Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Delivering low-energy carbon capture with photo-responsive hypercrosslinked polymers derived from polystyrene waste

Aotian Liu, [†,a] Guanchu Lu, [†,a] Xianfeng Fan [a,*] and Cher Hon Lau [a,*]

[a] School of Engineering, The University of Edinburgh, Robert Stevenson Road, Edinburgh, EH9 3BF, UK, E-mail: *cherhon.lau@ed.ac.uk*

[†] These authors contributed equally to this work.

Contents

1. Experimental Configuration for Photo-modulated Desorption

The experimental configuration for dynamic photo-modulated desorption was established by adding a visible light outside the metal retainer. The light rays can irradiate the spent adsorbents in the quartz container through the hole of the metal retainer.

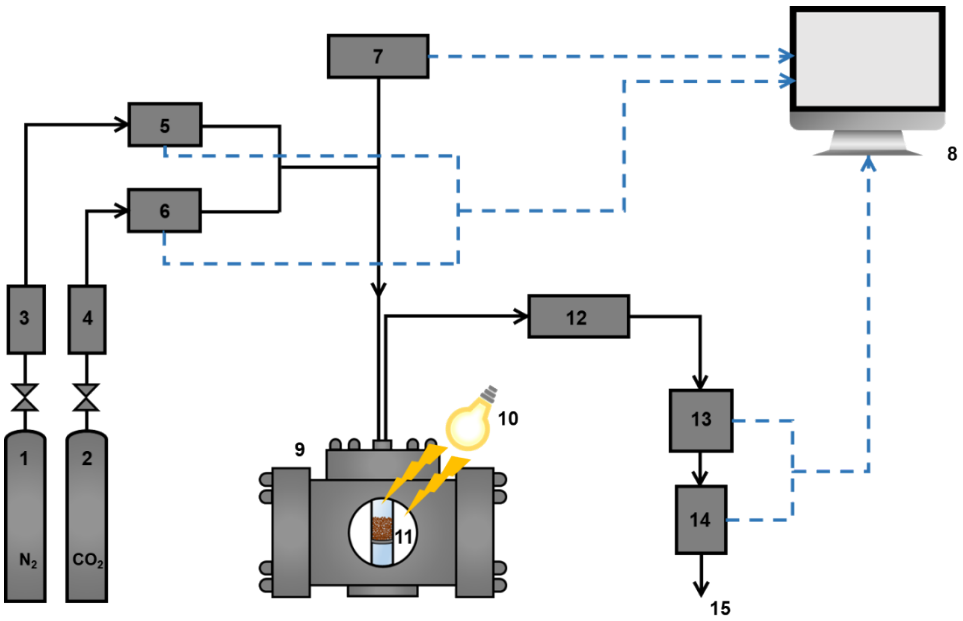

Figure S1. Experimental configuration for photo-modulated desorption: (1) N_2 gas cylinder and regular, (2) CO2 gas cylinder and regular, (3) zeolite/silica drying column of N_2 gas, (4) zeolite/silica drying column of CO2 gas, (5) mass flow controller of N_2, (6) mass flow controller of CO2, (7) fibre-optic temperature sensor and signal conditioner, (8) data analysis workstation, (9) metal retainer, (10) visible light, (11) quartz container, (12) water condenser, (13) non-dispersive infrared CO_2 sensor, (14) mass flow meter and (15) gas exit.

2. BET Analysis

N2 adsorption-desorption isotherms at 77 K and CO_2 adsorption isotherms at 273 K of HCPs, HCPs@Azo, *cis*-HCPs@Azo and *trans*-HCPs@Azo were measured on a Quadrasorb Evo Quantachrome in our previous paper [1]. The pore size distributions and pore volumes were obtained using the model of non-local density functional theory (NLDFT) [2].

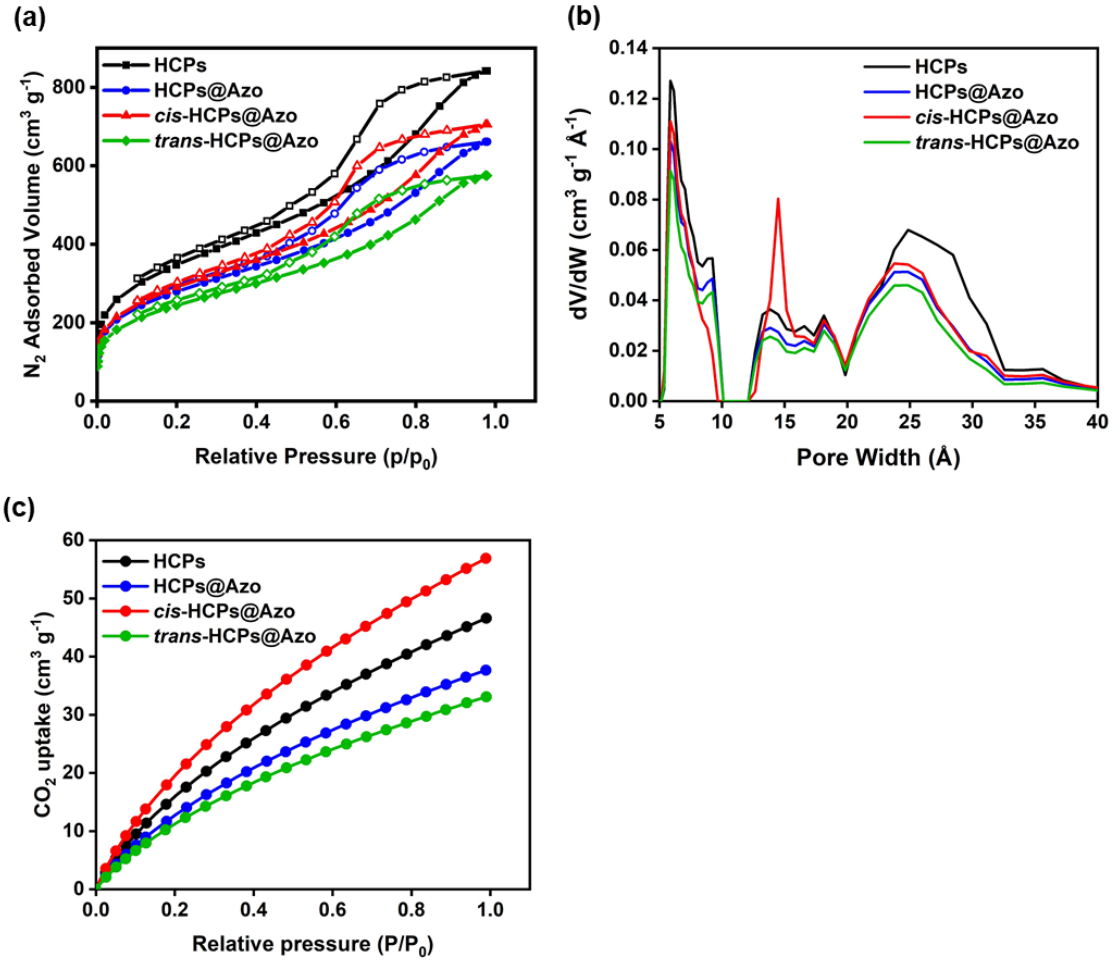

Figure S2. (a) N_2 adsorption and desorption curves at 77 K temperature, (b) pore size distribution and (c) CO2 adsorption curves at 273 K of HCPs, HCPs@Azo, *cis*-HCPs@Azo and *trans*-HCPs@Azo.

Table S1. BET surface areas, pore volumes of different size and total pore volumes of HCPs, HCPs@Azo, *cis*-HCPs@Azo and *trans*-HCPs@Azo.

	HCPs	HCPs@Azo	*cis*-HCPs@Azo	*trans*-HCPs@Azo
Pore volume (5 Å – 10 Å) (cm^3g^{-1})	0.308	0.254	0.228	0.223
Pore volume (10 Å – 20 Å) (cm^3g^{-1})	0.212	0.183	0.231	0.163
Pore volume (20 Å – 40 Å) (cm^3g^{-1})	0.64	0.462	0.488	0.398
Pore volume (> 40 Å) (cm^3g^{-1})	0.06	0.058	0.062	0.048
Total pore volume (cm^3g^{-1})	1.22	0.957	1.009	0.832
BET surface area (m^2g^{-1})	1225	984	1024	862

3. CO_2 adsorption and CO_2/N_2 Selectivity

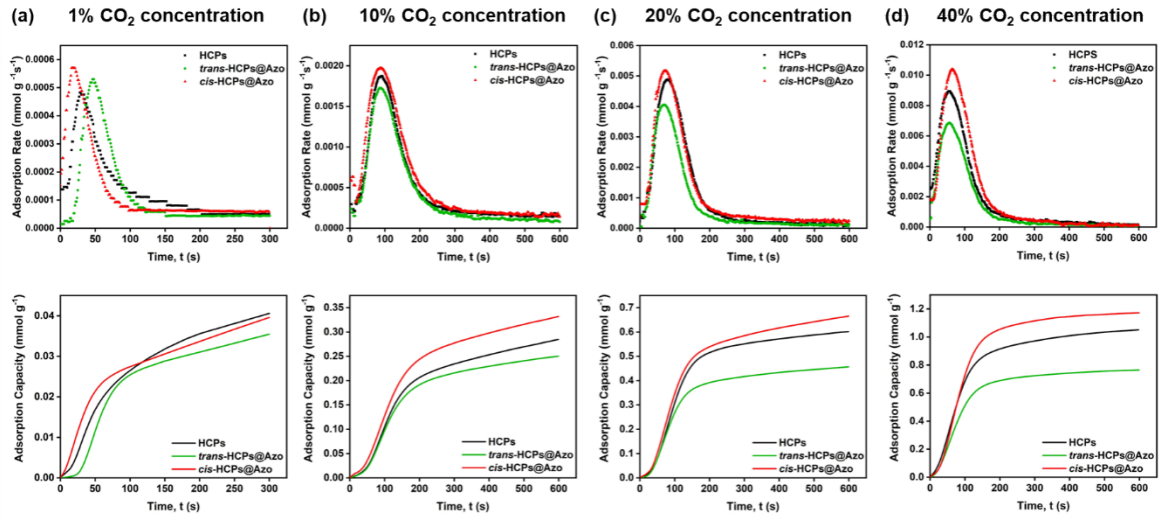

Figure S3. CO_2 adsorption rates and adsorption profiles of (black) HCPs, (green) visible light irradiated *trans*-HCPs@Azo and (red) UV light irradiated *cis*-HCPs@Azo at different CO_2 concentration of (a) 1 v/v %, (b) 10 v/v %, (c) 20 v/v %, (d) 40 v/v % at room temperature and atmosphere pressure.

The ideal CO_2/N_2 selectivity ($S_{CO2/N2\ ideal}$) can be calculated by dividing the adsorbed amounts of CO_2 and N_2 pure gas [3, 4] as the equations in the following table:

Table S2. Equations of adsorbed amounts of pure CO_2 and N_2 and CO_2/N_2 ideal selectivity

Pure CO_2 component	$V_{pure\ CO_2} = \int_0^t V_{gas\ blank} - \int_0^t V_{mfm}$	(1)
	$n_{pure\ CO_2} = \frac{P \times V_{pure\ CO_2}}{R \times T}$	(2)
Pure N_2 component	$V_{pure\ N_2} = \int_0^t V_{gas\ blank} - \int_0^t V_{mfm}$	(3)
	$n_{pure\ N_2} = \frac{P \times V_{pure\ N_2}}{R \times T}$	(4)
Ideal selectivity	$S_{co_2/N_2\ \ ideal} = \frac{n_{pure\ CO_2}}{n_{pure\ N_2}}$	(5)

, where $V_{pure\ CO2}$ (mL) and $V_{pure\ N2}$ (mL) are the adsorbed volumes of pure CO_2 and N_2, $n_{pure\ CO2}$ (mmol) and $n_{pure\ N2}$ (mmol) are the adsorbed amounts of CO_2 and N_2, $V_{gas\ blank}$ (mL s^{-1}) and V_{mfm} (mL s^{-1}) are the volumes of blank gas at input and mass flow meter reading at output, R is the gas constant (8.314 J mol^{-1} K^{-1}), P (KPa) and T (K) are the pressure and temperature of adsorption process, t (s) is the adsorption duration.

The practical selectivity of CO_2/N_2 ($S_{CO2/N2}$) in the mixed CO_2 and N_2 gas is determined by the ratio of the molar fractions of gas after and before adsorption process [5, 6], the equations are shown as following:

Table S3. Equations of adsorbed amounts of CO_2 and N_2 and CO_2/N_2 selectivity in the mixed gas

CO_2 component	$V_{CO_2} = \int_0^t V_{CO_2\ blank} - \int_0^t \frac{C_{CO_2}}{C_{CO_2\ blank}} V_{CO_2\ blank}$	(6)
	$n_{CO_2} = \frac{P \times V_{CO_2}}{R \times T}$	(7)
	$n_{CO_2\ blank} = \frac{P \times V_{CO_2\ blank}}{R \times T}$	(8)
N_2 component	$V_{N_2} = \int_0^t V_{gas\ blank} - \int_0^t V_{mfm} - \int_0^t V_{CO_2}$	(9)
	$n_{N_2} = \frac{P \times V_{N_2}}{R \times T}$	(10)
	$n_{N_2\ blank} = \frac{P \times V_{N_2\ blank}}{R \times T}$	(11)
Selectivity	$S_{co_2/N_2} = \frac{n_{CO_2}/n_{N_2}}{n_{CO_2\ blank}/n_{N_2\ blank}}$	(12)

, where V_{CO2} (mL) and V_{N2} (mL) are the adsorbed volumes of CO_2 and N_2 respectively in the mixed gas, n_{CO2} (mmol) and n_{N2} (mmol) are the adsorbed amounts of CO_2 and N_2, C_{CO2} (mg L^{-1} s^{-1})and $C_{CO2\ blank}$ (mg L^{-1} s^{-1})are the CO_2 concentrations at output and input, $V_{gas\ blank}$ (mL s^{-1})and V_{mfm} (mL s^{-1})are the volumes of blank total gas at input and mass flow meter reading at output, $V_{CO2\ blank}$ (mL s^{-1}) and $V_{N2\ blank}$ (mL s^{-1}) are the volumes of CO_2 and N_2 in blank gas, $n_{CO2\ blank}$ (mmol s^{-1})and $n_{N2\ blank}$ (mmol s^{-1})are the amounts of CO_2 and N_2 in blank gas, R is the gas constant (8.314 J mol^{-1} K^{-1}), P (KPa) and T (K) are the pressure and temperature of adsorption process, t (s) is the adsorption duration.

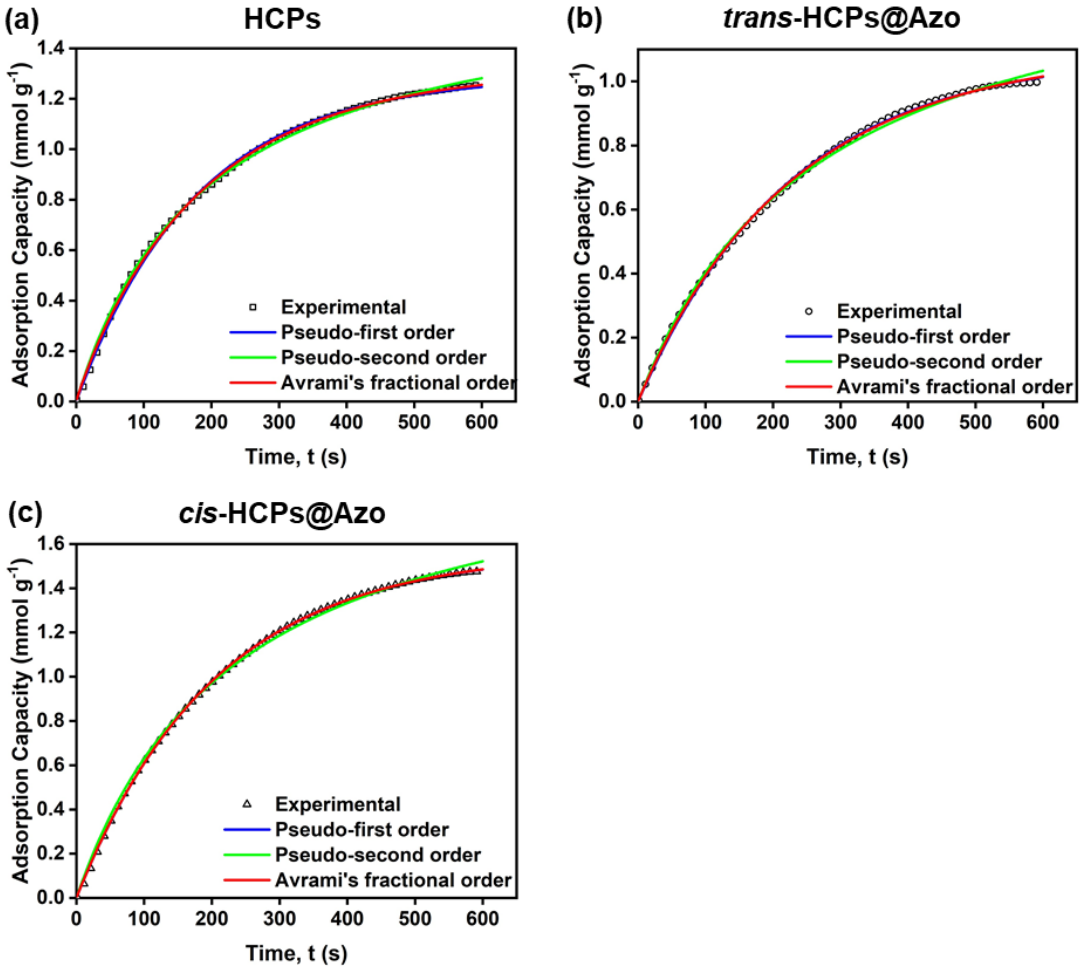

Figure S4. The CO_2 adsorption process experimental data of (a) HCPs, (b) *trans*-HCPs@Azo and (c) *cis*-HCPs@Azo was fitted by (blue) Pseudo-first order kinetic model, (green) Pseudo-second order kinetic order and (red) Avrami's fractional order kinetic model.

4. Adsorption Kinetic Models

5. Desorption Efficiency and Kinetic Models

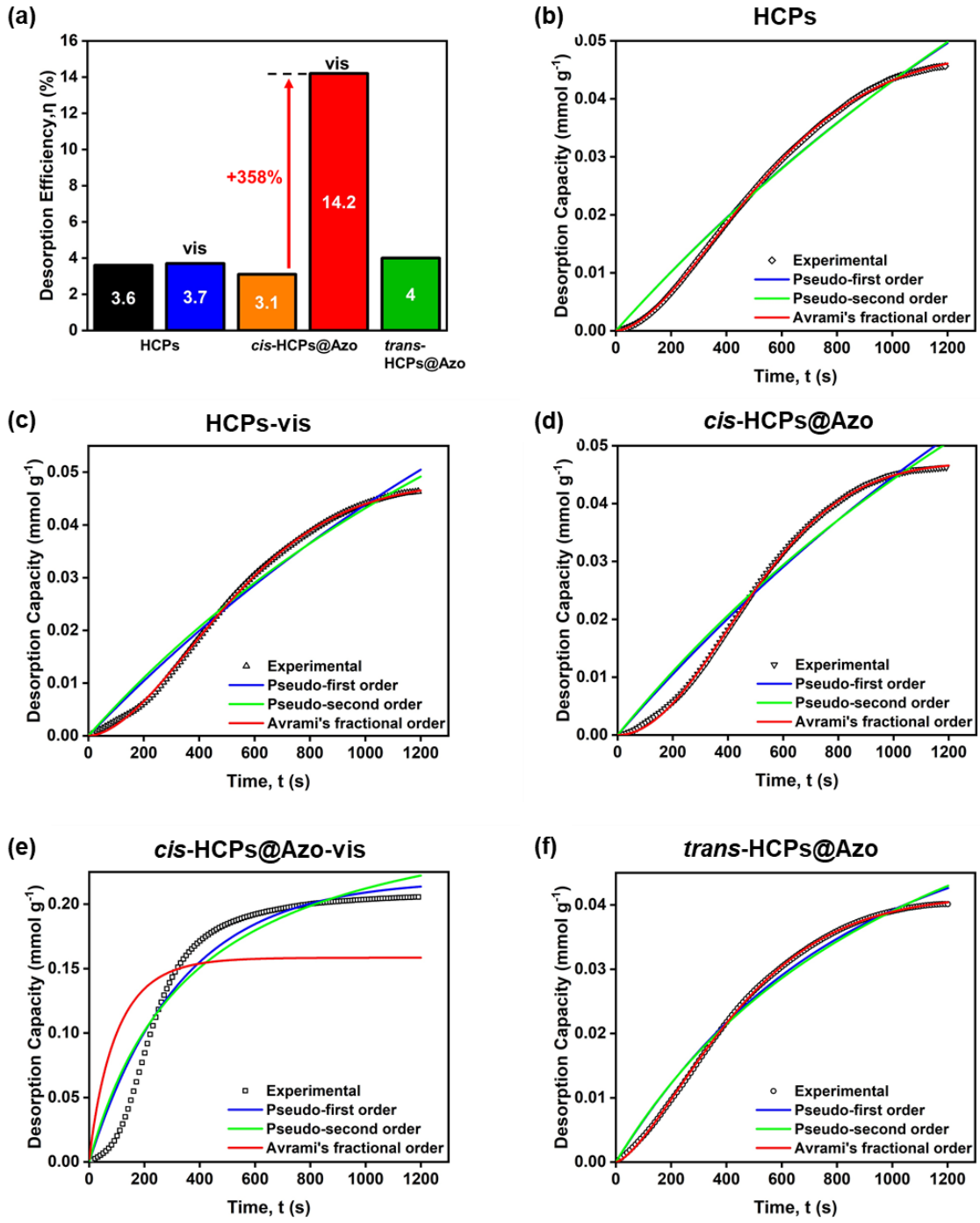

Figure S5. (a) The CO_2 desorption efficiency of HCPs, *cis*-HCPs@Azo and *trans*-HCPs@Azo with and without visible irradiation, and the desorption process experimental data of (b) HCPs, (c) HCPs-vis, (d) *cis*-HCPs@Azo, (e) *cis*-HCPs@Azo-vis and (f) *trans*-HCPs@Azo was fitted by (blue) Pseudo-first order kinetic model, (green) Pseudo-second order kinetic order and (red) Avrami's fractional order kinetic model.

6. Energy Consumption and Cost Evaluation

The energy consumption and cost of regenerating pristine HCPs and HCPs@Azo were evaluated. Pristine HCPs were regenerated using the traditional thermal approach where these adsorbents were regenerated in a vacuum environment at 110 C for 24 hours, while HCPs@Azo were regenerated using UV-vis irradiation. The equipment used in the thermal-vacuum regeneration method included a vacuum oven (Fistreem International Limited - OVA031.XX3.5) and a vacuum pump (KNF Neuberger - N816.3KT.18). The light used in our photo-modulated method included a UV light (ZLUV LAMP - 365nm, 6W) and a visible light (ZLUV LAMP– 450nm, 6W). Based on the Energy Guide UK [7], the price of electricity in the UK in 2023 was set at £0.34 per kWh.

Table S4. Energy consumption and cost evaluation of adsorption-desorption in traditional method of HCPs and photo-modulated method of HCPs@Azo

		Regeneration		Regeneration			
		Vacuum oven	Vacuum pump	UV light	Visible light	Total power consumption	Total cost
Power		0.4 kW	0.1 kW	6×10^{-3} kW	6×10^{-3} kW	-	£ 0.34 /kWh
HCPs	Adsorption	-	-	-	-	-	-
	Desorption	12 h	12 h	-	-	-	-
	Power consumption	4.8 kWh	1.2 kWh	-	-	6 kWh	£ 2.04
HCPs@Azo	Adsorption	-	-	1 h	-	-	-
	Desorption	-	-	-	1 h	-	-
	Power consumption	-	-	6×10^{-3} kWh	6×10^{-3} kWh	1.2×10^{-2} kWh	£ 4.08×10^{-3}

7. References

1. A. Liu, C. Mollart, A. Trewin, X. Fan and C. H. Lau, *ChemSusChem*, 2023, e202300019.
2. P. I. Ravikovitch, G. L. Haller and A. V. Neimark, *Advances in colloid and interface science*, 1998, **76**, 203-226
3. S. Saqib, S. Rafiq, N. Muhammad, A. L. Khan, A. Mukhtar, N. B. Mellon, Z. Man, M. H. Nawaz, F. Jamil and N. M. Ahmad, *Journal of Natural Gas Science and Engineering*, 2020, **73**, 103072.
4. L. A. Neves, J. G. Crespo and I. M. Coelhoso, *Journal of Membrane Science*, 2010, **357**, 160-170.
5. J. Liu, J. Tian, P. K. Thallapally and B. P. McGrail, *The Journal of Physical Chemistry C*, 2012, **116**, 9575-9581.
6. Y. Zhao, K. X. Yao, B. Teng, T. Zhang and Y. Han, *Energy & Environmental Science*, 2013, **6**, 3684-3692.
7. Average Cost Of Electricity Per KWh (UK 2023 Updated), https://energyguide.org.uk/average-cost-electricity-kwh-uk/).