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Adsorption of sodium diclofenac by chitosan with various electron-withdrawing substituents

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Introduction

Pharmaceutical compounds are increasingly recognized as emerging contaminants due to their continuous release into aquatic environments and their persistence in conventional wastewater treatment systems [1,2]. In this work, chitosan was chemically modified using three electrophilic reagents to introduce diester (DEEM), ester-nitrile (ECEA), and dinitrile (EMM) substituents [3], generating derivatives with progressively increasing degrees of substitution (Figure 1).

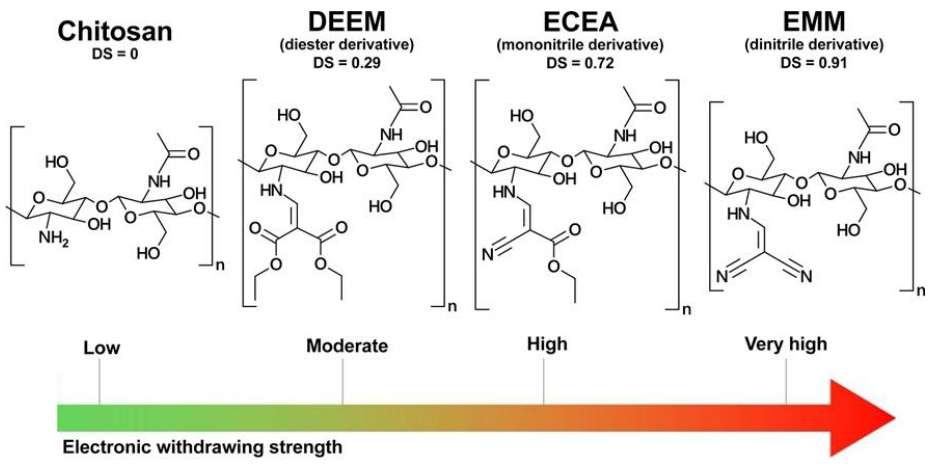


Figure 1. Schematic representation of chitosan and its derivatives with increasing electronic withdrawing character.

Objectives

The chitosan derivatives were evaluated as adsorbents for sodium diclofenac in aqueous solution, with the aim of establishing a direct correlation between functional group density and adsorption performance.

Methodology

Batch adsorption experiments were conducted using 25 mg of adsorbent dispersed in 25 mL of Sodium Diclofenac solution (adsorbent dosage: 1 $g \cdot L^{-1}$). All suspensions were agitated in Erlenmeyer flasks using an orbital shaker (150 rpm) at 25 °C for 24 h. For isotherm studies, ten initial diclofenac concentrations were investigated for each chitosan derivative. The concentration range was selected to adequately capture both low-coverage and near-saturation regimes (4-500 $mg \cdot L^{-1}$). Equilibrium adsorption data were analyzed using nonlinear least squares regression without linearization. The Langmuir, Freundlich, and Sips models were employed to describe adsorption isotherms.

References

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Results

The adsorption isotherms of sodium diclofenac onto pristine and modified chitosan materials revealed a pronounced dependence on functional group density (Table 1).

Table 1. Maximum removal efficiency of sodium diclofenac for pristine and modified chitosan derivatives under the investigated conditions.

Material	C_0 ($mg \cdot g^{-1}$)	Removal
Chitosan	353.12	2.381 ± 0.003 %
DEEM	268.37	9.06 ± 0.07 %
ECEA	477	32.31 ± 0.03 %
EMM	206.78	70 ± 0.8 %

The experimental equilibrium capacity increased markedly with progressive electronic modulation of the chitosan backbone through the incorporation of electron-withdrawing substituents, following the order: Chitosan < DEEM < ECEA < EMM (Figure 2).

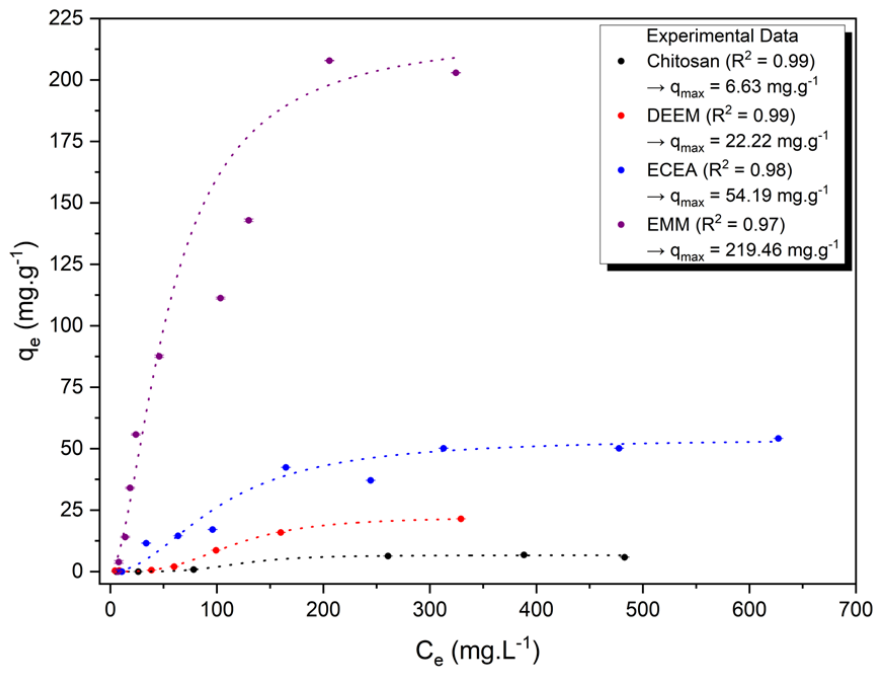


Figure 2. Adsorption isotherms of sodium diclofenac onto pristine chitosan and its derivatives. Symbols represent experimental data, and dotted lines correspond to Sips model fitting.

Conclusions

The present study indicates that progressive chemical functionalization of chitosan with electron-withdrawing substituents substantially enhances diclofenac adsorption under near-neutral conditions. The incorporation of ester- and nitrile-containing groups produced a marked increase in adsorption capacity and affinity, culminating in a maximum experimental q_e of 207.88 $mg \cdot g^{-1}$ for the highly substituted EMM derivative.

Acknowledgments

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