

Chitosan@Succinic Acid: A green adsorbent for Diclofenac removal from wastewaters

Anastasia D. Meretoudi¹, Athanasia K. Tolkou¹, Ioanna Koumentakou¹, Rigini Papi², Dimitra A. Lambropoulou², George Z. Kyzas^{1,*}

¹ Hephaestus Laboratory, School of Chemistry, Faculty of Sciences, Democritus University of Thrace, GR-65404 Kavala, Greece

² Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece.

*Corresponding author: kyzas@chem.duth.gr; Presenting author: ameretou@chem.duth.gr

INTRODUCTION

In last decades, the interest of scientist focused on chitosan modification. Chitosan is a natural cationic polymer which is a low-cost material, non-toxic, biodegradable and offers antimicrobial and adsorbent prosperities. Moreover, chitosan provides two different functional groups, $-NH_2$ and $-COOH$ that create new chemical bonds with other smaller chemical compounds to improve mechanical properties and adsorption capacity. Many researchers studied the chitosan modification with dicarboxylic acid such as itaconic acid, citric acid, malonic acid. In this study, the modification of chitosan with a tricarboxylic acid, i.e. succinic acid, was tested. In literature there are numerous research articles that refer the chitosan modification with succinic anhydride. However, succinic acid is less toxic (succinic acid is a GRAS-approved food additive by the FDA) than succinic anhydride and make the new adsorbent Chitosan@Succinic acid (CS@SA) more environmentally friendly. In this work, CS@SA was synthesized and characterized via FTIR technique. Thereafter, CS@SA was investigated for diclofenac removal. Batch experiments evaluated the effect of pH, kinetic and isotherm studies.

Chemical structure

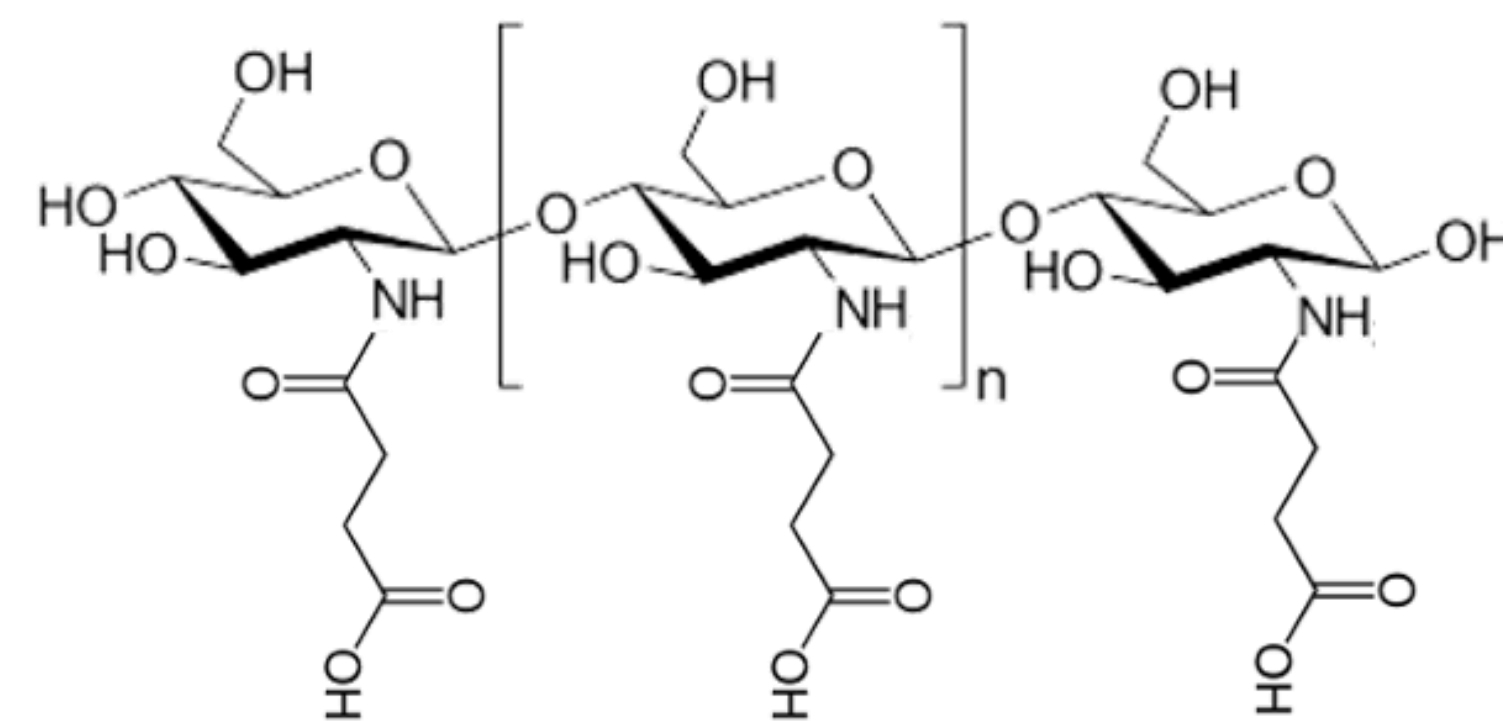


Figure 1. Chemical structure of CS@SA

RESULTS & DISCUSSION

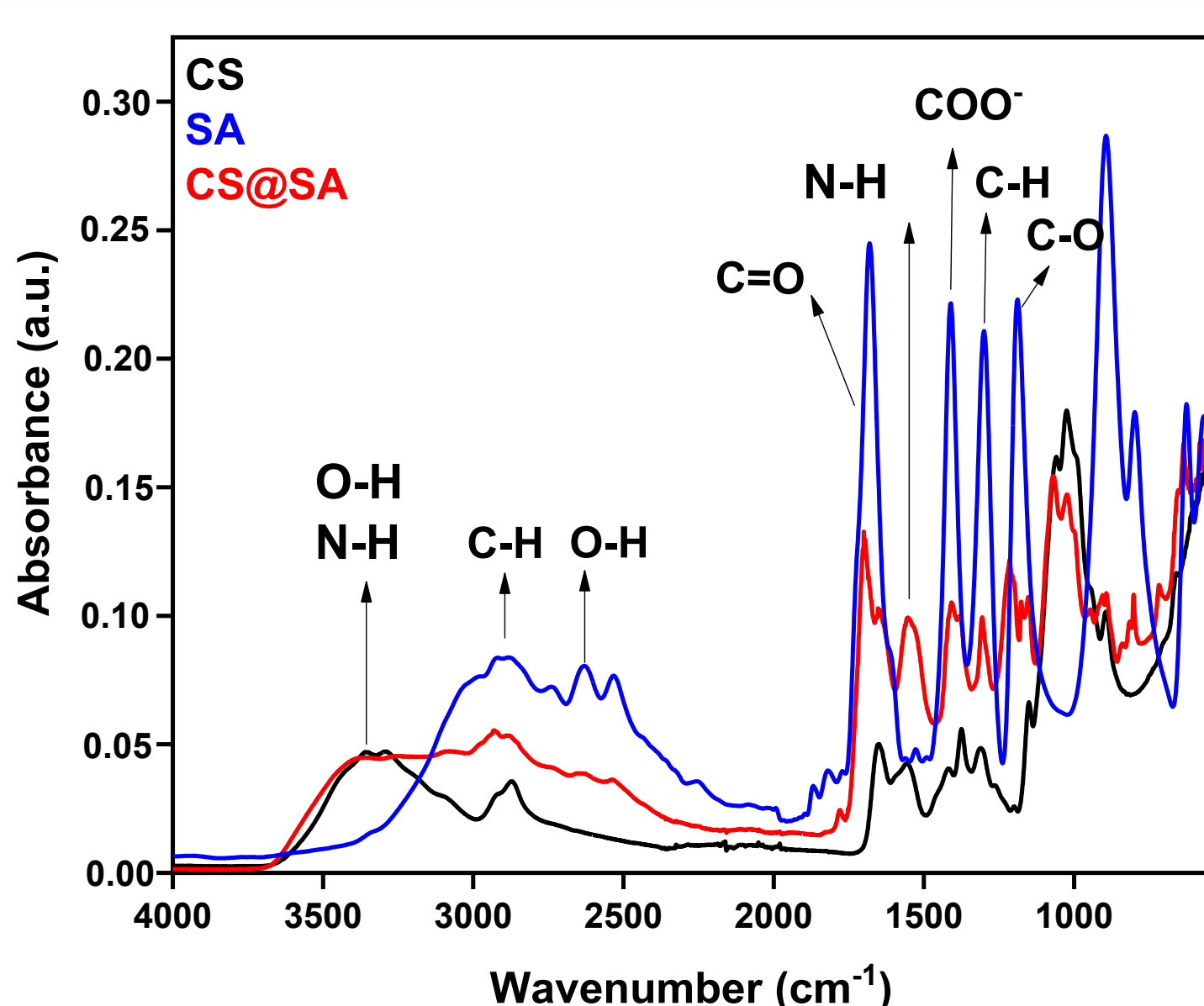


Figure 2. FTIR spectrum of CS, SA and CS@CS

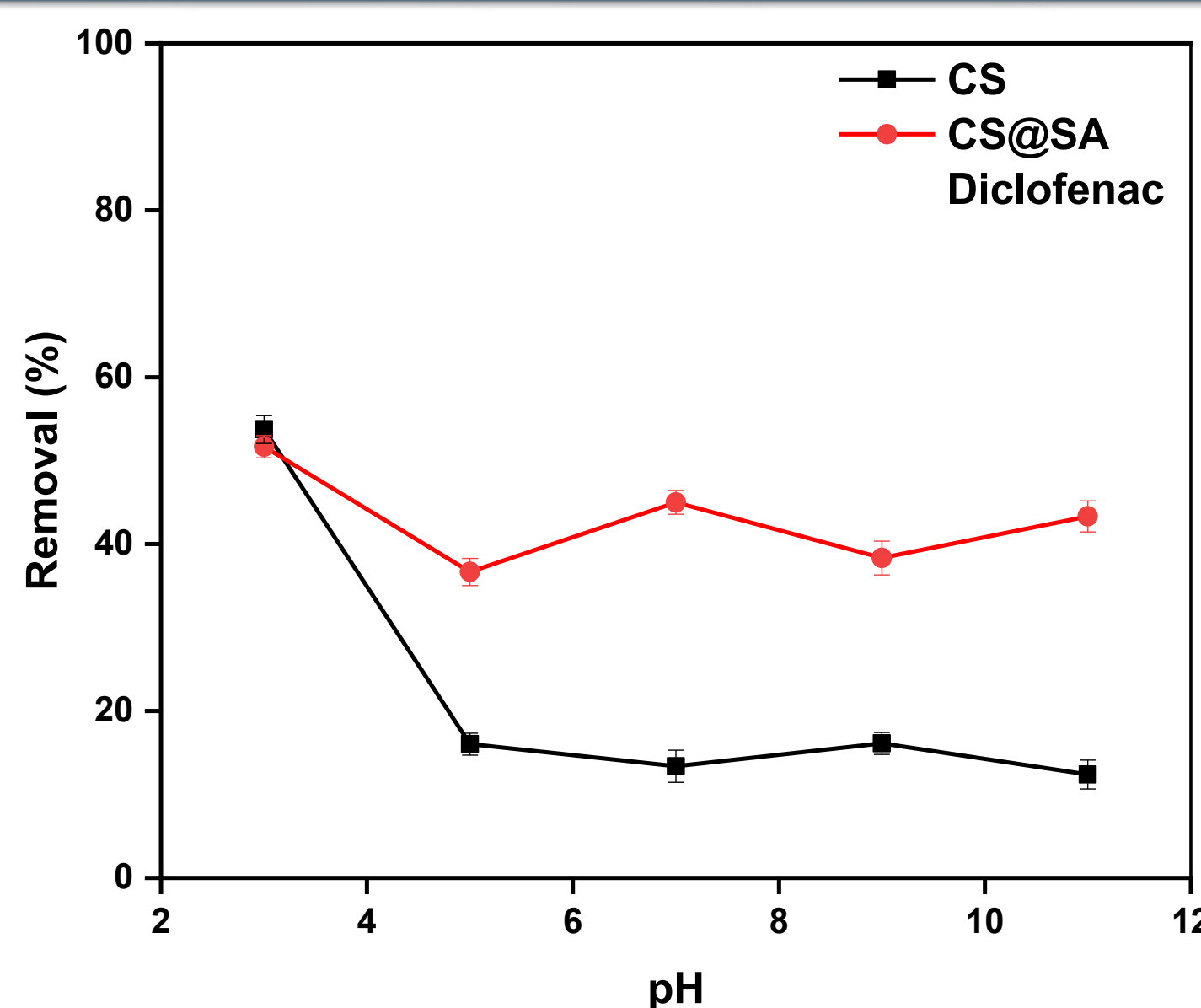


Figure 3. Effect of pH of removal diclofenac from CS and CS@SA ($C_0 = 50$ mg/L, $t = 24$ h, $T = 30^\circ\text{C}$)

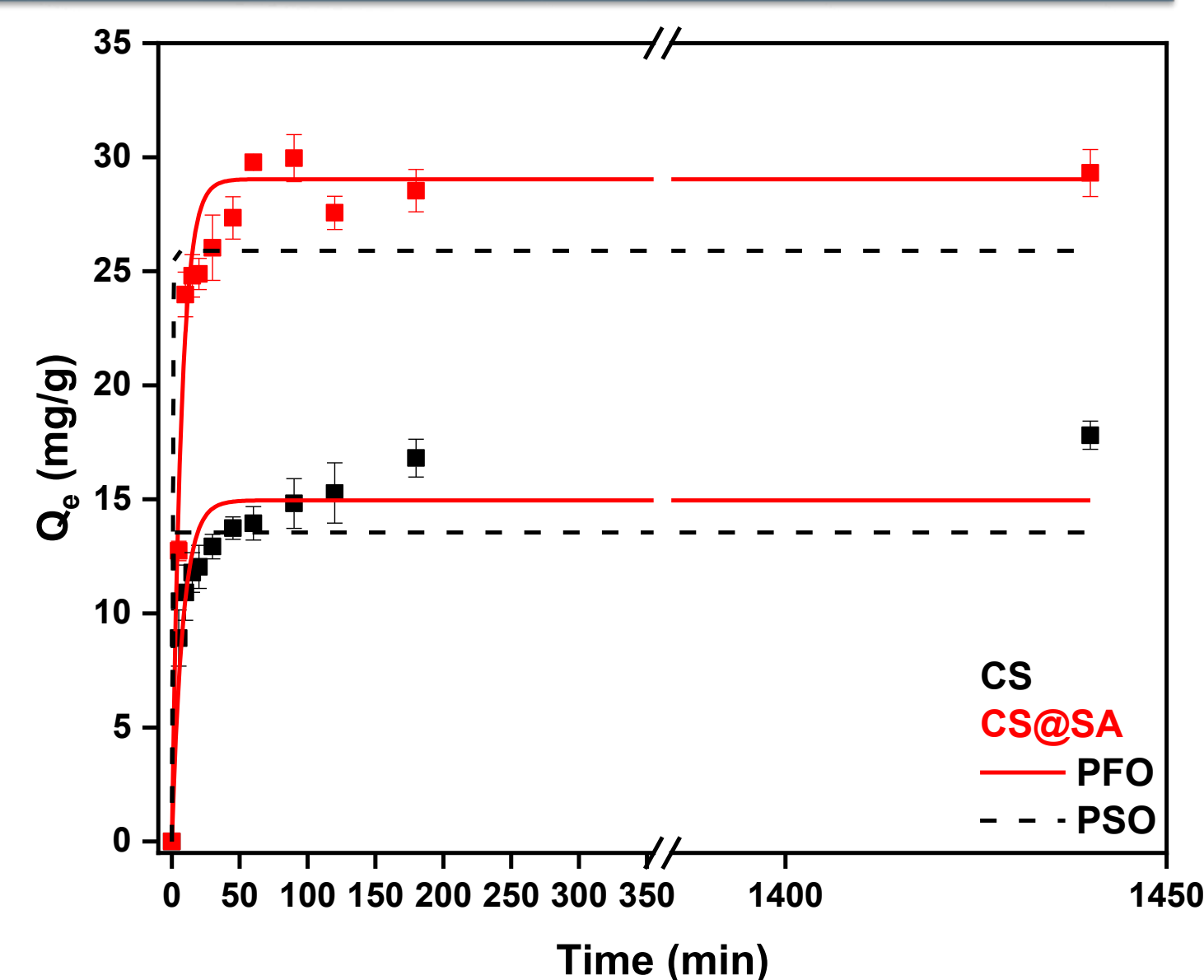


Figure 4. Contact time removal of diclofenac of CS and CS@SA adsorbents ($C_0 = 50$ mg/L, pH 7, $T = 30^\circ\text{C}$)

The FTIR analysis (Figure 2) demonstrates that the N–H bond vibration, which is absent in the SA spectrum and appears weakly in the CS spectrum, is prominently observed in the CS@SA spectrum. This vibration, recorded at 1546 cm^{-1} , confirms the formation of a chemical bond between CS and SA.

Figures 3, 4, and 5 present the results of diclofenac removal using the adsorbent materials CS and CS@SA. The maximum pollutant removal was achieved at neutral pH (Figure 4), with removal efficiencies of 13% and 45% for the respective adsorbent materials. The kinetic study (Figure 5) showed that the PFO model provided the best fit ($R^2 = 0.954$) for the CS@SA material, indicating that the process follows a physisorption mechanism. Finally, the isotherm study (Figure 6) demonstrated that the Langmuir model fits the experimental data best, confirming that the adsorption occurs as a monolayer process.

CONCLUSION

In this study, chitosan was chemically modified with succinic acid for the removal of diclofenac. FTIR spectroscopy confirmed that succinic acid was successfully grafted onto the polymeric chain of chitosan. The optimal experimental conditions were found to be pH 7 and a contact time of 120 min, following the physisorption model. The adsorption process was determined to be monolayer, with adsorption capacities of 0.78 mg/g for CS and 97 mg/g for CS@SA, respectively.

REFERENCES

- Gkika K.Á., 'Modified Chitosan Adsorbents in Pharmaceutical Simulated Wastewaters'.
- Das, Ghosh, and Pramanik, 'Chitosan Biopolymer and Its Composites'.
- Kyzas K.Á., 'Poly(Itaconic Acid)-Grafted Chitosan Adsorbents with Different Cross-Linking for Pb(II) and Cd(II) Uptake'.
- Patel, Pandey, and Uppaluri, 'Adsorption Behavior and Techno-Economic Analysis of Citric Acid-Modified Chitosan for Heavy Metal Removal from Wastewater'.
- Gomase K.Á., 'Efficient Multi-Ion Adsorption Using Chitosan-Malonic Acid Film'.
- Lima and Airolidi, 'Interaction of Copper with Chitosan and Succinic Anhydride Derivative—a Factorial Design Evaluation of the Chemisorption Process'.
- Xu K.Á., 'Adsorption and Assembly of Octenyl Succinic Anhydride Starch/Chitosan Electrostatic Complexes at Oil–Water Interface'.
- Fumagalli and Updated by Staff, 'Succinic Acid and Succinic Anhydride'.

ACKNOWLEDGMENT

We acknowledge support of this work by the project “Advanced Nanostructured Materials for Sustainable Growth: Green Energy Production/Storage, Energy Saving and Environmental Remediation” (TAEDR-0535821) which is implemented under the action “Flagship actions in interdisciplinary scientific fields with a special focus on the productive fabric” (ID 16618), Greece 2.0 – National Recovery and Resilience Fund and funded by European Union NextGenerationEU.