Supporting Information for

**Hydroxyl-Modified Chitosan Nanofiber Beads for Sustainable Boron Removal and Environmental Applications**

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A close-up of a test

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**Fig. S1.** Illustration of CGCNF beads (a) before and (b) after freeze-drying.

|  |  |
| --- | --- |
| a  b |  |

**Fig. S2.** Experiment of colloidal titration (a) before and (b) after adding indicator of toluidine blue.

A chemical structure with lines and dots

Description automatically generated with medium confidence

**Fig. S3.** *DA*%, *DD*%, and *DG*% of chitosan nanofibers and GCNF beads.

**Calculation details of degree of deacetylation (*DD*)**

*DD1*% of bare chitosan nanofibers was calculated according to **Eq. (S1)**:

(S1)

Where *d*1 is the mole of deacetylated unit (mol), *W*1 is the dry mass of bare chitosan nanofibers (g), and 161 and 204 are the molar weight of deacetylated unit and acetylated unit (g/mol), respectively.

*DD2*% of GC particles and GCNF beads was calculated based on **Eq. (S2):**

(S2)

Where *d*2 is the mole of deacetylated unit (mol), *a* is the mole of acetylated unit (mol), 340 is the molar weight of gluconated unit (g/mol), and *W*2 is the dry mass of GC particles or GCNF beads (g).

The degree of gluconated units (*DG*%) is therefore given as follows:

*DG*(%) = *DD*1(%) – *DD*2(%) (S3)

The level of grafted gluconted units (*LGG*%) is written as follows:

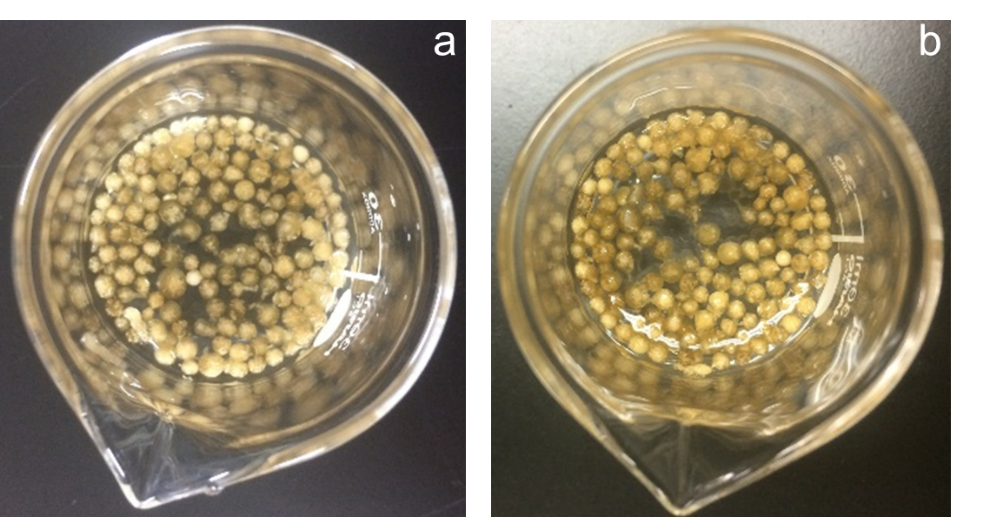
(S4)

**Table S1.** The solubility of various adsorbents.

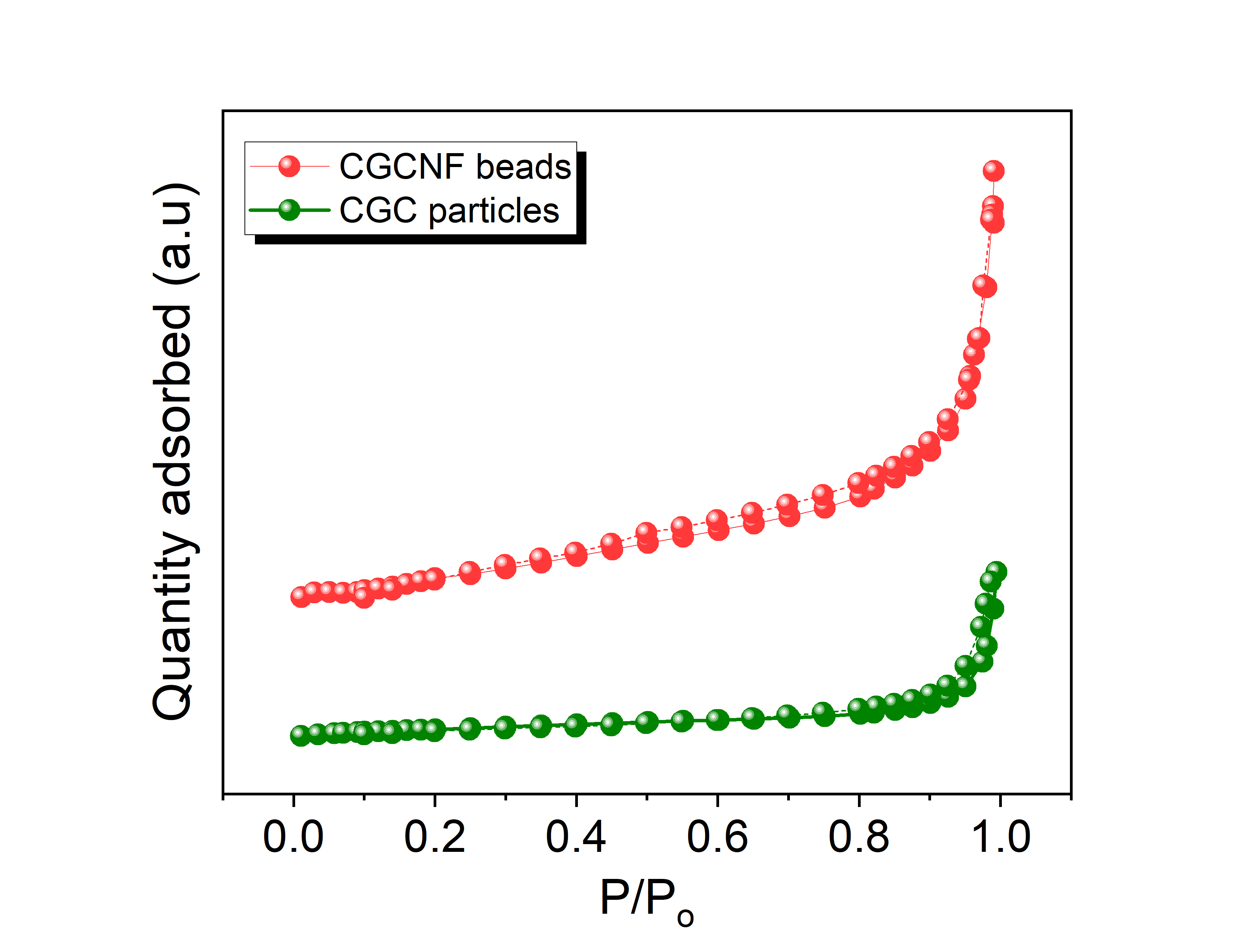
|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sample** | **Mili-Q water** | **0.1M NaOH** | **6M NaOH** | **0.1M HCl** | **6M HCl** |
| GC particles | + | + | + | - | - |
| GCNF beads | + | + | + | - | - |
| CGC particles | + | + | + | + | + |
| CGCNF beads | + | + | + | + | + |

“+”: insoluble.

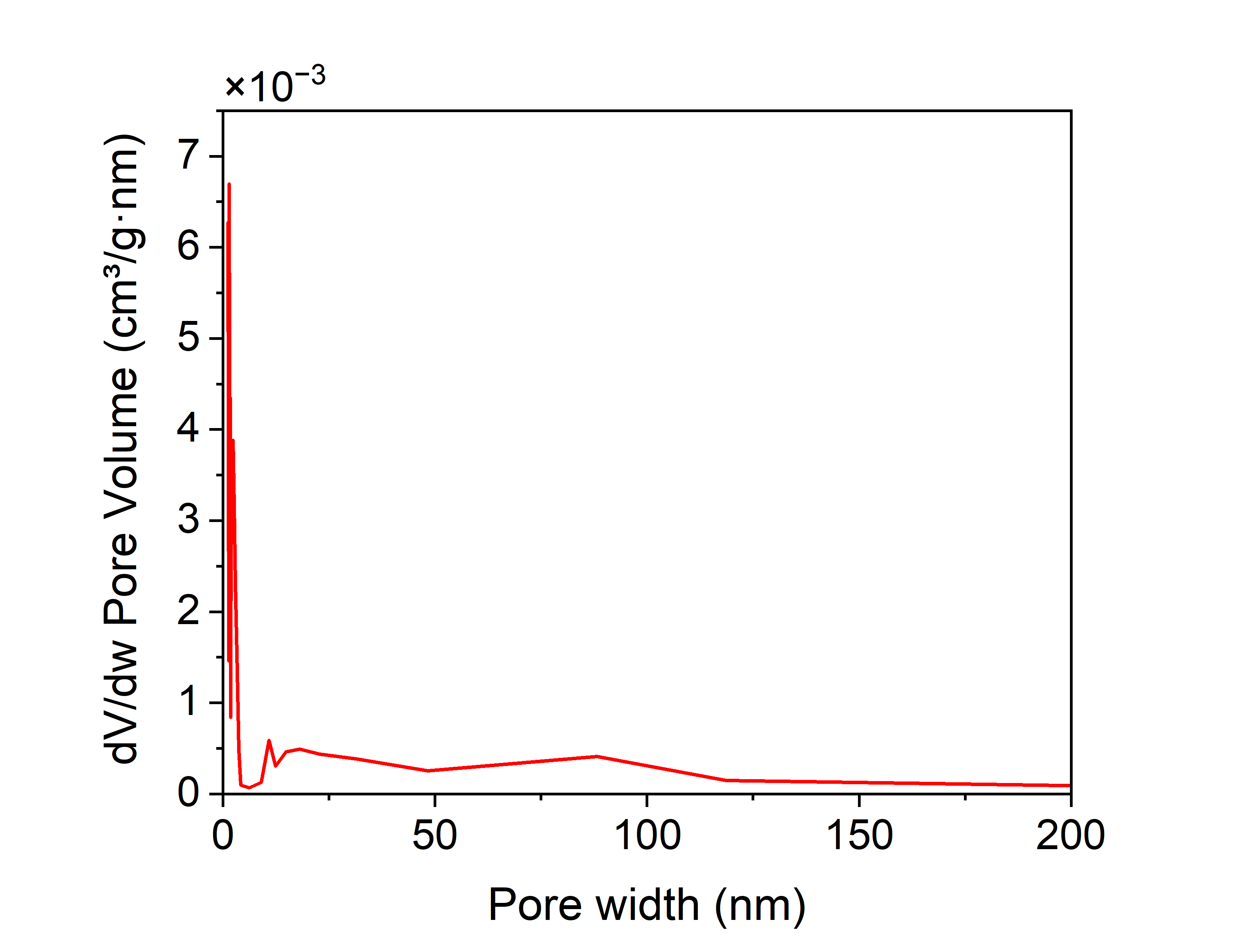
“-”: soluble.



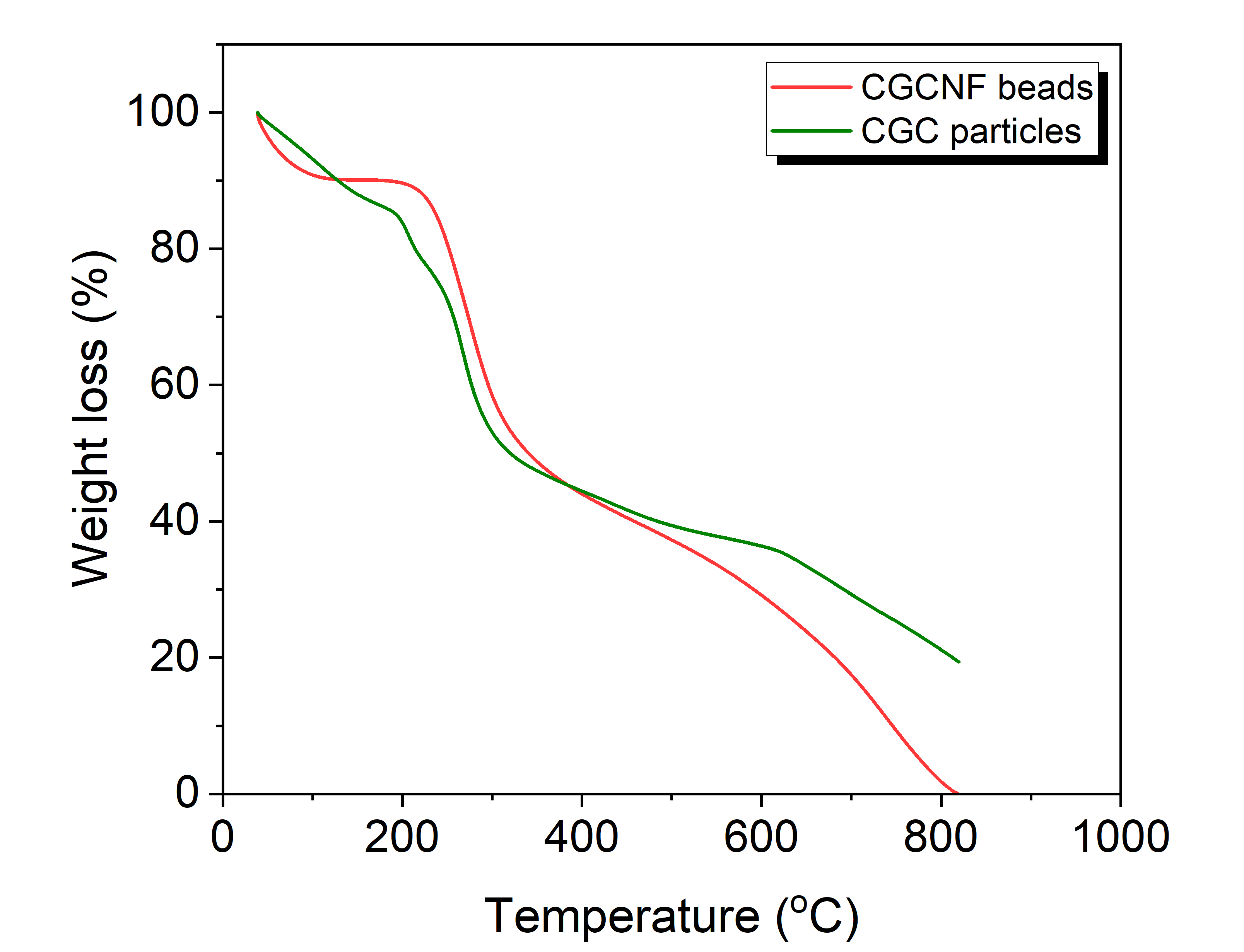
**Fig. S4.** CGCNF beads in 6M HCl solution after (**a**)1 min; and (**b**) 1 month.



**Fig. S5.** N2 adsorption-desorption isotherm curves of CGCNF beads and CGC particles samples.



**Fig. S6.** Pore size distribution of CGCNF sample.

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**Fig. S7.** TGA analysis for the prepared chitosan-based samples.

**Fig. S8.** Effect of initial pH solution on boron removal efficiency by using CGCNF beads and CGC particles (Initial concentration of boron:400 mg/L, mass of adsorbent: 0.8 g, initial pH solution: 2.03-12.03, solution volume: 20 mL, contact time: 24 h and temperature: 25 ºC).

**Table S2.** Langmuir, Freundlich, and Temkin isotherm constants and correlation coefficients of various adsorbents for boron adsorption.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Isotherm | Parameters | CGCNF beads | CGC particles | Amberlite IRA-743 |
| Langmuir | *q*exp (mg/g) | 5.53 | 3.96 | 5.42 |
| *q*max (mg/g) | 6.05 | 4.13 | 5.73 |
| *b* (L/mg) | 0.094 | 0.090 | 0.151 |
| *R*2 | 0.9976 | 0.9991 | 0.9997 |
| *R*L range | 0.027 - 0.513 | 0.028 - 0.524 | 0.016 - 0.385 |
| Freundlich | *K*F | 1.793 | 0.886 | 1.827 |
| *n* | 4.454 | 3.441 | 4.522 |
| *R*2 | 0.9441 | 0.8418 | 0.7764 |
| Temkin | *B* (J/mol) | 0.589 | 0.716 | 0.963 |
| *A*T (L/g) | 44.003 | 1.478 | 2.617 |
| *R*2 | 0.9687 | 0.9866 | 0.9111 |

c

**Fig. S9.** Experimental data of boron adsorption onto CGCNF beads fitted to linearized forms of **(a)** Langmuir, **(b)** Freundlich, and **(c)** Temkin isotherms (Initial concentration of boron: 10 - 400 mg/L, mass of adsorbent: 0.8 g, initial pH solution: 5.45, solution volume: 20 mL and contact time: 24h).

c

**Fig. S10.** Experimental data of boron adsorption onto CGC particles fitted to linearized forms of **(a)** Langmuir, **(b)** Freundlich, and **(c)** Temkin isotherms (Initial concentration of boron: 10 - 400 mg/L, mass of adsorbent: 0.8 g, initial pH solution: 5.45, solution volume: 20 mL and contact time: 24 h).

**Table S3.** Kinetics parameters for adsorption of boron by using various adsorbents.

|  |  |  |  |
| --- | --- | --- | --- |
| **Kinetic models** | **Parameters** | **CGCNF beads** | **CGC particles** |
| Pseudo-first order model | *k*1 (min-1) | 0.0648 | 0.0037 |
| *q*e (mg/g) | 5.47 | 4.06 |
| *R*2 | 0.9958 | 0.9137 |
| Pseudo-second order | *k*2 (g mg-1 min-1) | 0.0221 | 0.0007 |
| *q*e (mg/g) | 5.67 | 5.04 |
| *R*2 | 1.000 | 0.9901 |
| Intra-particle diffusion | *K*diff(mg g-1 min-1/2) | 0.0370 | 0.1231 |
| *C* (mg g-1) | 4.5003 | 0.0359 |
| *R*2 | 0.3860 | 0.9137 |

a

**Fig. S11.** Experimental data of boron adsorption onto CGCNF beads fitted to linearized forms of **(a)** Pseudo-first order, **(b)** Pseudo-second order, and **(c)** Intra-particle diffusion (Initial concentration of boron: 400 mg/L, mass of adsorbent: 0.8 g, initial pH solution: 5.56, solution volume: 20 mL, contact time: 0-24 h and temperature: 25 oC).

**Fig. S12.** Experimental data of boron adsorption onto CGC particles fitted to linearized forms of **(a)** Pseudo-first order, **(b)** Pseudo-second order, and **(c)** Intra-particle diffusion (Initial concentration of boron: 400 mg/L, mass of adsorbent: 0.8 g, initial pH solution: 5.56, solution volume: 20 mL, contact time: 0-24 h and temperature: 25 oC).

A graph of different colored lines

Description automatically generated with medium confidence

**Fig. S13.** Effect of ions Na+, K+, Ca2+ and Mg2+ on boron removal efficiency by using (a) CGCNF beads and (b) CGC particles.

**Fig. S14.** Adsorption performance of Se(VI), As(III), As(V), Cr(III)and Cr(VI) on CGCNF beads and CGC particles.

A graph of a number of blue bars

Description automatically generated with medium confidence

**Fig. S15.** Desorption and reusability of CGCNF beads and CGC particles (Initial concentration of boron: 400 mg/L, mass of adsorbent: 0.8 g, initial pH solution: 5.56, solution volume: 20 mL, contact time: 24h and temperature: 25 oC).

**Table S4.**Comparison of boron desorption efficiency by various adsorbents.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Adsorbent** | **Desorption condition** | **Regeneration condition** | **Desorption efficiency** | **Ref.** |
| Functional magnetic mesoporous silica hybrid nanoparticles | *C*i = 100 mg/L, dose = 0.1 g/50 mL, 0.1 M HCl, 12h, room temperature | 3% NH3.H2O then dried at 60oC | 65% after 7 cycles | [51] |
| Magnetic multi-hydroxyl  microbeads | *C*i = 150 mg/L, m = 0.1 g, 0.1 M HCl, 8h, 25 oC | Water at pH 9 then dried at 80 oC | 44.5% after 6 cycles | [51] |
| Zeolitic imidazolate framework | dose = 0.1 g/80 mL, water, 12h | 80 oC, overnight | 74.4% after 4 cycles | [52] |
| CGC particles | *C*i = 400 mg/L, dose = 0.8 g/50 mL, 0.1 M HCl, 24h, 25 oC | 0.1 M NaOH, 12 h, 25oC then freeze drying | 51.8% after 5 cycles | This work |
| CGCNF beads | *C*i = 400 mg/L, dose = 0.8 g/50 mL, 0.1 M HCl, 24h, 25 oC | 0.1 M NaOH, 12 h, 25oC then freeze drying | 65.1% after 20 cycles | This work |

**Table S5.** Characteristics of FGD wastewater (concentrations in mg/L).

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| --- | --- |
| **Parameters** | **FGD wastewater** |
| pH | 6.6 |
| Na+ | 1261.40 |
| Ca2+ | 3627.85 |
| Mg2+ | 1392.50 |
| B3+ | 133.29 |
| Se6+ | 850.38 |
| As3+ | 0.02 |
| Cr5+ | 0.04 |
| Zn2+ | 1.49 |
| Cu2+ | 0.44 |
| Cd2+ | 0.03 |
| Ni2+ | 0.15 |