Electronic Supplementary Information (ESI)

Eggshell incorporated agro-waste adsorbent pellets for sustainable orthophosphate capture from aqueous media

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This ESI material includes the following content:

S1. Methods

TGA

The ground samples were subjected to a heating rate of 10°C/min after equilibration of 1 min at 30 °C in an open aluminium pan in a N_2 atmosphere. Only the obtained TG curves were normalized via "divide by max".

XRD

A CuKα radiation (40 kV and 30 mA) with λ = 1970.1541 nm was used over a 2θ angle range from 5° to 80° to obtain the powder XRD (PXRD) profiles.

FT-IR Spectroscopy

Samples were ground with KBr (FT-IR grade) and a sample powder in a 10:1 ratio (KBr to sample) with a mortar and pestle. The spectra were recorded at 295 K over a spectral range of 400-4000 cm^{-1} with a 4 cm^{-1} resolution, including normalization, according to a [0,1] scale. A minimum of 64 scans were recorded and the spectral background was corrected against pure KBr.

NMR Spectroscopy

The CP-TOSS method (cross-polarization with total suppression of spinning sidebands) was used to collect the ^{13}C NMR spectra. The sample spinning speed was 7.5 kHz, and a ^{1}H 90° pulse on the ^{1}H channel. Spectral acquisition employed up to 20k scans with a cycle delay of 1 s with 50 kHz SPINAL-64 decoupling sequence. The ^{13}C shifts were referenced to adamantane (38.48 ppm low field signal). The spectra were normalized according to a [0,1] scale.

Surface Area via PNP Dye Adsorption

A fixed amount (20 mg) of the TWCs were added to 10 mL of PNP solution (0.5-20 mM, buffered with 30 mM acetic acid or carbonate at pH 4.5 or 8.5). The solutions were equilibrated overnight on an orbital shaker at ca. 22 °C and measured in duplicate.

***Table S1**: Isotherm parameter for orthophosphate adsorption at pH 4.5 ~~onto C22~~.*

Sips Parameter	**Q (mg/g)**	**K_a**	**n**	**R^2**
C72	22.9 ± 7.7	0.0018 ± 0.001	2.1 ± 1.3	0.967
C20	28.1 ± 6.1	0.0014 ± 0.0004	2.3 ± 0.7	0.989
C21	30.1 ± 12	0.0015 ± 0.001	1.7 ± 0.9	0.971
C22	22.2 ± 2.1	0.0095 ± 0.0009	1.3 ± 0.3	0.969
Langmuir Parameter	**Q**	**K**		**R^2**
C72	62.0 ± 38.6	0.0005 ± 0.0004		0.949
C20	65.4 ± 64.0	0.0005 ± 0.0007		0.778
C21	73.5 ± 47.5	0.0003 ± 0.0003		0.966
C22	31.5 ± 3.7	0.0021 ± 0.00048		0.954
Freundlich Parameter	**K**		**n**	**R^2**
C72	0.077 ± 0.10		1.3 ± 0.3	0.936
C20	0.013 ± 0.02		1.0 ± 0.2	0.973
C21	0.050 ± 0.05		1.2 ± 0.2	0.960
C22	0.68 ± 0.48		2.0 ± 0.4	0.880

***Table S2:** Isotherm parameters for orthophosphate adsorption at pH 8.5 onto the agro-waste composites.*

Sips Parameter	**Q (mg/g)**	**K_a**	**n**	**R^2**
C72	12.1 ± 0.7	0.005 ± 0.001	2.02 ± 0.26	0.98132
C20	11.6 ± 1.2	0.005 ± 0.001	2.31 ± 0.21	0.93548
C21	8.90 ± 1.4	0.007 ± 0.002	1.28 ± 0.36	0.92976
C22	10.3 ± 1.1	0.009 ± 0.001	3.11 ± 0.46	0.98837
Langmuir Parameter	**Q**	**K**	**R^2**	
C72	29.5 ± 7.0	0.0008 ± 0.0003	0.94827	
C20	25.3 ± 6.3	0.0009 ± 0.0004	0.92938	
C21	16.4 ± 2.6	0.0018 ± 0.0006	0.91077	
C22	10.8 ± 1.3	0.0080 ± 0.0026	0.83442	
Freundlich Parameter	**K**		**n**	**R^2**
C72	0.05 ± 0.01		1.2 ± 0.1	0.98009
C20	0.07 ± 0.04		1.3 ± 0.2	0.91198
C21	0.16 ± 0.07		1.6 ± 0.2	0.91329
C22	0.49 ± 0.28		2.1 ± 0.4	0.75437

Table S3: *Equations and parameters of both Freundlich and Langmuir adsorption isotherm models.*

Freundlich Isotherm	$q_e = K_f C_e^{\frac{1}{n}}$	q_e = monolayer adsorption capacity at equilibrium C_e = equilibrium adsorbate concentration K_f = Freundlich constant n = Freundlich exponent
Langmuir Isotherm	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	q_m = equilibrium monolayer adsorption capacity K_L = Langmuir adsorption constant C_e = adsorbate concentration at equilibrium q_e = bound adsorbate concentration

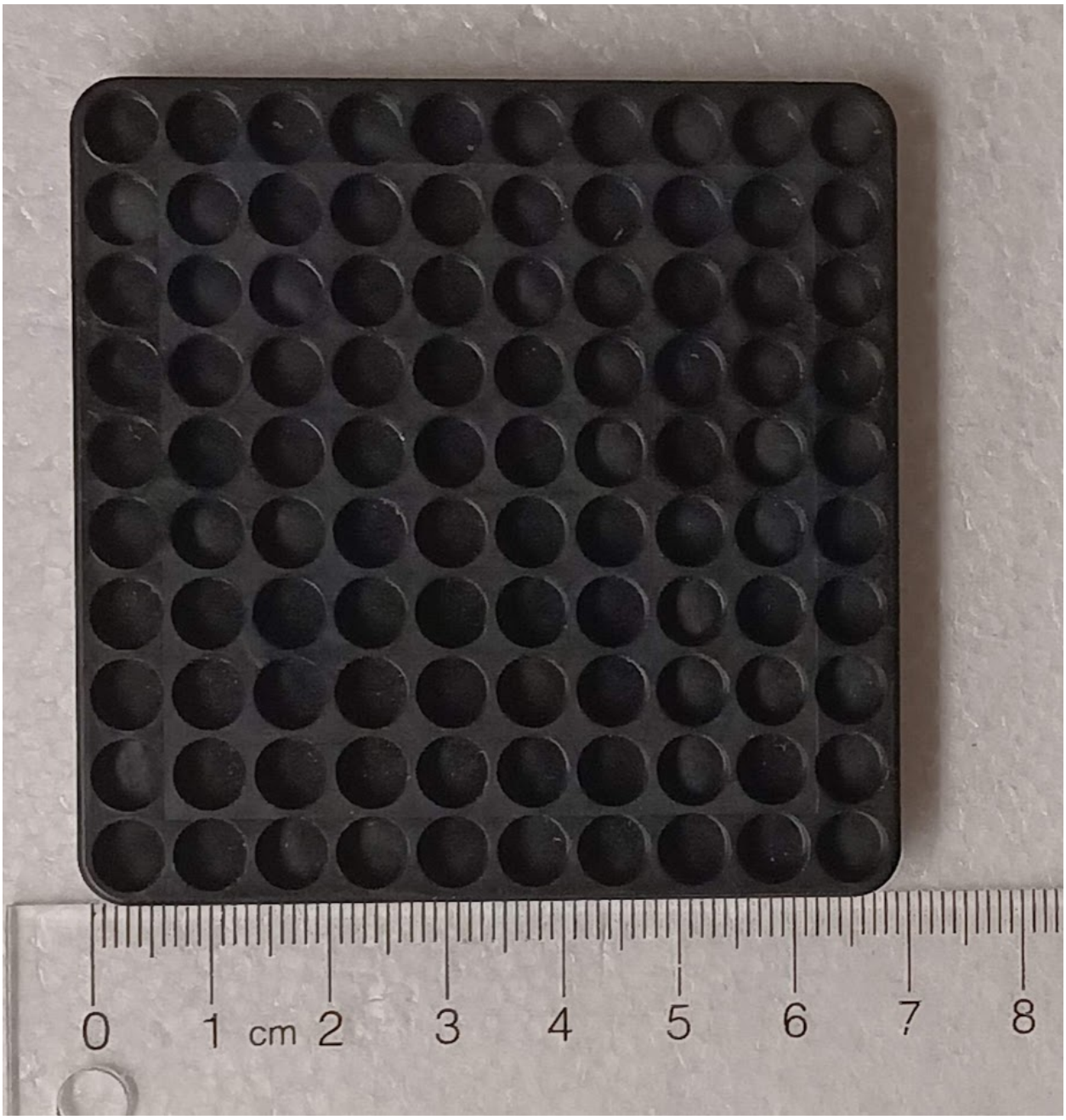

Figure S1: *Digital image of the mold/tray used to prepare the samples with scale.*

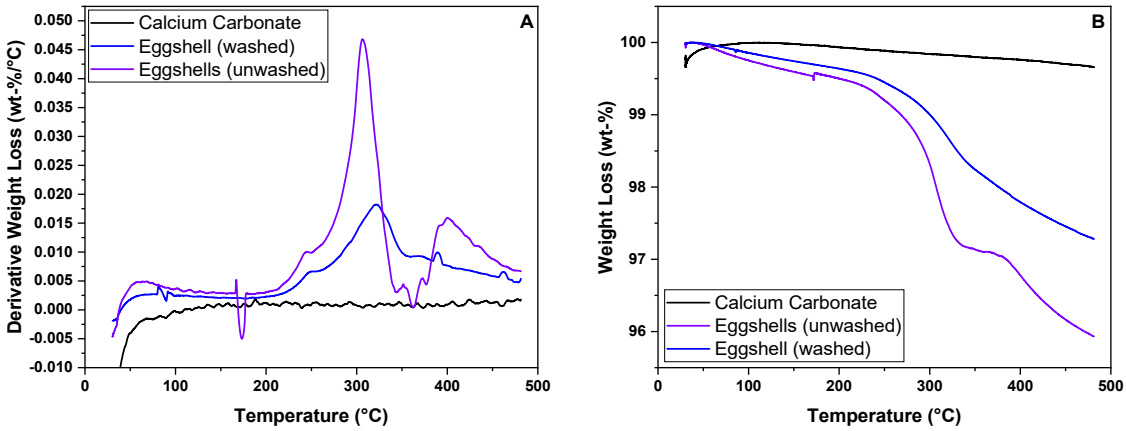

Figure S2: *DTG profiles (A) of pristine calcium carbonate as comparison to eggshells (washed) and their respective weight loss profiles (B). Note. 2.7 wt-% of organic matter was estimated on the ES sample after washing, which compares to ca. 4.1 wt-% before washing.*

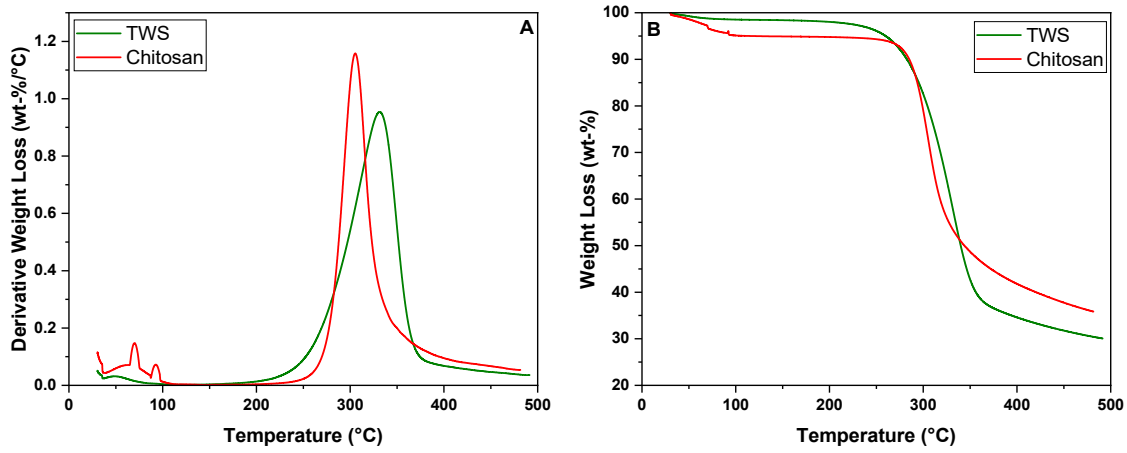

Figure S3: *DTG profiles (A) of torrefied wheat straw (TWS) and chitosan and their TG profiles (B) respectively.*

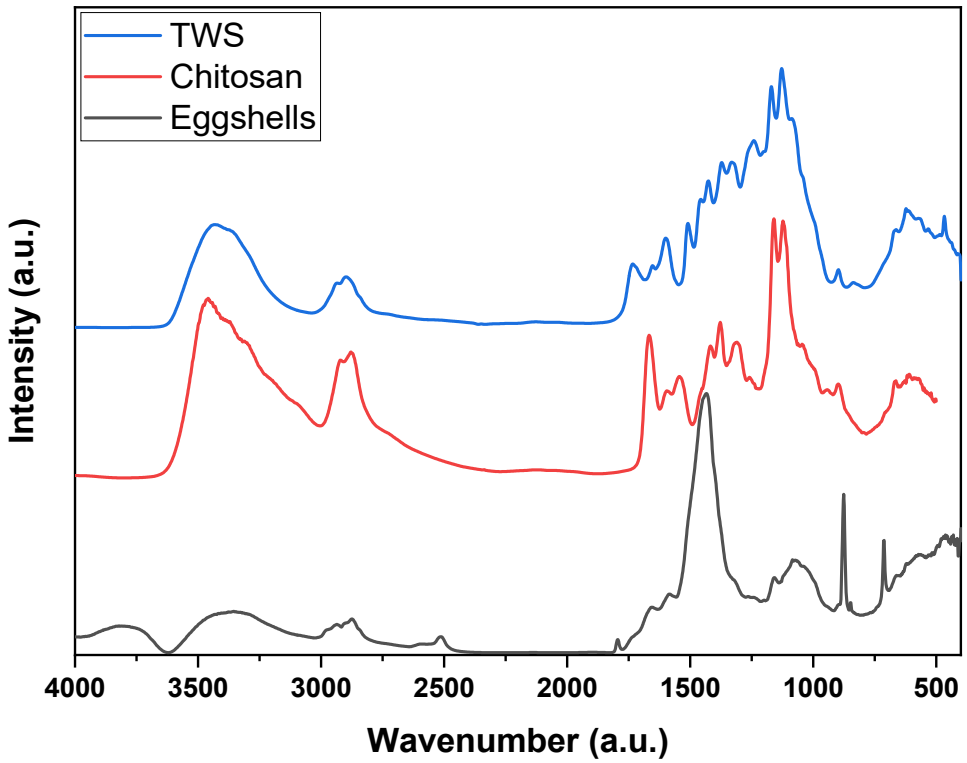

Figure S4: *FT-IR spectra of the raw materials used to prepare the pelletized adsorbents.*

Orthophosphate Adsorption Isotherms of composites at pH 4.5

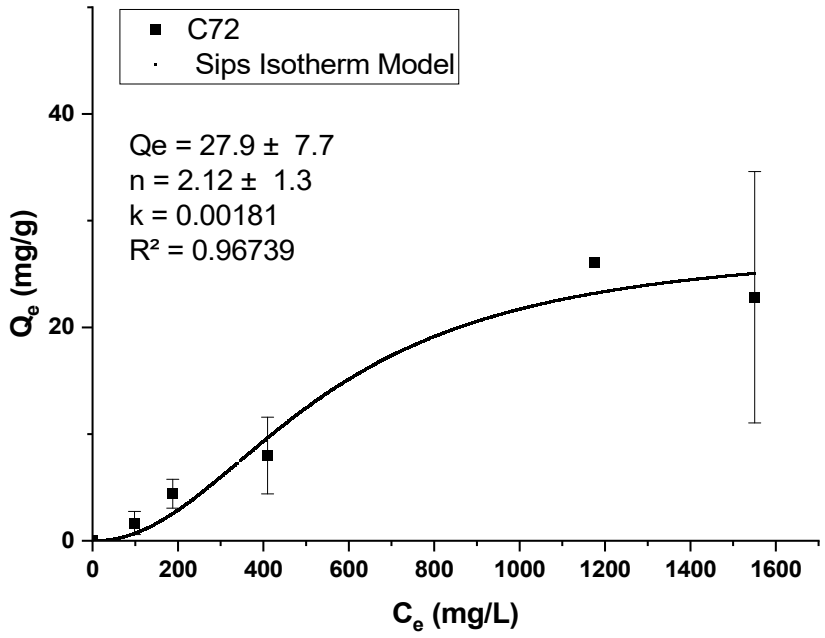

Figure S5: *Orthophosphate adsorption isotherm study of C72 at pH 4.5.*

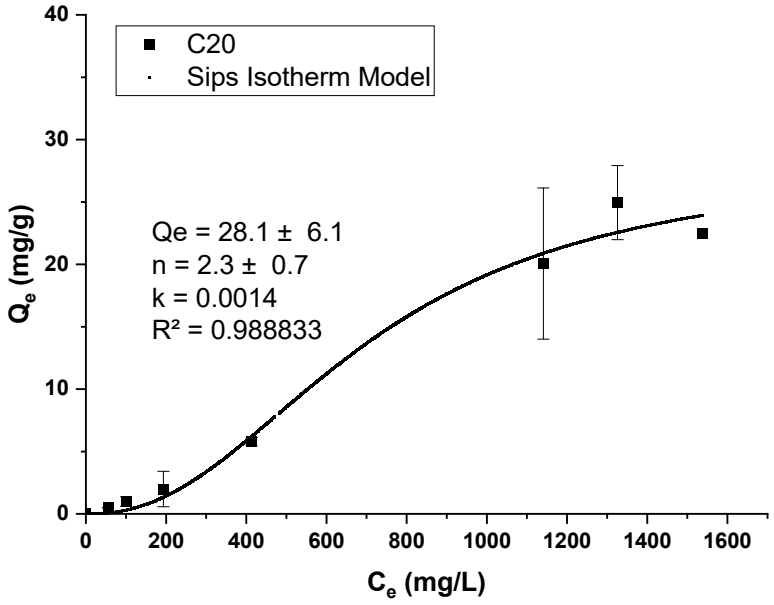

Figure S6: *Orthophosphate adsorption isotherm study of C20 at pH 4.5.*

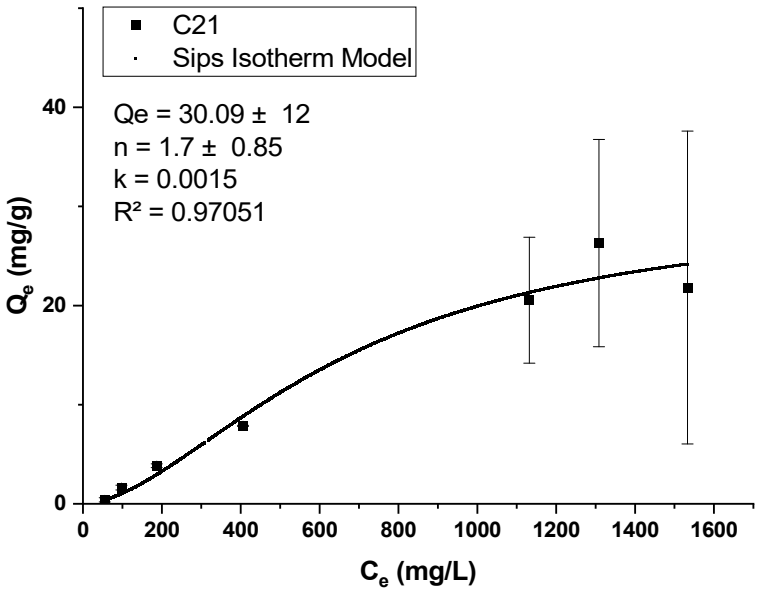

Figure S7: *Orthophosphate adsorption isotherm study of C21 at pH 4.5.*

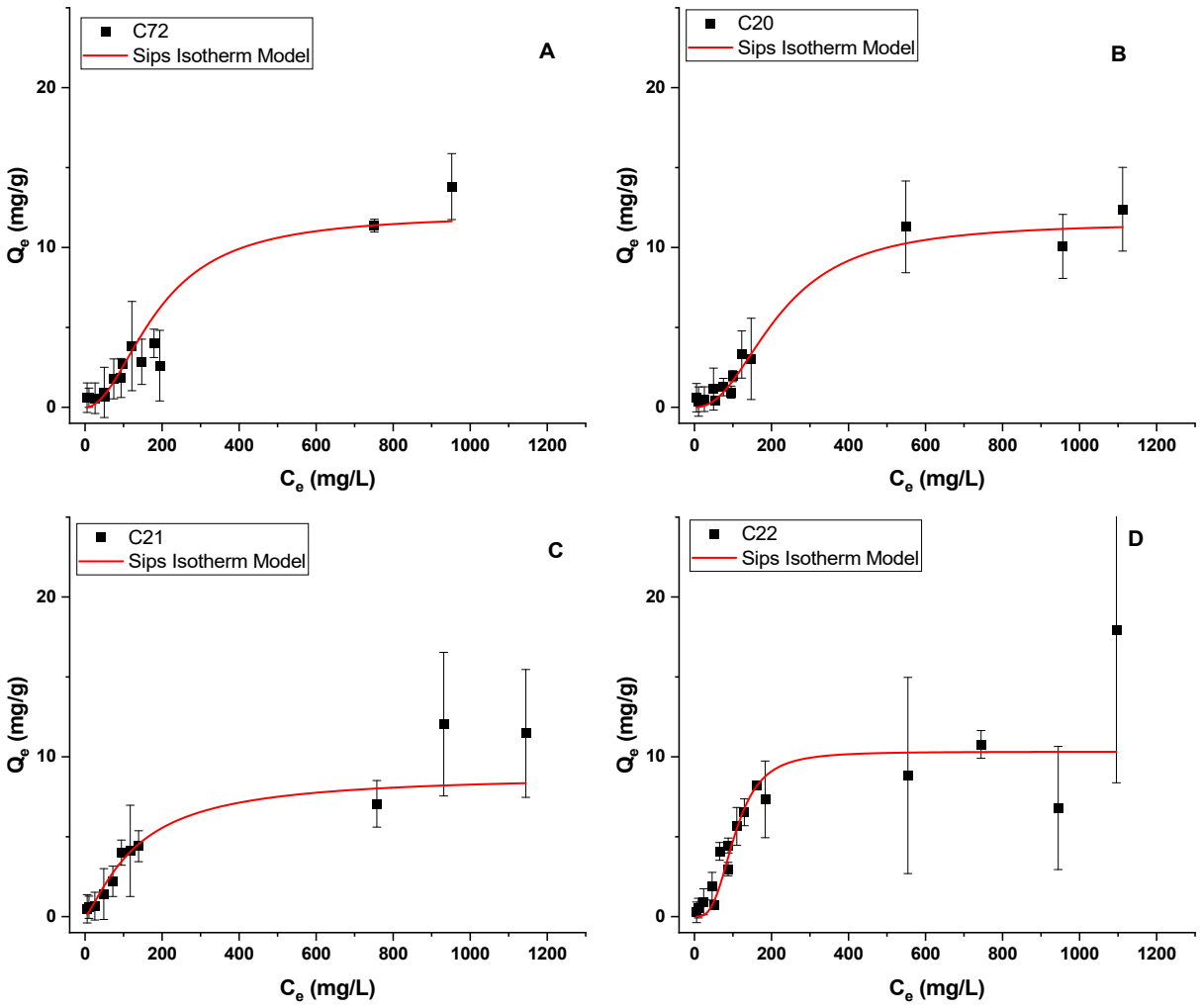

Figure S8: *Orthophosphate isotherms (Sips Isotherm Model) at pH 8.5 on C72 (A), C20 (B), C21 (C) and C22 (D).*