

## Adsorption isotherms and kinetics of activated carbons produced from coals of different ranks

### MATERIALS AND METHODS

#### Preparation of activated carbon

All of the chemicals used were analytical grade. The coal samples were obtained from Baganuur, Shariin, Nariinsukhait, Ereen, Tavantolgoi, and Saikhaovoo deposits in Mongolia. Table 1 in the main paper shows the basic coal sample information. The raw coals were treated with 130%  $\text{ZnCl}_2$  solutions at room temperature. Continued mixing of the raw coals with  $\text{ZnCl}_2$  for 24 h was maintained using a magnetic stirrer. After mixing, the solutions were allowed to dry at in an oven for 2 h at approximately  $105^\circ\text{C}$ . Then, the coal samples were pyrolyzed in a vertical cylindrical container. The experiments were conducted at a temperature of  $700^\circ\text{C}$  and a heating rate of  $20^\circ\text{C min}^{-1}$ . Carbonized coal samples were then placed in quartz tubes. The oxygen in the tubes was removed using nitrogen, and the tubes were heated until the temperature reached  $800^\circ\text{C}$ . The samples were processed using heated water steam for 120 min. After being cooled, all the carbonized samples were washed several times with hot water until the pH became neutral, and finally washed with cold water to remove residual chemicals.

**Table S1** | Atomic percentages of carbon (C1s) and oxygen (O1s) obtained by XPS analysis of AC-I

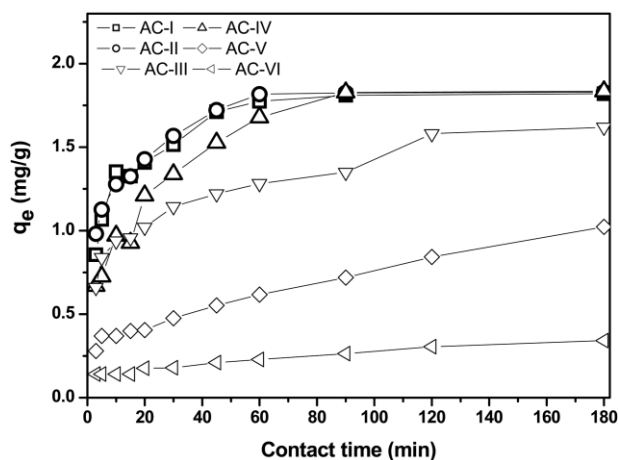
| Functional group     | Binding energy (eV) | Atomic percentage (%) |
|----------------------|---------------------|-----------------------|
| <b>C1s</b>           |                     |                       |
| Carbideic            | 283.5               | 5.9                   |
| Graphitic            | 284.6               | 70.9                  |
| C-OH, C-O-C          | 285.5               | 5.9                   |
| C=O                  | 287.4               | 6.7                   |
| C-O-C=O              | 289                 | 10.6                  |
| <b>O1s</b>           |                     |                       |
| C=O                  | 531.1               | 27.1                  |
| C-OH, C-O-C          | 532.3               | 23.4                  |
| C-O-C=O              | 533.4               | 48.3                  |
| $\text{H}_2\text{O}$ | 535.9               | 1.2                   |

#### Proximate and ultimate analysis

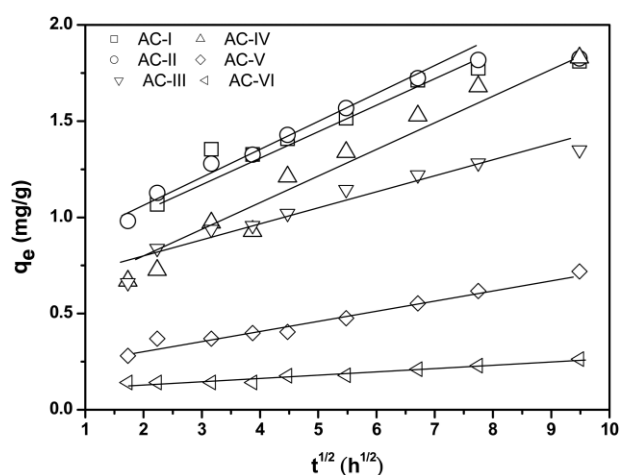
Proximate analysis was carried out with a micro thermogravimetric analyzer (SDT Q600, TGA, TA instruments) similar to the procedure of ASTM D 5142-04 for coal and coke (ASTM 2002a). Elemental analysis of the samples was performed according to the ASTM D3176-89 standard test method for coal and coke (ASTM 2002b). The C, H, N, and S contents were measured using an elemental analyzer (Flash 2000, Thermo Scientific). Oxygen was estimated by the difference.

#### Determination of acidic and basic sites

The procedure for Boehm titration was adopted from Boehm (1994). A total of 1.0 g of the ACs was added to 15 mL solutions composed of 0.1 M  $\text{NaHCO}_3$ , 0.05 M  $\text{Na}_2\text{CO}_3$ , and 0.1 M NaOH for acidic groups and 0.1 M HCl for basic groups at room temperature. These solutions were maintained



**Figure S1** | MB adsorption rate using the prepared ACs. The contact time is up to 3 h given an initial concentration of  $10 \text{ mg L}^{-1}$  and a shaking speed of 125 rpm. The solutions were well-mixed after 3 h; thus, external mass transport limitations were negligible. The concentration gradient decreased over time as a result of the accumulation of MB particles in vacant sites; thus, adsorption rate dropped in the latter stage of adsorption. With the exception of AC-V and AC-VI, adsorption on all of the samples was initially extremely rapid and then slowed down throughout the adsorption process.



**Figure S2** | Intra-particle diffusion plots for MB removal by the prepared ACs.

for over 2 days. Acidic and basic solutions were then back-titrated with 0.1 M HCl and 0.1 M NaOH, respectively.

### Textural and chemical characterization

The adsorption capacities of ACs obtained from different coals were characterized via nitrogen adsorption at  $-196^{\circ}\text{C}$  using an ASAP2010 apparatus (Micrometrics). Brunauer–Emmett–Teller (BET) total surface area and  $t$ -method micropore surface area were calculated based on adsorption isotherms using the BET equation and de Boer's  $t$ -method, respectively. Micropore fraction (percentage ratio of micropore surface area to BET total surface area) was also tabulated to investigate pore development. Scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis were used to determine the surface textural characteristics and elemental composition of ACs, respectively. Organic surface structures were studied using Fourier transform infrared (FTIR) spectroscopy at a wavelength range of  $4000$  to  $400\text{ cm}^{-1}$ . The X-ray photoelectron spectroscopy (XPS) measurements were performed using a Vacuum Generators ECSALAB MKII photoelectron spectrometer (VG Co., East Grinstead, UK) with an ALK $\alpha$ X-ray source ( $1486.6\text{ eV}$ ) under  $10^{-7}$  torr vacuum. A pass energy of  $100\text{ eV}$  was used in recording the scan spectra.

### Batch equilibrium studies

For the batch adsorption studies, appropriate AC was added to a series of Erlenmeyer flasks filled with  $50\text{ mL}$  MB. The MB concentrations ranged from  $1$  to  $10\text{ mg L}^{-1}$ . Adjustment of pH 7 of the MB solutions prior to degradation was carried out with  $0.1\text{ M NaOH}$  or  $\text{H}_2\text{SO}_4$  from Merck. The final pH

ranged from  $7.0$  to  $7.5$ . The flasks were sealed with parafilm and then shaken at  $125\text{ rpm}$  in an orbital shaker incubator under  $30^{\circ}\text{C}$  until equilibrium was reached. The samples were precipitated ( $15\text{ min}$ ) and analyzed using a UV/V is spectrometer at a wavelength corresponding to the maximum absorbance of  $664\text{ nm}$ . The remaining dye solution concentrations were subtracted from the initial concentration to determine the amount of dye adsorbed onto the AC. Each experiment was duplicated under identical conditions. The amount of MB adsorption at equilibrium,  $q_e\text{ (mg g}^{-1}\text{)}$ , was calculated by:

$$q_e = \frac{(C_0 - C_e) \times V}{W} \quad (1)$$

where  $C_0$  and  $C_e\text{ (mg L}^{-1}\text{)}$  are the MB concentration at initial and equilibrium, respectively,  $V$  is the volume of the solution (L), and  $W$  is the mass of AC used in gram (g). Two widely used error functions, the non-linear regression RMSE (Ng *et al.* 2002) and sum of SSE (Kumar and Sivanesan 2006) have been applied to assess the quality of fit.

$$\text{RMSE (\%)} = \sum_1^n \left[ \frac{(q_{e(\text{exp})} - q_{e(\text{cal})})^2}{N - 2} \right]^{1/2} \quad (2)$$

$$\text{SSE (\%)} = \sum_1^n \left[ \frac{(q_{e(\text{exp})} - q_{e(\text{cal})})^2}{N} \right]^{1/2} \quad (3)$$

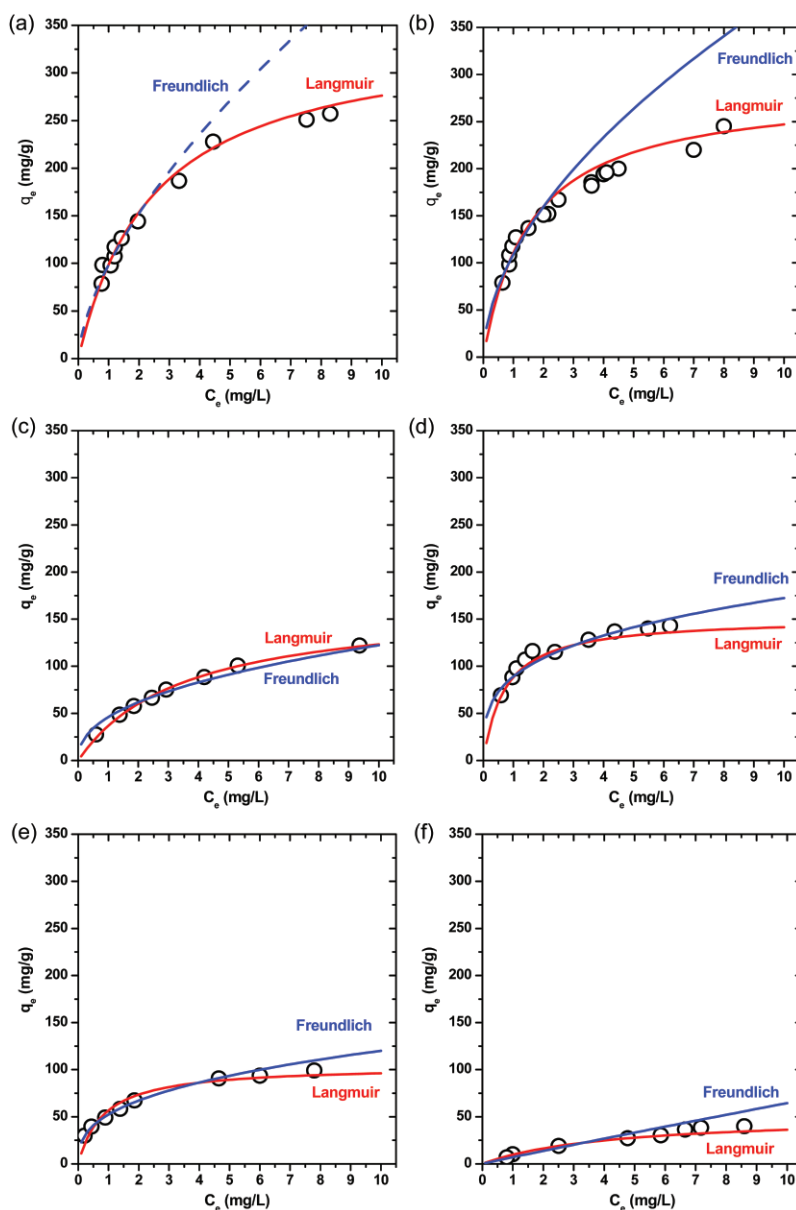
where  $q_{e(\text{exp})}\text{ (mg g}^{-1}\text{)}$  is the experimental value of MB adsorption,  $q_{e(\text{cal})}\text{ (mg g}^{-1}\text{)}$  is the calculated value of MB adsorption, and  $N$  is the number of data points.

### Batch kinetic studies

Kinetic analysis was conducted at room temperature. Appropriate AC doses were introduced into  $250\text{ mL}$  amber glass bottles, which were then filled with  $10\text{ mg L}^{-1}$  MB solution to exclude headspace and capped with Teflon septum caps. Next, the bottles were shaken in a rotary tumbler at a rotation speed of  $125\text{ rpm}$ . Samples were collected at predetermined intervals for up to  $3\text{ h}$  and subjected to filtration through prewashed  $0.45\text{ }\mu\text{m}$  filters to remove the AC and determine residual MB concentration. The amount of MB adsorption at time  $t$ ,  $q_t\text{ (mg g}^{-1}\text{)}$ , was calculated by

$$q_t = \frac{(C_0 - C_t) \times V}{W} \quad (4)$$

where  $C_t\text{ (mg L}^{-1}\text{)}$  are the MB concentration at any time  $t$ .



**Figure S3** | Adsorption isotherms for MB onto the prepared ACs: (a) AC-I; (b) AC-II; (c) AC-III; (d) AC-IV; (e) AC-V; (f) AC-VI.

## REFERENCES

- ASTM- D5142-04 2002a Standard test methods for proximate analysis of the analysis sample of coal and coke by instrumental procedures Annual Book of ASTM Standards, Section 5, vol. 05.06. American Society for Testing and Materials, West Conshohocken, PA.
- ASTM- D3176-89 2002b Standard practice for ultimate analysis of coal and coke. Annual Book of ASTM Standards, Section 5, vol. 05.06. American Society for Testing and Materials, West Conshohocken, PA.
- Boehm, H. P. 1994 Some aspects of the surface-chemistry of carbon-blacks and other carbons. *Carbon* **32** (5), 759–769.
- Kumar, K. V. & Sivanesan, S. 2006 Pseudo second order kinetics and pseudo isotherms for malachite green onto activated carbon: comparison of linear and nonlinear regression methods. *J. Hazard. Mater.* **136** (3), 721–726.
- Ng, J. C. Y., Cheung, W. H. & McKay, G. 2002 Equilibrium studies of the sorption of Cu(II) ions onto chitosan. *J. Colloid Interface Sci.* **255** (1), 64–74.