent for simultaneous removal of zinc and cationic/basic dye from effluents was investigated. The adsorption experiments showed a strong increase of maximum adsorption capacity of the material after grafting (CSUC) both for single-component solutions (either CR or Zn) and mixture (Mix). The interesting concluding remark of the nearly constant reuse behavior of the material for 40 cycles demonstrated the reuse potential of this material. The competitive adsorption phenomenon was confirmed both in SEM distribution maps of Zn, where the number of dots (traces of Zn existence) was clearly larger and more intense in the case of CSUC-Zn than in CSUC-Mix. The latter confirmed that in the case of Mix adsorption, the metal ions competed with dye molecules for possibly the same adsorption sites.

## ADSORPTION EXPERIMENTS

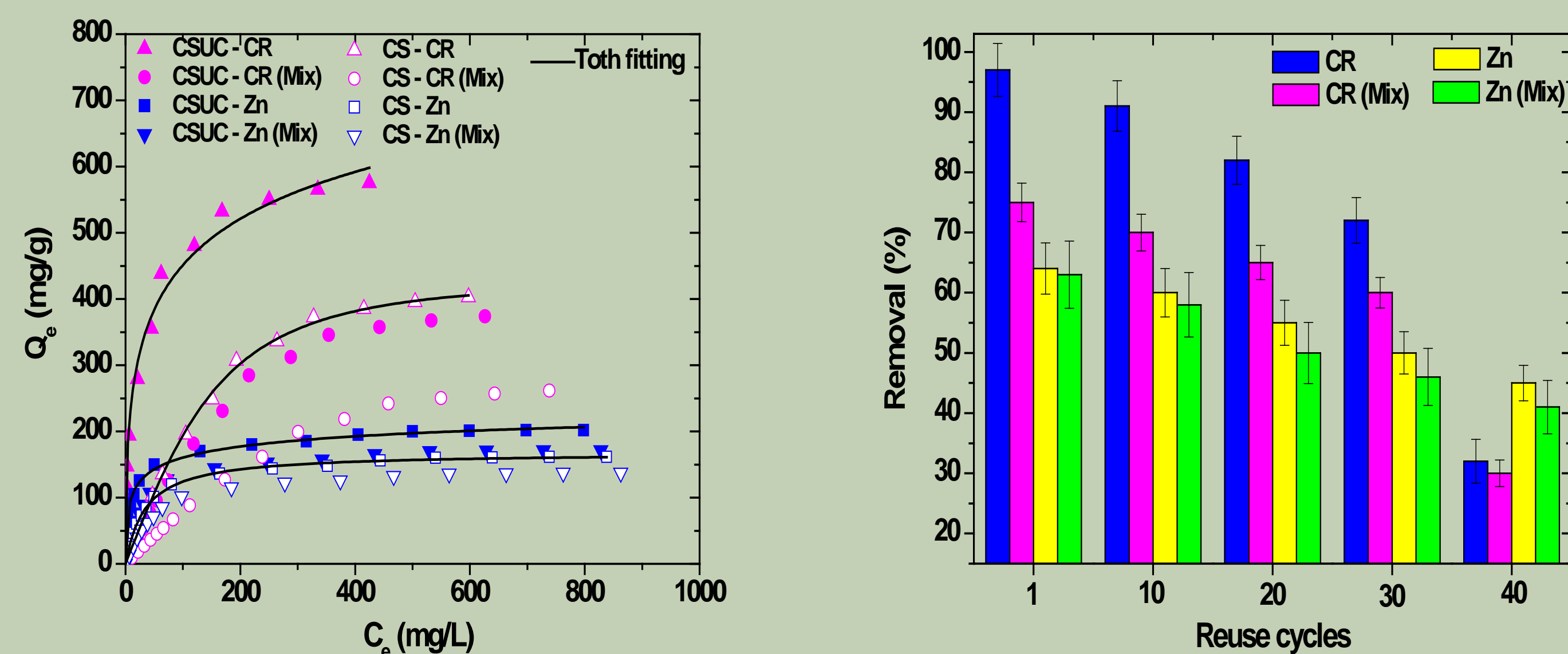
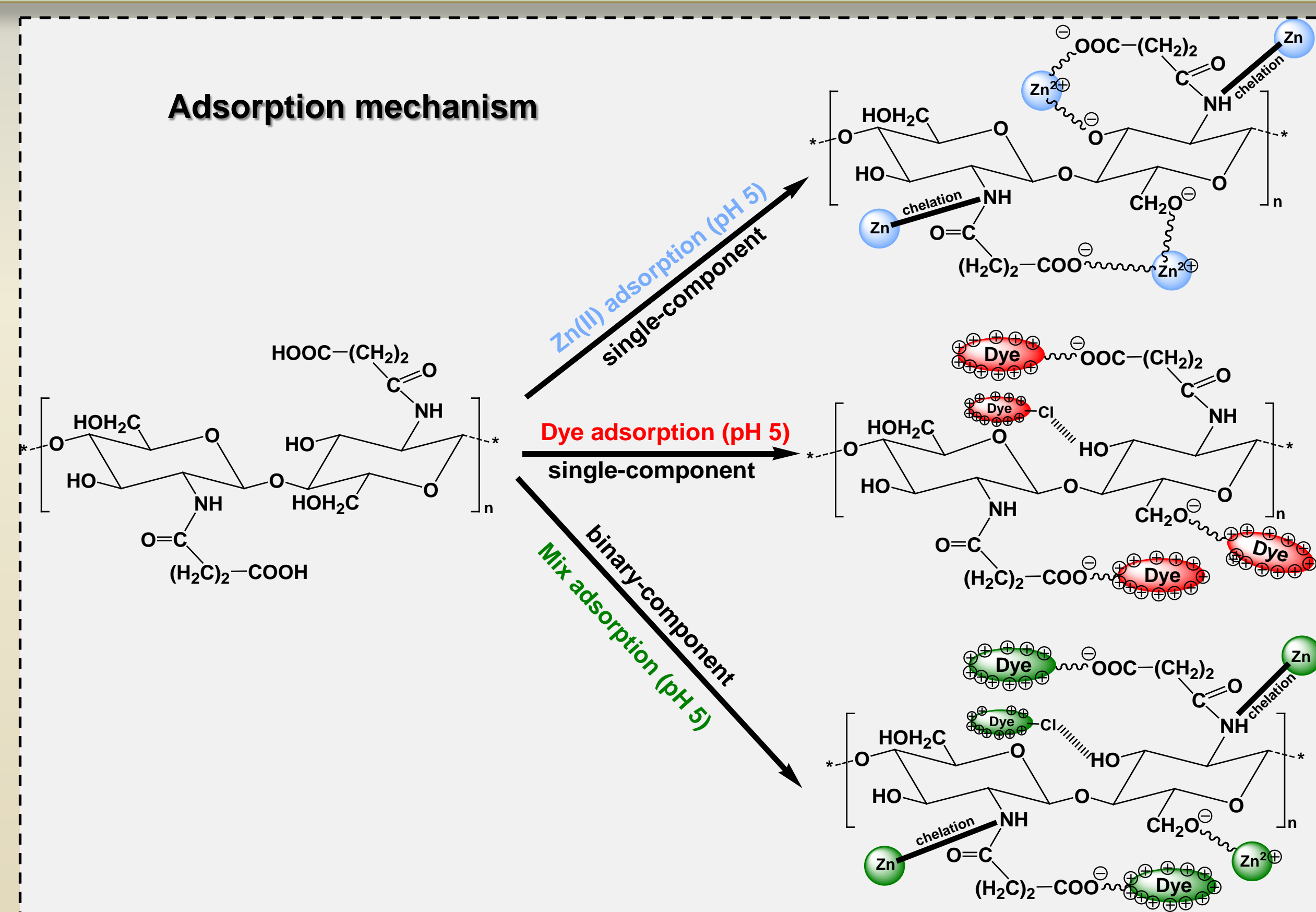


Figure 3.a) Isotherms (fitting to L-F equation) for the adsorption onto CS and CSUC of CR, Zn, and Mix b) Cycles of adsorption-desorption for the reuse of CSUC as super-adsorbent for CR, Zn, and MIX adsorption

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