# IHSS
## NATURAL ORGANIC MATTER RESEARCH
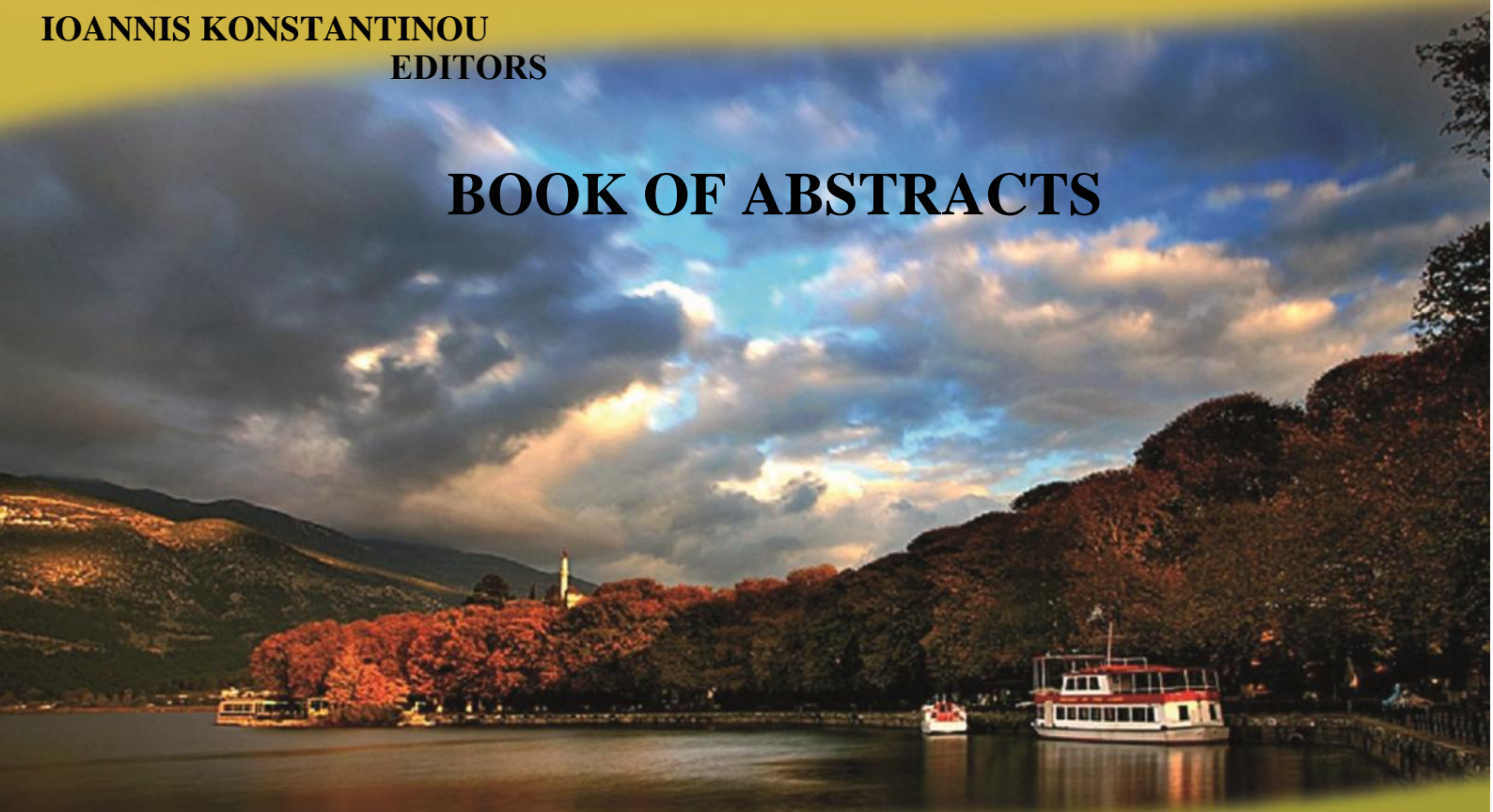
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YIANNIS DELIGIANNAKIS

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# BOOK OF ABSTRACTS

# NATURAL ORGANIC MATTER:
## *Structure-Dynamics*
## *Innovative Applications*

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# The effect of humic acid on the removal of pharmaceuticals from aqueous solutions

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**ABSTRACT SUMMARY**:
A modified chitosan (grafted with sulfonate groups and cross-linked with glutaraldehyde) was synthesized in order to examine the effect of humic acid (HA) on the adsorption equilibrium of a pharmaceutical compound. The results show that increasing the concentration of HA, the maximum adsorption capacity decreases.

**INTRODUCTION**:

Pharmaceuticals are of scientific and public concern as newly recognized classes of environmental pollutants and are receiving considerable attention with respect to their environmental fate and toxicological properties over the last 15 years. This problem is directly linked with the existence in waters/wastewaters of humic compounds and especially humic acids (HA).

Humic acid is a principal component of humic substances, which are the major organic constituents of soil (humus), peat, coal, many upland streams, dystrophic lakes, and ocean water. It is produced by biodegradation of dead organic matter. It is not a single acid; rather, it is a complex mixture of many different acids containing carboxyl and phenolate groups so that the mixture behaves functionally as a dibasic acid or, occasionally, as a tribasic acid. The presence of humic acid in water intended for potable or industrial use can have a significant impact on the treatability of that water and the success of chemical disinfection processes. Therefore, industrial effluents are even mis-treatable.

In this study, a chitosan derivative (poly-$\beta$-(1$\rightarrow$4)-2-amino-2-deoxy-D-glucose) grafted with sulfonate groups was synthesized and tested as adsorbent for the removal of a particular pharmaceutical compound; Pramipexole dihydrochloride ((6S)-N6-propyl-4,5,6,7-tetrahydro-1,3-benzothiazole-2,6-diamine, PRM) is used widely all over the world for its unique pharmaceutical activity and on the basis of recent drug usage trends [1]; therefore, treatment of wastewater by high polluted levels of PRM is required and urgent needed.

The novelty of this study is based on the co-existence of humic acids on the adsorbate (PRM) in various concentrations. Which is the effect of humic acids on the adsorbent use of chitosan derivatives? How did humic acids influence the crucial parameters of adsorption (isotherm etc)? The latter are some of crucial questions replied with this study.

**EXPERIMENTAL METHODS**:

For the synthesis of sulfonate-grafted chitosan adsorbent (CsSLF) [2], a mixture of dichloroacetic acid (5 mL) and formamide (50 mL) was added into chitosan (4.0 g) and stirred to be an homogenized solution. This was then mixed with a complex of chlorosulfonic acid-dimethylformamide and stirred for 1 h in a water bath at 50 °C. The reaction mixture was then diluted by a small quantity of deionized water, filtered, and precipitated by pouring into ethanol 95% (400 mL). The precipitate was dissolved in deionized water, neutralized by a saturated $Na_2CO_3$ solution, and dialyzed against deionized water. After dialysis, the product was dried and stored in a desiccator. Then, a cross-linking procedure was realized with GLA as reagent (0.5 wt%) at 60 °C for 1.5 h. The final grafting degree (GD) was determined on the basis of the percentage weight increase of the final product relative to the initial weight of chitosan GD = $(W_2-W_1)/W_1$ (where $W_1$ and $W_2$ denote the weight of chitosan before and after grafting reaction, respectively). So, the grafting degree was found 2.2.

Adsorption/desorption experiments were conducted in 20-mL amber vials using a batch approach. All experiments were run in duplicate. The residual concentration of PRM was measured spectrophotometrically by monitoring its UV absorbance at 263 nm (model U-2000, Hitachi). A detailed description of experimental procedure is given below, where $[PRM]_0$ (mg/L) is the initial PRM concentration, pH is the pH of the aqueous solutions (fixed with micro-additions of HCl or NaOH), T (°C) is the temperature, m (g) is the mass of the adsorbent used, V (mL) is the volume of adsorbate, N (revolutions or full rotations per minute, abbreviated as rpm ) is the agitation rate of the shaking machine and t (h) is the contact time. For all experiments three different values of HA concentrations (2.5, 5.0, 20 mg/L) were selected to investigate their influence to adsorption of PRM onto CsSLF. Effect of initial PRM concentration: $[PRM]_0$=0-500 mg/L; pH=10 (optimum value found from (i)); m=0.02 g; V=20 mL; T=25 °C; N=160 rpm; t=24 h. The equilibrium data resulted were fitted to the Langmuir-Freundlich (L-F) isotherm model [3]:

$$Q_e = \frac{Q_m bC_e^{1/n}}{1+bC_e^{1/n}}$$

where $Q_e$ (adsorbed PRM weight/adsorbent weight) is the equilibrium concentration in the solid phase; $Q_m$ is the maximum amount of adsorption (adsorbed PRM weight/adsorbent weight); b is the L-F constant; n is the L-F heterogeneity constant.

The adsorption capacity in equilibrium ($Q_e$) was calculated using the mass balance equation:

$$Q_e = \frac{(C_0 - C_e)}{\frac{V}{m}}$$

where $C_0$ and $C_e$ (PRM weight/liquid volume) are the initial and equilibrium PRM concentrations in the liquid phase, respectively.

**RESULTS AND DISCUSSION**:

The effect of grafting reactions to the physical structure and the appearance of chitosan can be observed from SEM images. All derivatives of chitosan (Cs, CsSLF) had an irregular shape owing to the grinding. The nearly total smooth surface of Cs (Fig. 1a) was changed to CsSLF. It is readily observed that the drying method caused the collapse of any porous microstructure of the particles. This is possibly due to hydrophilic interactions between the water molecules and the carboxyl, hydroxyl and amino groups on the macromolecular chains of the prepared materials. According to BET analysis, the surface area of CsSLF was $2.9\pm0.3$ m$^2$/g, while the non-grafted derivative (Cs) had only $0.9\pm0.2$ m$^2$/g. The above values belong to the typical ones of non-porous materials, as bibliographically chitosan is characterized.

In the field of swelling, CsSLF showed swelling ~300% at pH=10. The above percentages are commonly observed in chitosan adsorbents, given the powdered–nature of the adsorbents and the single cross-linking method with GLA followed in the current study (and not dual cross-linking with GLA and some ionic reagent as sodium tripolyphosphate).
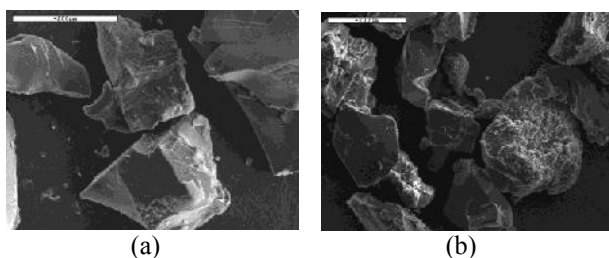


<div align="center">(a)          (b)</div>

Fig. 1: *SEM images of (a) Cs, and (b) CsSLF.*

Based on previous study, the optimum pH for the system Cs (or CsSLF) – PRM was alkaline (10). Therefore, all isotherm tests were carried out at pH=10. The most crucial parameter of each adsorbent-adsorbate system is the adsorption isotherms. The maximum theoretical adsorption capacity shows how suitable is a material for the pollutant studied. Fig. 2 shows the effect of the presence of humic acid on the adsorption isotherm of Cs. The experimental were fitted to L-F fitting. Based on L-F theoretical calculation, $Q_m$ was 181 mg/g without existence of HA in the adsorbate solution ($C_{HA}$ = 0 mg/L). However, increasing the HA concentration to 2.5 mg/L, a decrease was observed for the maximum adsorption capacity of Cs ($Q_m$ = 151 mg/g), which corresponds to 17% reduction. Increasing the HA concentration to 5.0 and 20.0 mg/L, a sharp decrease was observed for the maximum adsorption capacity of Cs ($C_{HA}$ = 5.0 mg/L: $Q_m$ = 74 mg/g, $\Delta Q_m$ = 51%; $C_{HA}$ = 20.0 mg/L: $Q_m$ = 50 mg/g, $\Delta Q_m$ = 33%). As it was shown, the after a gradual decrease in the cased of 2.5 mg/L HA, the next reduction was very intense, implying complex antagonistic interactions between HA and PRM for the adsorption onto Cs. Similar observations were taken for the case of CsSLF. ($C_{HA}$ = 0.0 mg/L: $Q_m$ = 339 mg/g; $C_{HA}$ = 2.5 mg/L: $Q_m$ = 252 mg/g, $\Delta Q_m$ = 25%; $C_{HA}$ = 5.0 mg/L: $Q_m$ = 146 mg/g, $\Delta Q_m$ = 43%; $C_{HA}$ = 20.0 mg/L: $Q_m$ = 134 mg/g, $\Delta Q_m$ = 8%).
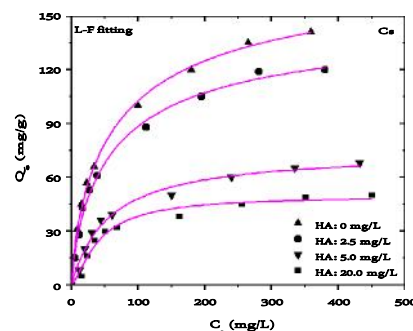


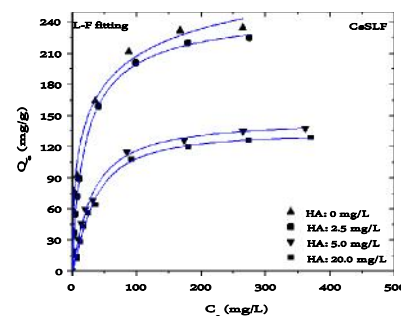Fig.2: *Isotherms of Cs under various concentrations of HA.*



Fig.3: *Isotherms of CsSLF under various concentrations of HA*

It is obvious that the phenomenon is antagonistic, but the $Q_m$ of the chitosan derivative remains high.
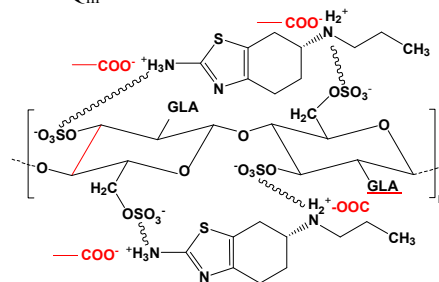


Fig.4: *Antagonistic adsorption of PRM versus HA for adsorption onto CsSLF.*

**CONCLUSIONS**:

Chitosan grafted with sulfonate groups and cross-linked with glutaraldehyde was synthesized in order to examine the effect of humic acid (HA) on the adsorption equilibrium of a pharmaceutical compound. The results show that increasing the concentration of HA, $Q_m$ decreases. The higher reduction was for CsSLF: ($C_{HA}$ = 2.5 mg/L: $\Delta Q_m$ = 25%; $C_{HA}$ = 5.0 mg/L: $\Delta Q_m$ = 43%; $C_{HA}$ = 20.0 mg/L: $\Delta Q_m$ = 8%).

**REFERENCES**:
[1] S.A. Hollingworth, et al., Pharmacoepidemiology and Drug Safety, 20 (2011) 450-456.
[2] J. Miao, et al., Desalination, 181 (2005) 173-183.
[3] C. Tien, Adsorption Calculations and Modeling, Butterworth-Heinemann, Boston, U.S.A., 1994.

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## Abstract / Aim / Novelty

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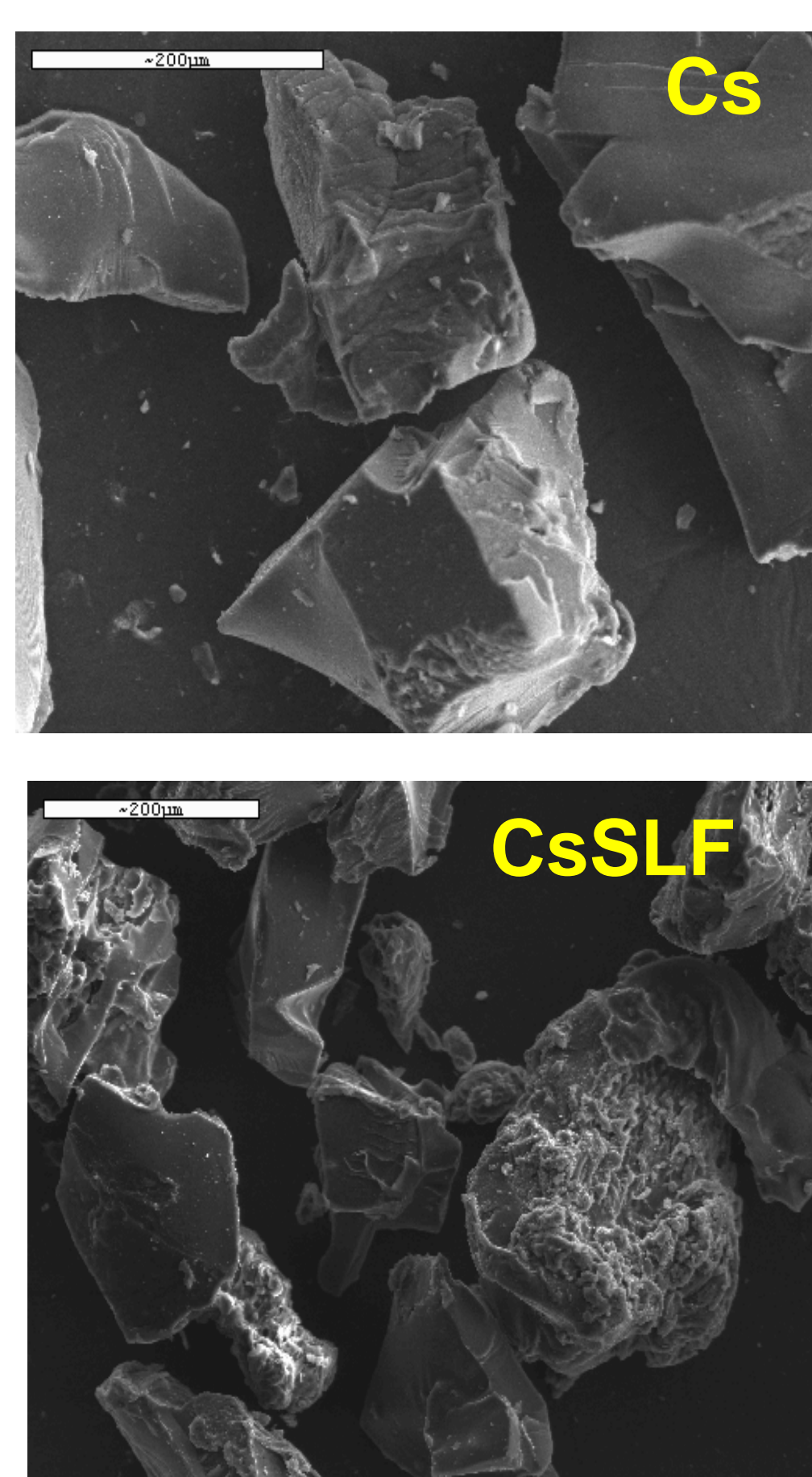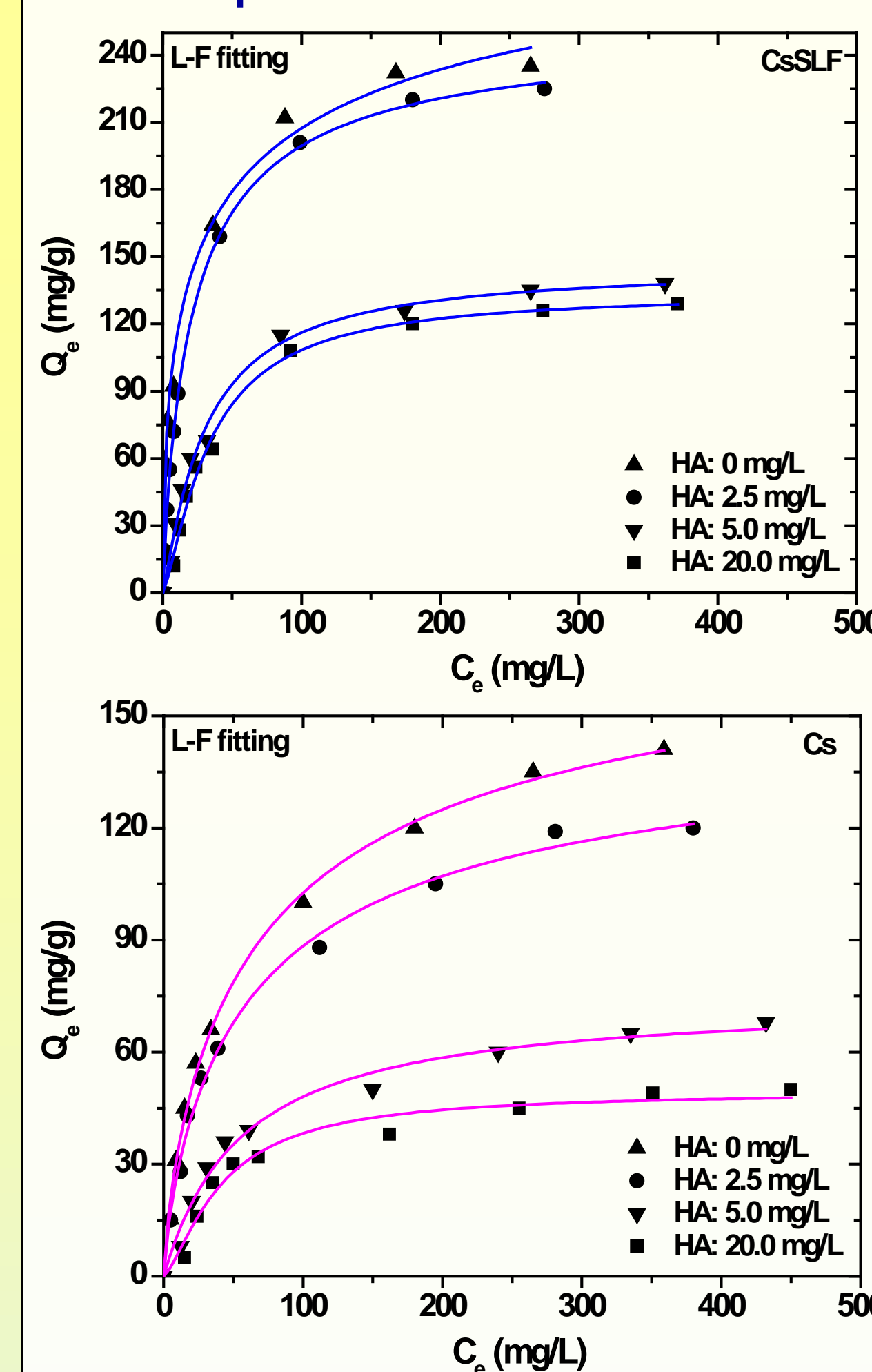

Cs


CsSLF

## Characterization

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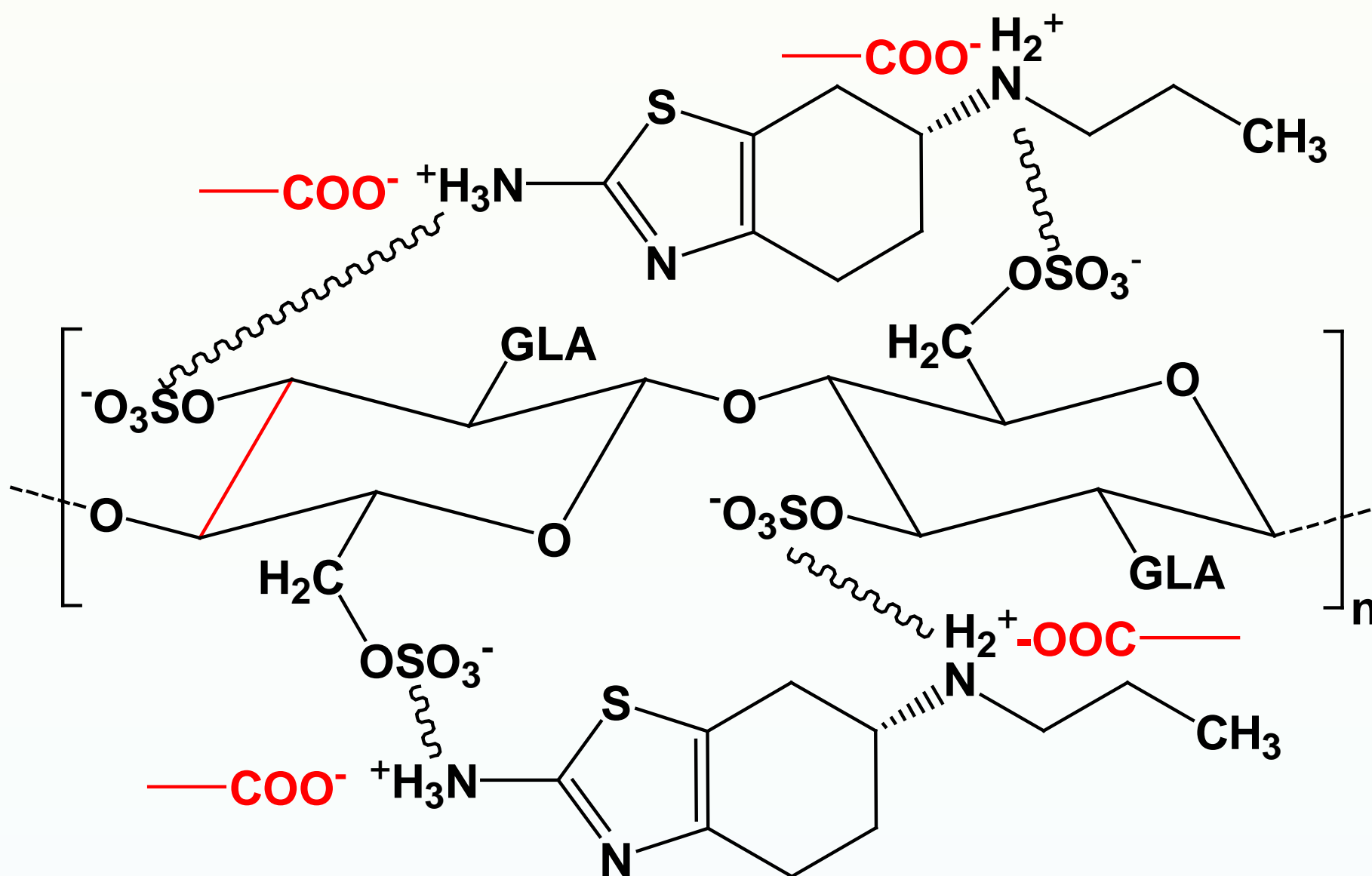
## Effect of HA on adsorption

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The experimental were fitted to L-F fitting. Based on L-F theoretical calculation, $Q_m$ was 181 mg/g without existence of HA in the adsorbate solution ($C_{HA}$ = 0 mg/L). However, increasing the HA concentration to 2.5 mg/L, a decrease was observed for the maximum adsorption capacity of Cs ($Q_m$ = 151 mg/g), which corresponds to 17% reduction. Increasing the HA concentration to 5.0 and 20.0 mg/L, a sharp decrease was observed for the maximum adsorption capacity of Cs ($C_{HA}$ = 5.0 mg/L: $Q_m$ = 74 mg/g, $\Delta Q_m$ = 51%; $C_{HA}$ = 20.0 mg/L: $Q_m$ = 50 mg/g, $\Delta Q_m$ = 33%). As it was shown, the after a gradual decrease in the cased of 2.5 mg/L HA, the next reduction was very intense, implying complex antagonistic interactions between HA and PRM for the adsorption onto Cs.

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## Acknowledgment

## Conclusions

Chitosan grafted with sulfonate groups and cross-linked with glutaraldehyde was synthesized in order to examine the effect of humic acid (HA) on the adsorption equilibrium of a pharmaceutical compound. The results show that increasing the concentration of HA, $Q_m$ decreases. The higher reduction was for CsSLF: ($C_{HA}$ = 2.5 mg/L: $\Delta Q_m$ = 25%; $C_{HA}$ = 5.0 mg/L: $\Delta Q_m$ = 43%; $C_{HA}$ = 20.0 mg/L: $\Delta Q_m$ = 8%).