

Supplementary Information

for

“Eco-friendly and facile one-step synthesis of three dimension net-like magnetic mesoporous carbon derived from wastepaper as renewable adsorbent”

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Synthesis of carbon material (C) without magnetism. Carbon material (C) without magnetism was also prepared by dry-production method. The carbon source was filter paper. Firstly, paper was immersed in ethanol, and placed into the 300Hz ultrasonic system for 30 min. After 3 times washing, the treated paper was dried in a 60°C oven. The dried filter paper was heated at 750 °C in a tubular furnace under N₂ atmosphere with a heating rate 3 °C/min to the final products.

Adsorption kinetics. Kinetic study on adsorption can provide important information about the mechanism of the whole adsorption process. The adsorption kinetic models used in this study include the Lagergren pseudo-first order kinetics and the pseudo-second order kinetics,¹ which are expressed in equations (S1)-(S2) as listed below:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (\text{Eq. S1})$$

$$t / q_t = 1 / (k_2 q_e^2) + t / q_e \quad (\text{Eq. S2})$$

Where k_1 and k_2 , are the pseudo-first order, pseudo-second order rate constant, respectively; q_e is the amount of solute adsorbed (mg g⁻¹) at equilibrium and q_t is the amount of solute on the surface of the adsorbent (mg g⁻¹) at any time t .

Isotherm adsorption models.

Langmuir isotherm model. Langmuir model treats the adsorption process uniform and leads to a monolayer. The linear expression for the Langmuir model is given by

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (\text{Eq. S3})$$

Where q_m (mg g^{-1}) is the maximum adsorption capacity (mg g^{-1}), and K_L ($\text{mg}^{-1} \text{L}$) stands for the equilibrium adsorption constant.²

Using the Langmuir isotherm was possible to determine the equilibrium parameter known as the separation factor (R_L), which is a dimensionless constant related to the propitiousness of the adsorption. This parameter can be calculated using Eq. S4

$$R_L = \frac{1}{1 + K_L C_0} \quad (\text{Eq. S4})$$

R_L values indicate the adsorption process to be unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$, and irreversible if $R_L = 0$.³

Freundlich isotherm model. The Freundlich isotherm model was used to investigate the non-ideal and reversible adsorption on a heterogeneous surface.⁴ The linear Freundlich equation is expressed as

$$q_e = K_F C_e^{1/n} \quad (\text{Eq. S5})$$

where K_F (mg g^{-1}) and n are the Freundlich constants that are related to the sorption capacity and intensity, respectively.

Sips isotherm model. It is a generalized nonlinear equation containing Langmuir and Freundlich isotherm models.⁵ The model elucidates the surface heterogeneity in the heterogeneous systems and the equation was described by

$$q_e = \frac{q_m (K_s C_e)^{1/n_s}}{1 + (K_s C_e)^{1/n_s}} \quad (\text{Eq. S6})$$

where k_s (L mg⁻¹) is the Langmuir median association constant, and n_s^{-1} is the Freundlich heterogeneity factor.

Redlich-Peterson isotherm model. It is a hybrid of Langmuir and Freundlich isotherm model.⁶

The empirical equation for Redlich-Peterson model is given by

$$q_e = \frac{AC_e}{(1 + BC_e^\beta)} \quad (\text{Eq. S7})$$

Where A (L g⁻¹), B (L mg⁻¹) and β are Redlich-Peterson constants and the exponent β ranges from 0 to 1. This model applies to both homogeneous and heterogeneous systems.

Adsorption thermodynamics.

Adsorption thermodynamics were measured by varying the temperature of the reaction systems.

Thermodynamic parameters including standard Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated by the following equations:

$$\Delta G^\circ = -RT \ln k_d \quad (\text{Eq. S8})$$

$$\Delta G^\circ = \Delta H^\circ - \Delta S^\circ \quad (\text{Eq. S9})$$

$$k_d = (C_0 - C_e) / C_e \quad (\text{Eq. S10})$$

$$\ln k_d = -\left(\frac{\Delta H^\circ}{RT}\right) + \frac{\Delta S^\circ}{R} \quad (\text{Eq. S11})$$

where R (8.314 J/K mol) is the universal gas constant, T (K) is the temperature of adsorption interaction system, k_d is the equilibrium constant, C_0 (mg/L) is the initial concentration in solution and C_e (mg/L) is the equilibrium concentration. Values of ΔH° and ΔS° were calculated from the $\ln k_d$ versus $1/T$ plot by the linear regression method.⁷

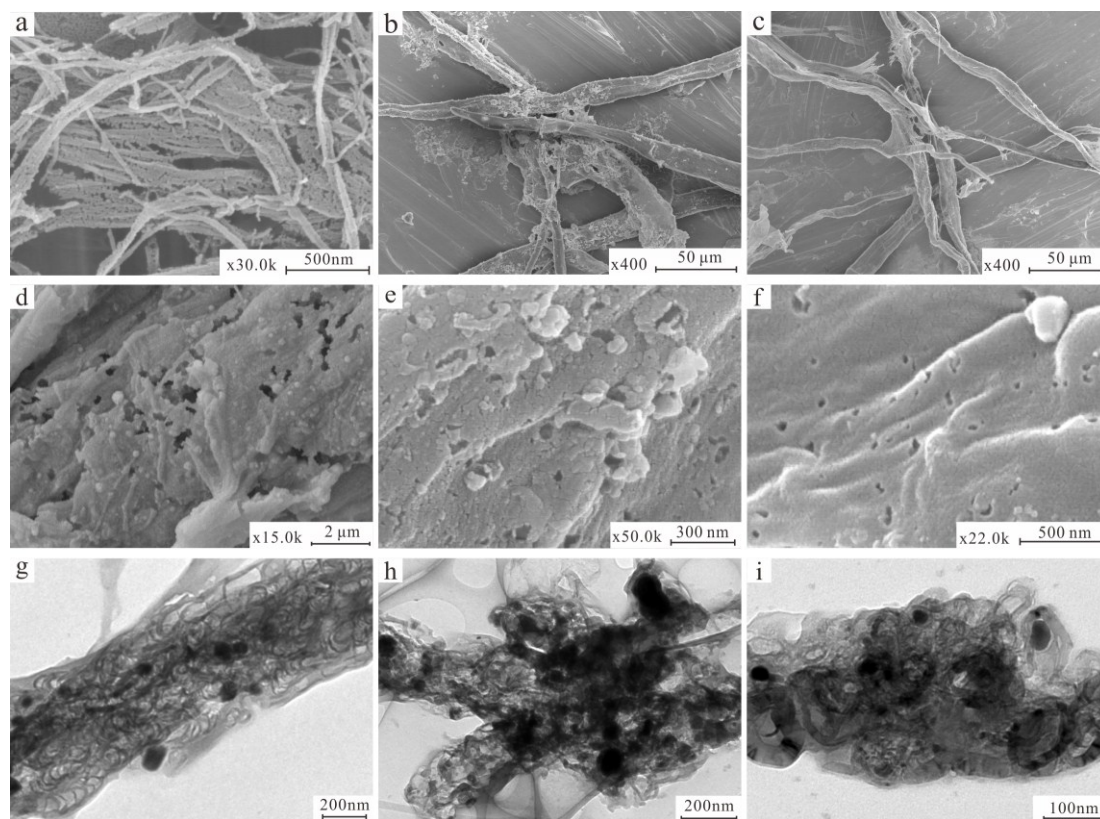


Fig. S1 SEM and TEM images of filter paper, printer paper and napkins. SEM images of filter paper (a), printer paper (b) and napkins (c) immersed in ferric nitrate solution for 2 h and then dried. SEM images of filter paper (d), printer paper (e) and napkins (f) immersed in ferric nitrate solution and then calcined at 750°C in a nitrogen atmosphere. TEM images (g~i) corresponding to d~f, respectively.

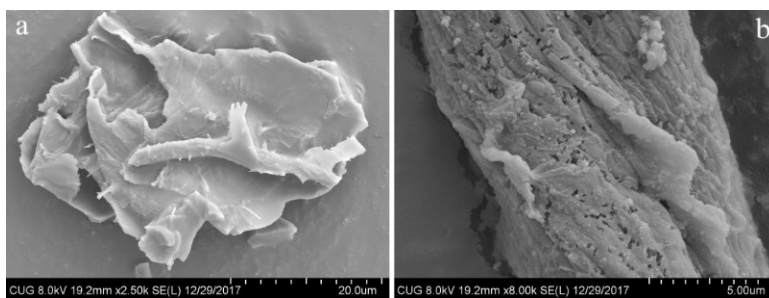


Fig. S2 SEM images of carbon material derived from filter paper after calcination. (a) filter paper without immersion of ferric nitrate solution; (b) iron ion saturated filter paper.

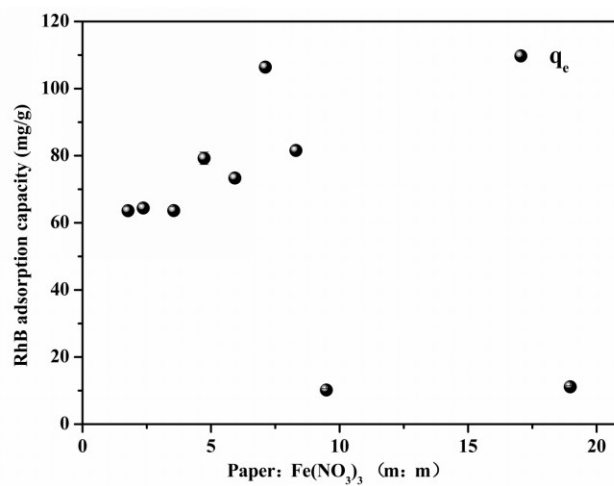


Fig. S3 Optimization of the Paper:Fe(NO₃)₃ (m:m) ratio.

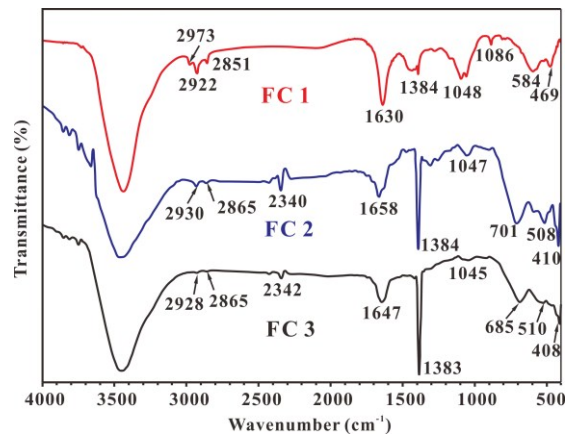


Fig. S4 FTIR spectra of FC1, FC2 and FC3.

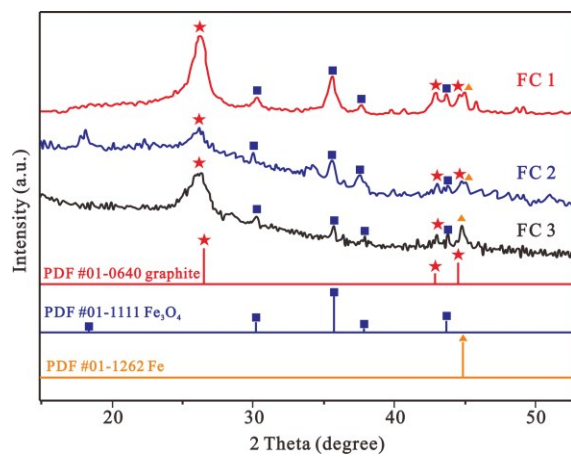


Fig. S5 XRD patterns of FC1, FC2 and FC3.

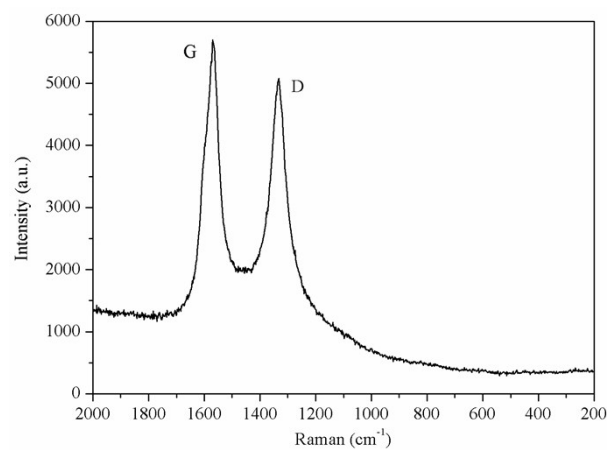


Fig. S6 Raman spectrum of the 3D net-like magnetic mesoporous carbon derived from filter paper.

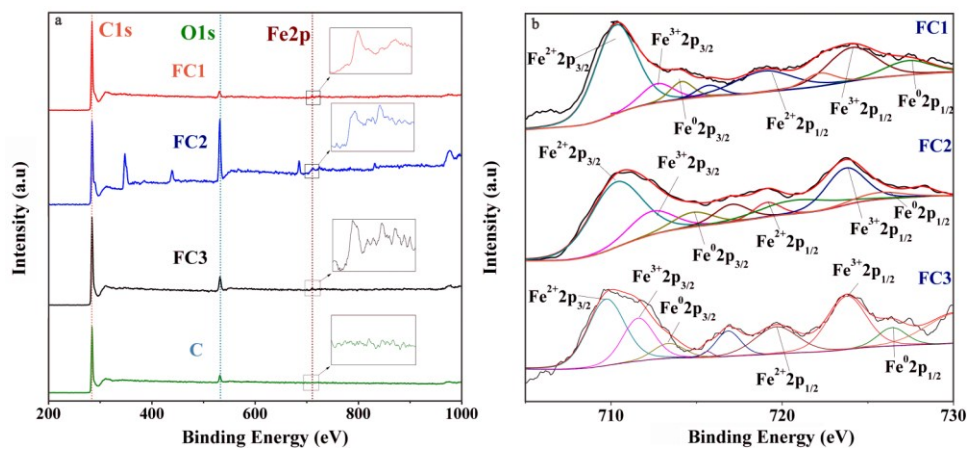


Fig. S7 XPS spectra (a) and Fe 2p spectra (b) of FC1, FC2, FC3 and C.

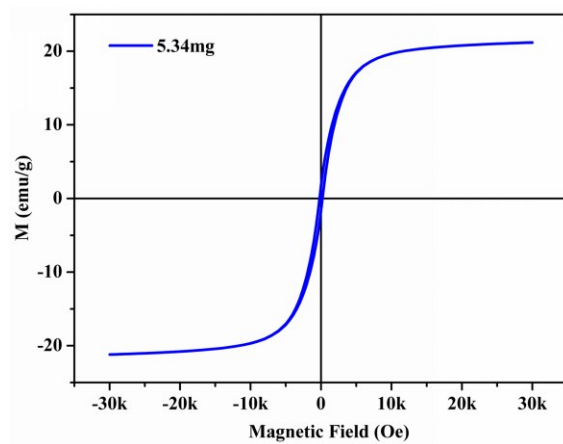


Fig. S8 VSM magnetization curve of 3D net-like magnetic mesoporous carbon derived from filter paper.

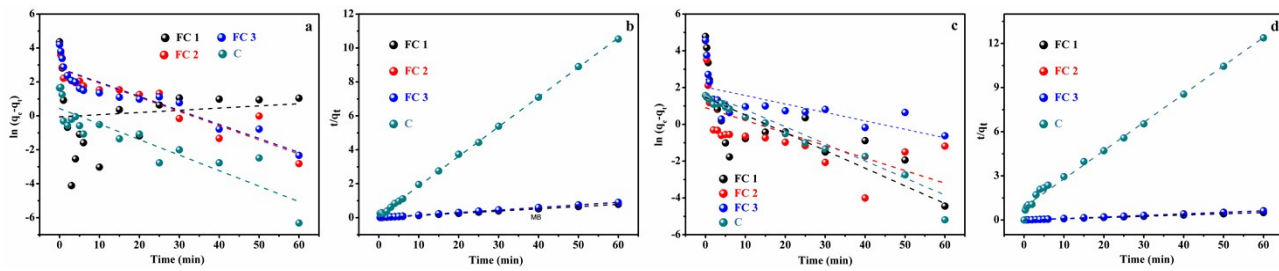


Fig. S9 Pseudo-first-order kinetics (a and c) and pseudo-second-order kinetic models (b and d) for the adsorption of MB and RhB onto FC1, FC2, FC3 and C. (Conditions: initial concentration of MB and RhB: 50 mg L⁻¹; amount of adsorbents for MB and RhB: 8 mg; sample volume of MB and RhB: 20 mL; pH of MB and RhB: 7; Temperature: 25°C)

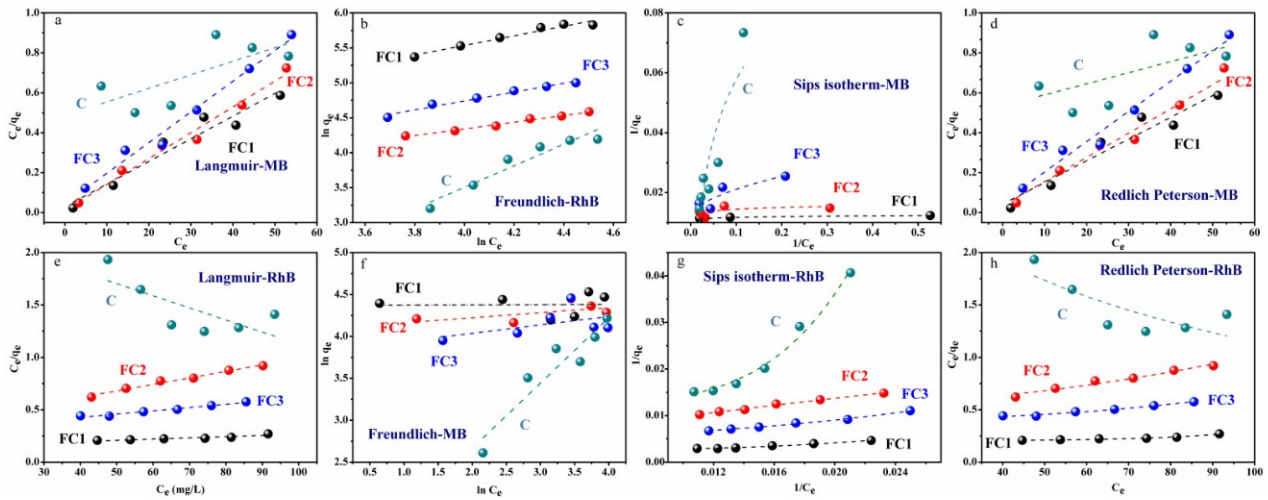


Fig. S10 Fitting curve of Langmuir, Freundlich, Sips isotherm and Redlich-Peterson model for the equilibrium adsorption data of MB (a~d) and RhB (e~h) by FC1, FC2, FC3 and C. (Conditions: amount of adsorbents for MB: 8 mg; amount of adsorbents for RhB: 2 mg; sample volume of MB and RhB: 20 mL; pH of MB and RhB: 7; temperature: 50°C)

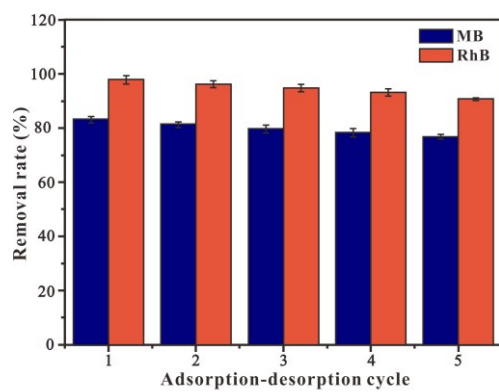


Fig. S11 Reusability of FC1 after 5 cycles. Error bars represent the standard error of the average value for measurement carried out in triplicate.

Table S1 Chemical structures and selected properties of MB and RhB.

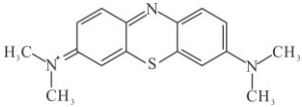
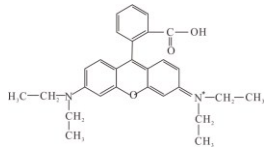
| Dye | Structure | ρ | M_W | $D_m(\text{\AA})$ |
|-----|---|--------|--------|-------------------|
| MB |  | 1.00 | 319.86 | 15.10 |
| RhB |  | 0.79 | 479.01 | 17.08 |

Table S2 Adsorption kinetic parameters of MB and RhB adsorption by FC1, FC2, FC3 and C.

| Dye | Adsorbent | Pseudo-first-order | | | Pseudo-second-order | | | $q_{e,exp}$ (mg g ⁻¹) |
|-----|-----------|-------------------------------|--------------------------------------|----------------|--------------------------------------|--|----------------|--------------------------------------|
| | | K_1 (min ⁻¹) | $q_{e,cal}$ (mg g ⁻¹) | R ² | $q_{e,cal}$ (mg g ⁻¹) | K_2 (g mg ⁻¹ min ⁻¹) | R ² | |
| MB | FC1 | 2.77 | 80.64 | 0.9791 | 76.34 | 0.12 | 0.9999 | 78.80 |
| | FC2 | 0.08 | 15.96 | 0.8284 | 68.03 | 0.03 | 0.9995 | 67.54 |
| | FC3 | 0.08 | 16.61 | 0.8454 | 66.67 | 0.03 | 0.9998 | 66.40 |
| | C | 0.09 | 1.55 | 0.7840 | 5.88 | 0.23 | 0.9995 | 5.70 |
| RhB | FC1 | 0.09 | 5.10 | 0.4823 | 119.05 | 0.08 | 0.9999 | 117.76 |
| | FC2 | 0.07 | 2.40 | 0.3486 | 94.97 | 0.27 | 0.9999 | 94.06 |
| | FC3 | 0.08 | 2.12 | 0.4611 | 96.81 | 0.27 | 0.9999 | 95.78 |
| | C | 0.04 | 13.7 | 0.5984 | 5.20 | 0.04 | 0.9926 | 4.8 |

Table S3 Isotherm parameters for adsorption of MB and RhB by FC1, FC2, FC3 and C.

| Model | MB | | | | RhB | | | |
|-----------------------------|------------------------|-----------------------|-------|----------------------|------------------------|------------------------|------------------------|-------|
| | FC1 | FC2 | FC3 | C | FC1 | FC2 | FC3 | C |
| Langmuir | | | | | | | | |
| q_m (mg g ⁻¹) | 82.1 | 71.4 | 65.4 | 147.5 | 862.1 | 161.3 | 322.6 | 100.0 |
| K_L (mg ⁻¹ L) | 0.38 | 1.00 | 0.35 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 |
| R^2 | 0.928 | 0.977 | 0.980 | 0.387 | 0.826 | 0.980 | 0.957 | 0.425 |
| Freundlich | | | | | | | | |
| K_F (mg g ⁻¹) | 79.0 | 60.4 | 46.3 | 3.0 | 16.3 | 11.3 | 9.0 | 0.1 |
| n | 331.12 | 16.67 | 9.94 | 1.28 | 1.46 | 2.09 | 1.58 | 0.65 |
| R^2 | 0.249 | 0.161 | 0.069 | 0.864 | 0.949 | 0.985 | 0.972 | 0.911 |
| Sips | | | | | | | | |
| q_m (mg g ⁻¹) | 2.0 | 0.2 | 83.1 | 0.1 | 377.4 | 100.0 | 177.0 | 77.5 |
| k_s (L mg ⁻¹) | 2.06×10^{-11} | 2.81×10^{-9} | 0.16 | 75.99 | 0.016 | 0.024 | 0.018 | 0.017 |
| $1/n_s$ | 7.6×10^{-4} | 1.4×10^{-4} | 0.6 | 2.5×10^{-3} | 1.1 | 0.9 | 1.2 | 1.3 |
| R^2 | 0.251 | 0.095 | 0.350 | 0.679 | 0.976 | 0.990 | 0.990 | 0.987 |
| Redlich-Peterson | | | | | | | | |
| A (L g ⁻¹) | 23.4 | 29.0 | 19.2 | 1.9 | 4.8 | 1.8 | 2.5 | 0.03 |
| B (L mg ⁻¹) | 0.25 | 0.35 | 0.29 | 0.01 | 6.61×10^{-11} | 2.19×10^{-11} | 2.29×10^{-11} | 0.87 |
| β | 0.99 | 0.98 | 0.97 | 0.99 | 4.91 | 1.81 | 2.22 | 0.02 |
| R^2 | 0.941 | 0.978 | 0.984 | 0.488 | 0.961 | 0.982 | 0.971 | 0.387 |

Table S4 R_L values calculated from Eq. S4.

| C_0 (mg/L) | FC1 | FC2 | FC3 |
|--------------|-------|-------|-------|
| 10 | 0.208 | 0.091 | 0.969 |
| 20 | 0.116 | 0.048 | 0.984 |
| 30 | 0.081 | 0.032 | 0.989 |
| 40 | 0.062 | 0.024 | 0.992 |
| 50 | 0.050 | 0.020 | 0.993 |
| 60 | 0.042 | 0.016 | 0.994 |

References:

1. F. Zhao, E. Repo, Y. Song, D. Yin, S. Ben Hammouda, L. Chen, S. Kalliola, J. Tang, K. C. Tam and M. Sillanpaa, *Green Chem.*, 2017, **19**, 4816-4828.
2. I. Langmuir, *J. Am. Chem. Soc.* 1916, **38**, 2221–2295.
3. E. F. Lessa, M. S. Gularte, E. S. Garcia and A. R. Fajardo, *Carbohydr. Polym.*, 2017, **157**, 660-668.
4. X. Zheng, E. Liu, F. Zhang, Y. Yan and J. Pan, *Green Chem.*, 2016, **18**, 5031-5040.
5. R. Sips, *J. Chem. Phys.* 1948, **16**, 490–495.
6. O. Redlich, D.L. Peterson, *J. Phys. Chem.* 1959, **63**, 1024.
7. B. C. Melo, F. A. A. Paulino, V. A. Cardoso, A. G. B. Pereira, A. R. Fajardo and F. H. A. Rodrigues, *Carbohydr. Polym.*, 2018, **181**, 358-367.