Supporting Information

Chitosan Deposited onto Fumed Silica Surface as Sustainable Hybrid Biosorbent for Acid Orange 8 Dye Capture: Effect of Temperature in Adsorption Equilibrium and Kinetics

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FTIR analysis

FTIR spectra of the initial chitosan and synthesized composite were obtained in order to confirm the chitosan coating formation on the surface of fumed silica (Figure S1). In the FTIR spectrum of chitosan, the band at 3429 cm^{-1} corresponds to the stretching vibrations O–H of hydroxyl groups bound with carbon atoms. Intensive absorption bands at 2800 to 3000 cm^{-1} are observed due to the C–H stretching vibrations. The band at 1580 cm^{-1} corresponds to the deformation vibrations of $–NH_2$; 1420 and 1380 cm^{-1} for C–H bending vibrations, 1310 cm^{-1} for asymmetric C–O–C stretching vibrations, and 1080 cm^{-1} for C–O stretching vibration of CH–OH were observed. The FTIR spectrum of the synthesized composite have shown a shift of the band 1553 cm^{-1} of aminogroups deformation vibrations in comparison with the spectrum of the initial chitosan. An intensive absorbance at 1100 cm^{-1} represents the Si–O stretching vibrations.

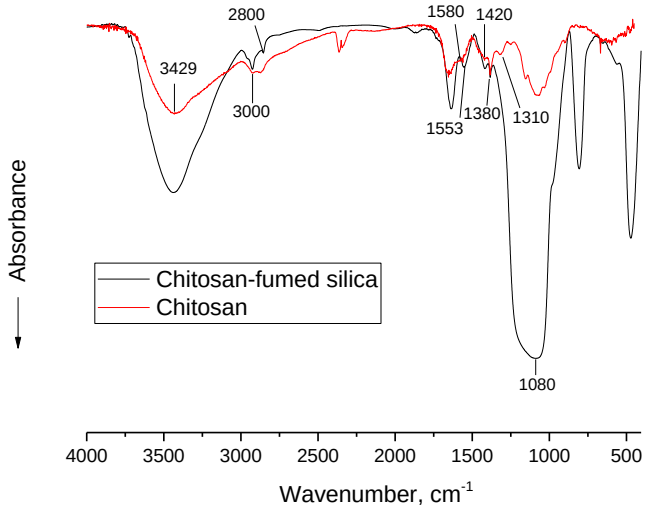
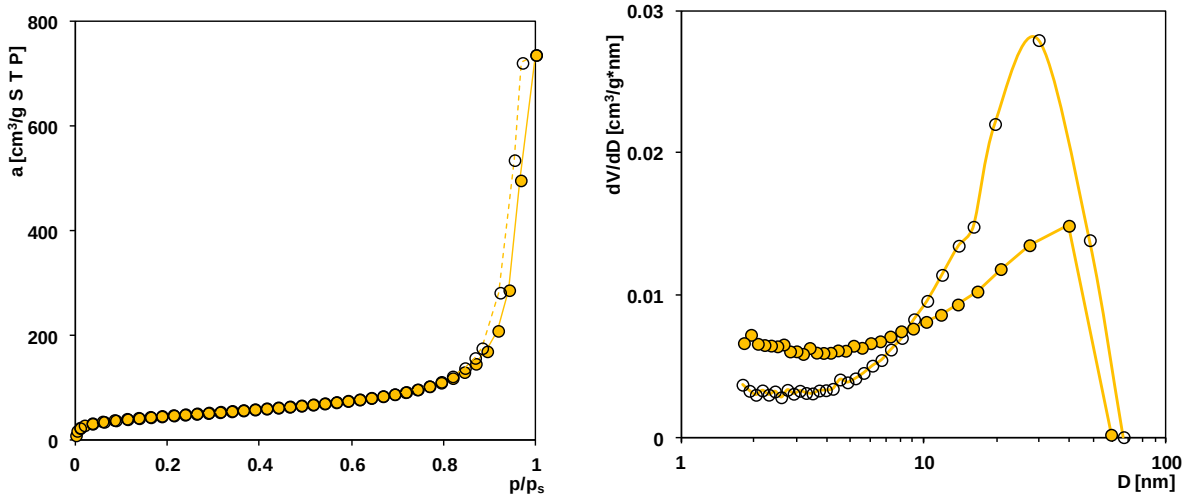


Figure S1. FTIR of pure chitosan and chitosan-fumed silica composite. Reprinted with permission from our previous work[5]; Blachnio et al., *Langmuir* **2018,** *34*, 2258. Copyright American Chemical Society.

Nitrogen adsorption/desorption measurement

The results of surface area and average pore diameter analysis of chitosan-fumed silica composite are presented in Figure S2. According to the results the BET surface area of the chitosan-fumed silica composite is 170 m^2 g^{-1}. The shape of the isotherm corresponds to the Langmuir isotherm, type II of the IUPAC classification. This type of isotherm is commonly observed in materials, in which mesopores and macropores are present. The presence of mesopores and macropores for the sample is confirmed by the diagrams of pore size distribution (Figure 2*b*), which were obtained from adsorption and desorption branch of the isotherm using the BJH method.



a *b*

Figure S2. (*a*) The nitrogen adsorption/desorption isotherms and (*b*) Pore size distributions from adsorption (closed symbols) and desorption branch (open symbols) for chitosan-fumed silica composite calculated using BJH method. Reprinted with permission from our previous work[5]; Blachnio et al., *Langmuir* **2018,** *34*, 2258. Copyright American Chemical Society.

Scanning electron microscopy (SEM)

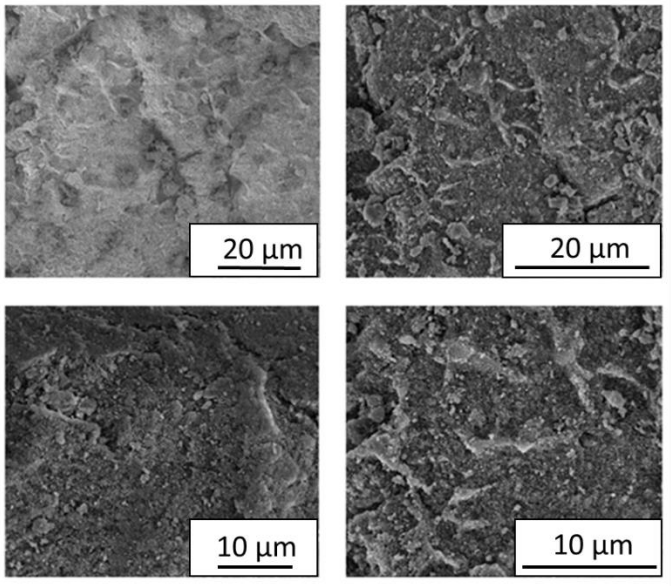


Figure S3. SEM micrographs of chitosan-fumed silica composite.

Adsorbate characteristics

For the equilibrium adsorption and kinetic studies anionic dye acid orange 8 (AO8), was used. The physicochemical characteristics of the compound is as follows: molecular weight: 364.35 g·mol; acidity constant: –1; 13.5; water solubility: highly soluble; distance between the most remote atoms in dye molecules: 1.3 nm. Chemical structure of the Acid Orange 8 dye is shown in Figure S4.

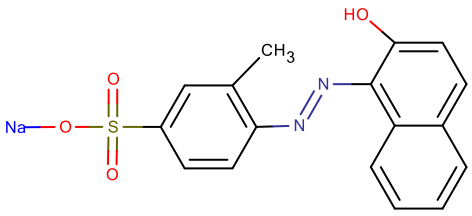


Figure S4. Chemical structures of Acid Orange 8 dye. Reprinted with permission from our previous work[5]; Blachnio et al., *Langmuir* **2018,** *34*, 2258. Copyright American Chemical Society.

Potentiometric titration measurement

In Figure S5 dependence of surface charge density *vs.* pH for chitosan-fumed silica composite determined by potentiometric titration is shown. The value of pH_{PZC} is 6.0 indicates that modification applied in the study totally changed surface charge of silica (for pure silica the pH_{PZC} = 2.5–3.5).

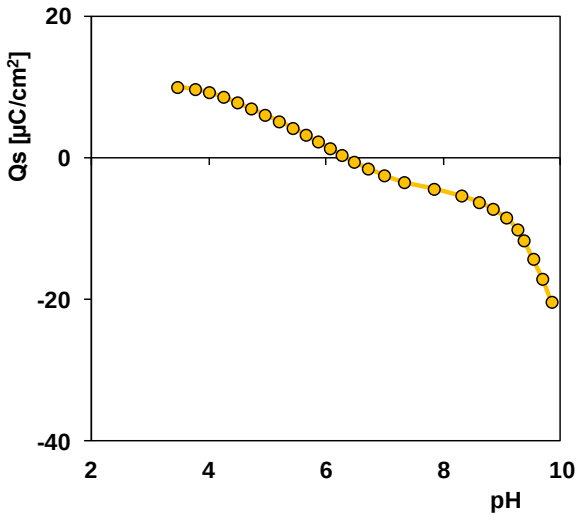


Figure S5. Dependence of surface charge density on pH for chitosan-fumed silica composite determined by potentiometric titration. Reprinted with permission from our previous work[5]; Blachnio et al., *Langmuir* **2018,** *34*, 2258. Copyright American Chemical Society.

Acid Orange 8 dye (AO8) adsorption study

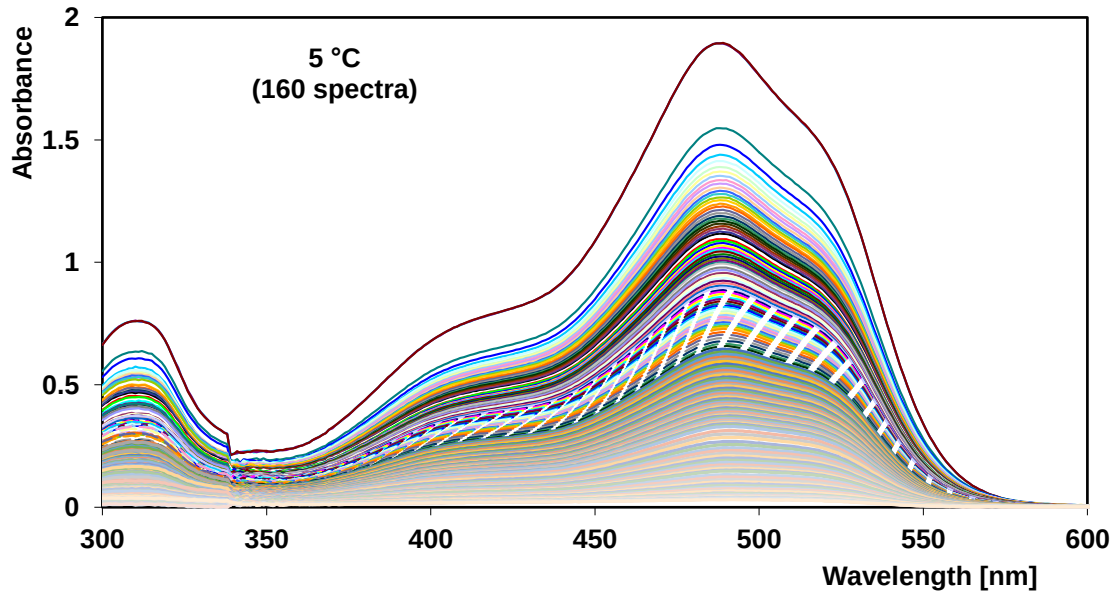


Figure S6. The exemplary absorption spectra in the UV-Vis range measured for the Acid Orange 8 adsorption process on the chitosan-fumed silica composite at 5 °C.

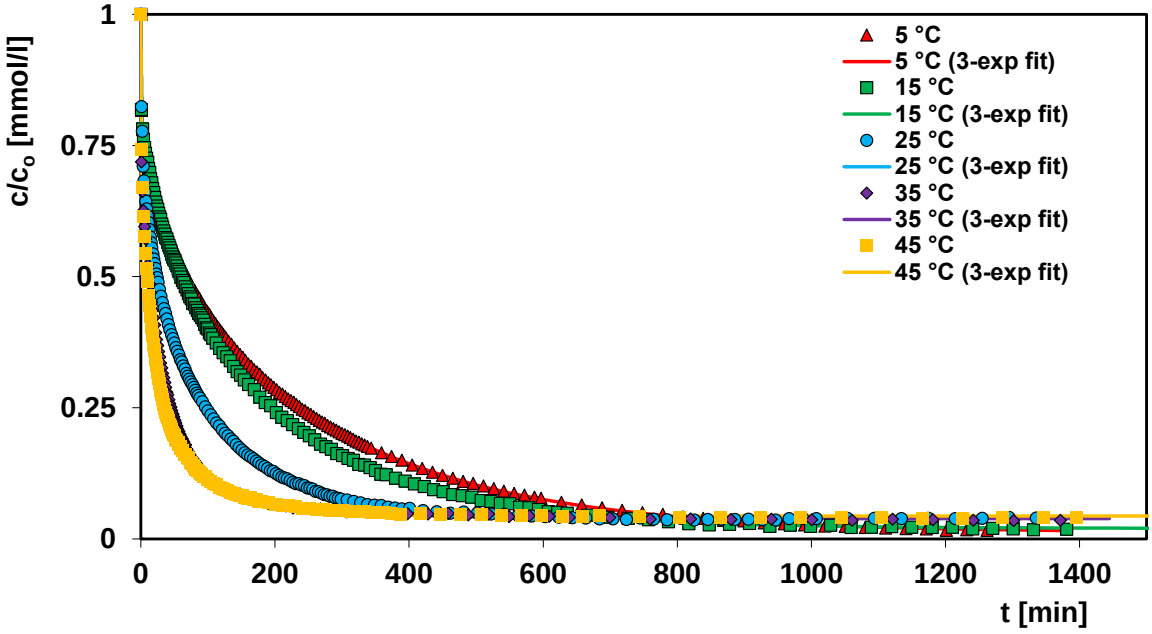


Figure S7. Comparison of adsorption kinetics for Acid Orange 8 on the chitosan-fumed silica composite at various temperatures at coordinates: relative concentration ~ time. Lines correspond to the fitted multi-exponential equation.

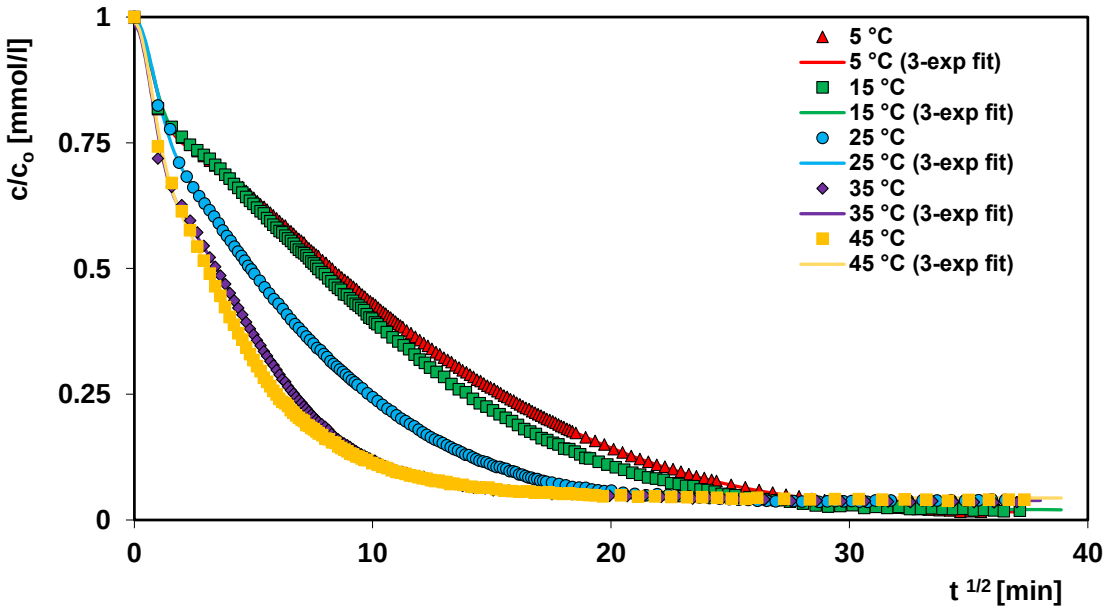


Figure S8. Comparison of adsorption kinetics for Acid Orange 8 on the chitosan-fumed silica composite at various temperatures at coordinates: relative concentration ~ square root of time. Lines correspond to the fitted multi-exponential equation.

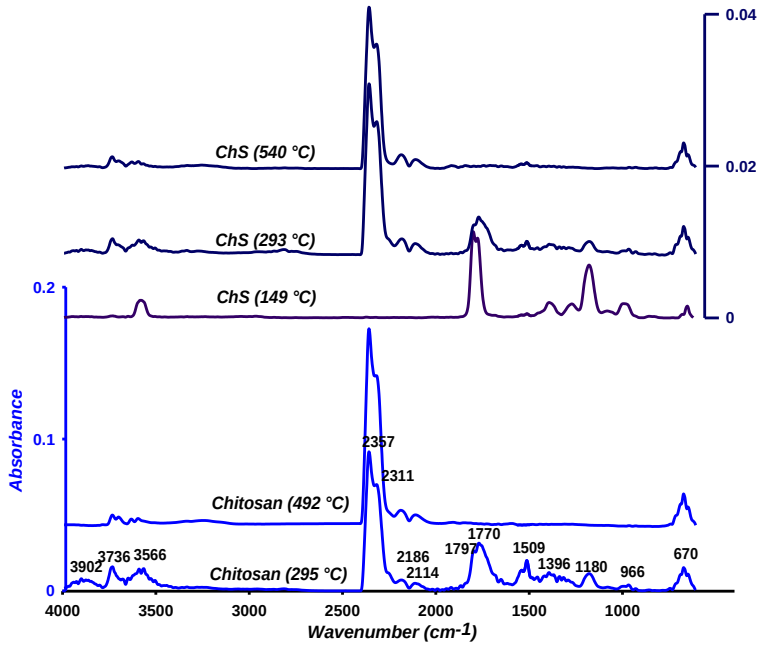


Figure S9. FTIR spectra of gas products generated during pyrolysis of chitosan and chitosan-fumed silica composite ChS at the temperatures corresponding to maximum rate of process.

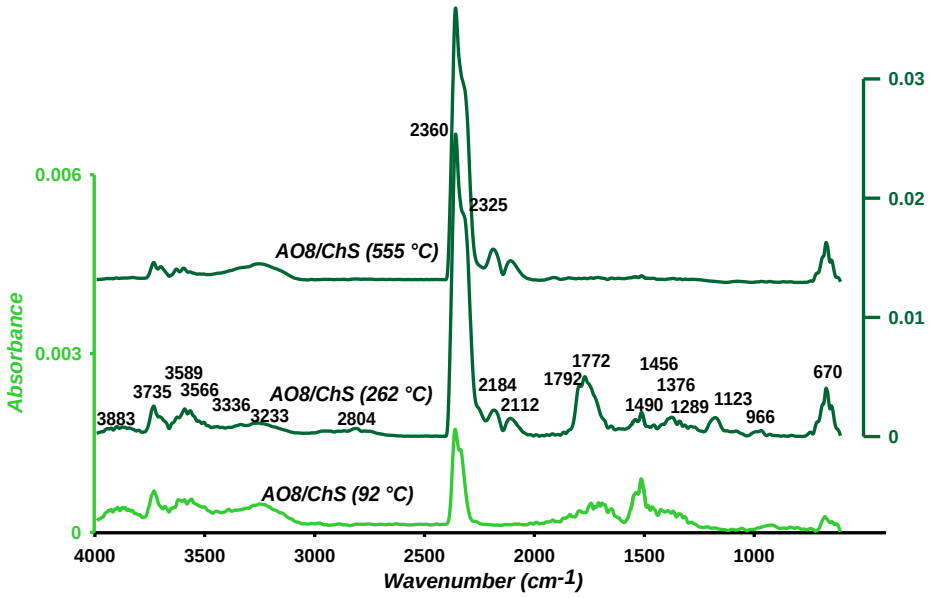


Figure S10. FTIR spectra of gas products generated during pyrolysis of the sorbent-dye system (AO8(ChS)) at the temperatures corresponding to maximum rate of process.

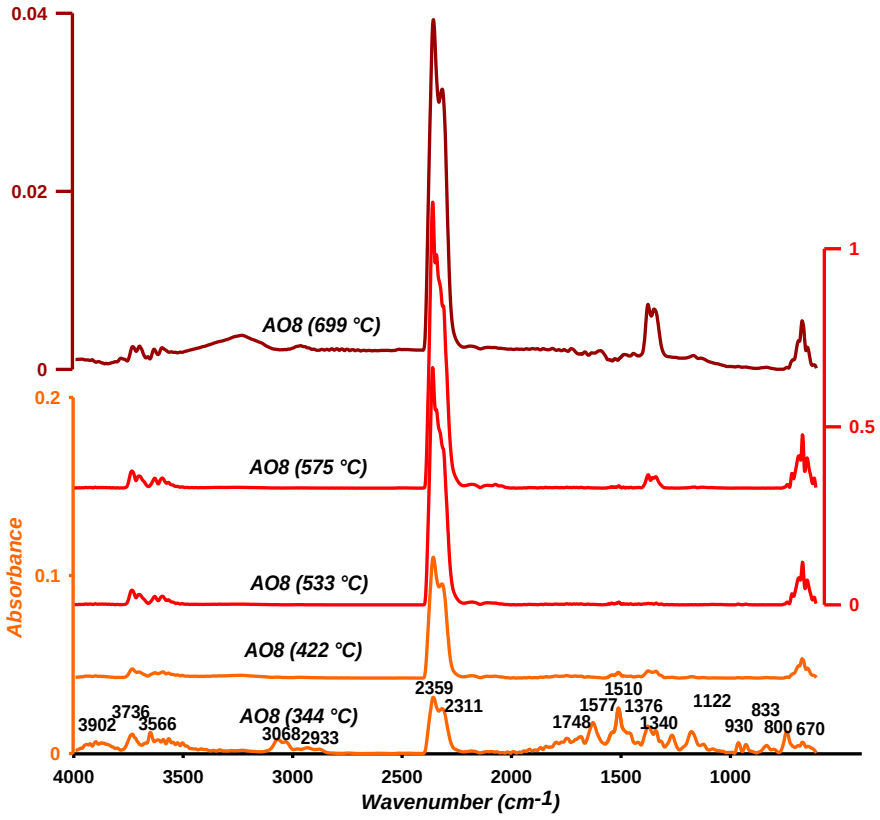


Figure S11. FTIR spectra of gas products generated during pyrolysis of pure AO8 dye at the temperatures corresponding to maximum rate of process.