Supporting Information

A Novel Synthesis of MIL 53 (Al)@SiO2: An Integrated Photo Catalyst Adsorbent to Remove Bisphenol A from Wastewater

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Table S1 Details of the chemicals used

Component	CAS Reg. No.	Suppliers	Purity (%)	Purification method
Nitric acid (HNO_3)	7697-37-2	Merck	70	Used as received
N,N-Dimethylformamide (DMF)	68-12-2	Merck	98	Used as received
Terepthealic acid (H_2BDC)	100-21-0	Merck	98	Used as received
Bisphenol-A (BPA)	1675-54-3	Merck	98	Used as received

Table S2 Experimental range and levels of independent variables

Factor	Name	Minimum	Maximum	Coded Low	Coded High	Mean	Std. Dev.
A	Aluminium foil : fly ash	0.20	1	-1 ↔ 0.32	+1 ↔ 0.88	0.6	0.231
B	Water : DMF	0	4	-1 ↔ 0.59	+1 ↔ 3.41	2	1.154

Table S3 Responses for different experimental runs

Run	Factor 1	Factor 2	Response
	A : (Aluminium foil : fly ash)	B: (Water : DMF)	Adsorption uptake of BPA
1	0.60	2.00	45.20
2	0.89	0.59	16.61
3	0.60	2.00	45.20
4	1.00	2.00	15.00
5	0.60	2.00	45.20
6	0.89	3.41	18.25
7	0.32	3.41	24.54
8	0.20	2.00	41.20
9	0.60	2.00	45.20
10	0.60	2.00	45.20
11	0.32	0.59	26.88
12	0.60	4.00	14.07
13	0.60	0.00	12.30

Table S4 ANOVA for BPA adsorption uptake

Sources	Sum of Squares	df	Mean Square	F Value	p-value Prob>F	
Model	2373.29	5	474.46	59.85	<0.0001	Significant
A- aluminium foil : fly ash	359.29	1	359.29	45.32	0.0003	359.29

B- water : DMF	0.41	1	0.41	0.051	0.8273	0.41
AB	3.96	1	3.96	0.50	0.5026	3.96
A^2	481.33	1	481.33	60.71	0.0001	481.33
B^2	1731.27	1	1731.27	218.38	<0.0001	1731.27
Residual	55.50	7	7.93			55.50
Lack of Fit	55.50	3	18.50			55.50
Pure Error	0.000	4	0.000			0.000
Cor Total	2427.79	12				2427.79

The probability plot of residual in Figure S1, shows the residuals are normally distributed and no response transformation is needed. The studentized residual measures the number of standard deviations, which separates the actual and predicted values.

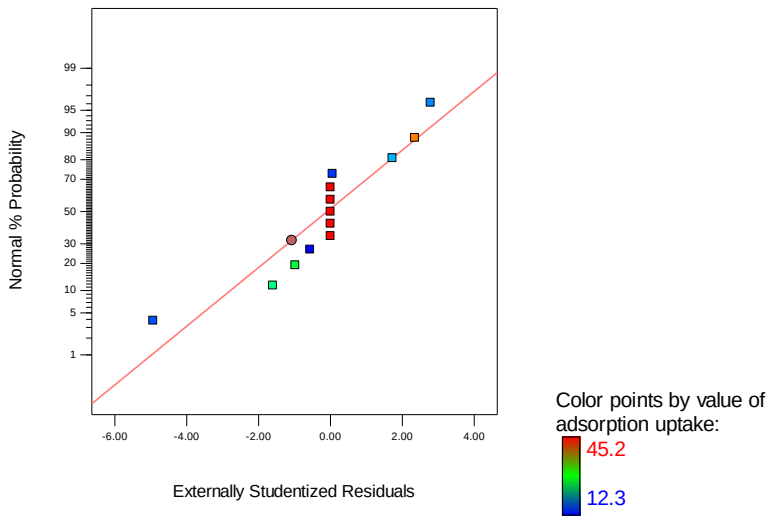

Figure S1 The studentized residuals and normal percentage probability plot for BPA adsorption uptake

Figure S2 represents the plot of studentized residual versus the predicted value of BPA uptake. The constant variance of observation for all the values of response is confirmed by the random scatter of the plot. Hence, there no transformation is required for the response variables.

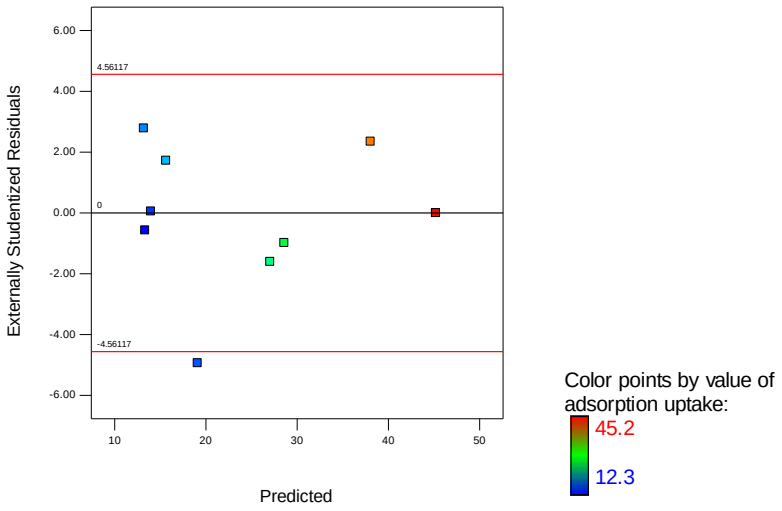

Figure S2 The predicted uptake of BPA and studentized residuals' plot

Figure S3 shows the plot of actual versus predicted values of BPA uptake. This figure confirms that the predicted values are quite close to the actual ones. This signifies that the model is successful to predict the adsorption uptake of BPA.

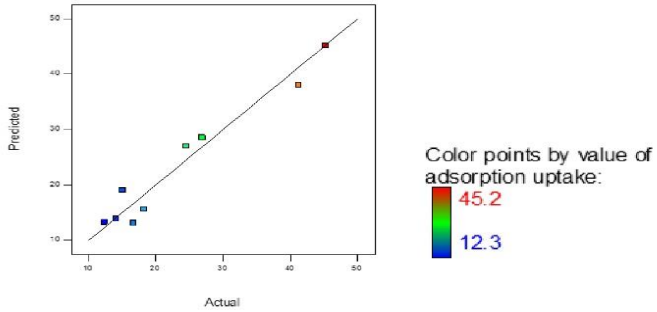

Figure S3 The plot of actual and predicted values of BPA uptake

Table S5 The optimum process variables for MIL 53 (Al)@SiO_2 synthesis

Aluminium foil : fly ash	Water : DMF	BPA adsorption uptake(mg g^{-1})	
		Predicted	Experimental
0.6	2	45.2	44.9

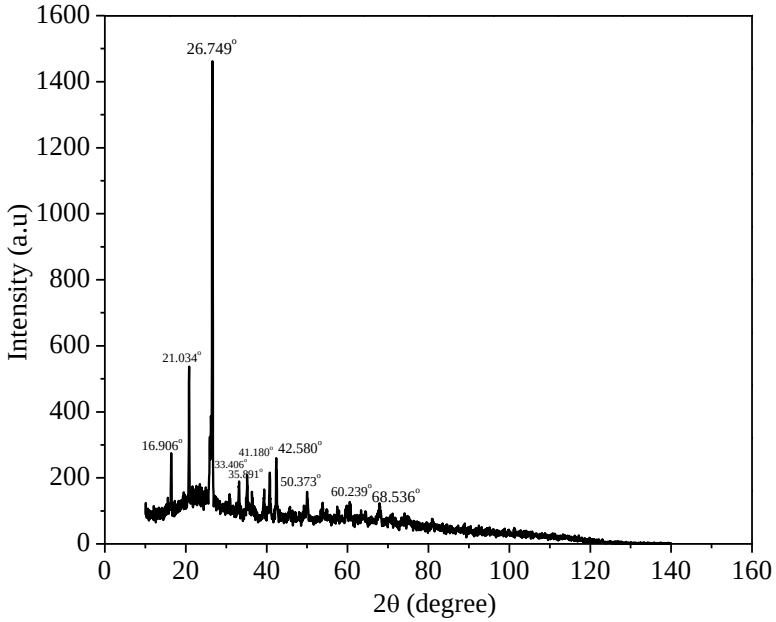

Figure S4 XRD pattern of raw fly ash

The PXRD pattern of fly ash shown in Figure S4 confirms the majority of aluminium silicate (sillimanite) [ICDD card no. 000010626] at 33.406^o corresponding to (220) facet and 41.180^o corresponding to (122) facet, silicon oxide (cristobalite) [ICDD card no. 000040379] peak at 35.891^o corresponding to (110) plane, peak at 42.58 corresponding to (211) facet, 60.239^o

corresponding to (311) facet and 68.536^{o} corresponding to (214) facet, aluminium oxide hydrate [ICDD card no. 000010259] at peaks 26.75^{o} corresponding to (202) facet, 36.65^{o} corresponding to (021) facet and 50.37^{o} corresponding to (015) facet. On the other hand the peak at 16.91^{0} corresponding to (020) plane signifies the presence of iron silicate oxide [ICDD card no. 000110262] and potassium aluminium silicate [ICDD card no. 000500437] at 21.03^{0} corresponding to (211) plane.

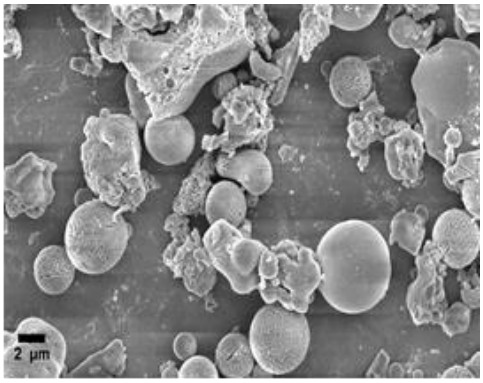

Figure S5 SEM image of Fly ash

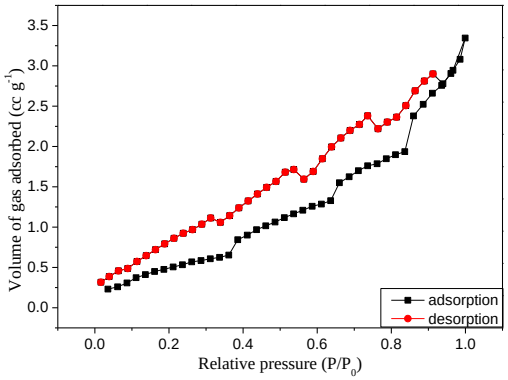

Figure S6 The Nitrogen adsorption desorption isotherm plots of fly ash

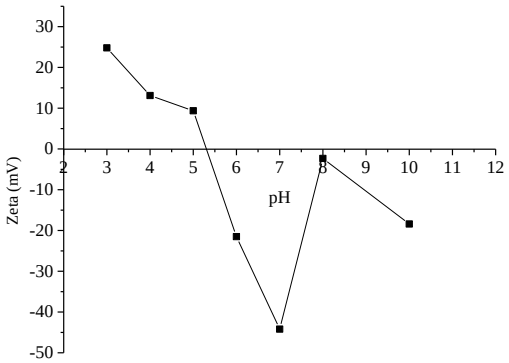

Figure S7 PZC of MIL 53 (Al)@SiO_2

BPA adsorption experiment

$$\%R = \frac{(C_0 - C_e)}{C_0} \times 100 \quad \text{(S1)}$$

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad \text{(S2)}$$

$$q_t = \frac{(C_0 - C_t)}{m} \times V \quad \text{(S3)}$$

where, R and q_e represent the percentage BPA removal and BPA uptake by MIL 53 (Al)@SiO_2 at adsorption equilibrium (mg g^{-1}), respectively. While the symbol q_t represents BPA uptake by MIL 53(Al)@SiO_2 at time t. The quantities C_0 and C_e are the initial and equilibrium concentration of BPA in the aqueous solution, while V and m are the volume of the solution and adsorbent dosage, respectively.

Asdorption isotherm models

The Langmuir adsorption isotherm model based on the assumption of identical and energetically equivalent active sites and monolayer adsorption, which follows the equation:

$$q_e = \frac{q_m C_e}{\left(\frac{1}{b} + C_e\right)} \quad \text{(S4)}$$

Where q_e and q_m are the dye or metal equilibrium uptake (mg L^{-1}) and maximum monolayer adsorption capacity (mg L^{-1}), respectively. b (l/mg) represents Langmuir equilibrium constant. Whereas, Freundlich adsorption isotherm model describes a heterogeneous adsorption model, which is represented as:

$$q_e = K_f C_e^{\frac{1}{N}} \quad \text{(S5)}$$

Where K_f is the empirical constant, which is used to indicate the adsorption capacity ($mg^{1-1/N}.L^{1/N}.g^{-1}$) and N is the heterogeneity factor depending on the adsorbent and adsorbate of the system. Concurrently Temkin adsorption isotherm follows the equation:

$$q_e = \frac{RT}{b_T}\ln(AC_e) \quad \text{(S6)}$$

(RT/b_T) and A are Tempkin constants, here (RT/b_T) depends on the heat of adsorption (J mol^{-1}) and A is the equilibrium of binding constant corresponding the maximum binding energy (L g^{-1}). R and T are the universal gas constant and the absolute temperature [1,2], respectively.

Table S6 Adsorption isotherm parameters for BPA adsorption on MIL 53 (Al)@SiO_2

Adsorption isotherm Model	Parameters	Values		
		Temperature (K)		
		283	303	318
Langmuir adsorption isotherm	q_m*(mg/g)*	125.52	134.68	95.41
	B	0.010	0.021	0.011
	R^2	0.940	0.970	0.970
Freundlich adsorption Isotherm	k_f	3.45	7.71	3.06
	N	1.58	1.83	1.65
	R^2	0.891	0.952	0.921
Tempkin adsorption isotherm	B	128.28	94.26	131.57
	A_t	0.240	0.270	0.125
	R^2	0.909	0.957	0.961

Adsorption kinetics model

The pseudo first order model [2] is established on the assumption that the rate of change of adsorption over time is directly proportional to the difference in saturation concentration and the amount of solid uptake over time. The model follows the equation:

$$\ln\left(\frac{q_e}{q_e - q_t}\right) = k_1 t \quad \text{(S7)}$$

Where, q_e (mg g^{-1}) and q_t (mg g^{-1}) are the mass of solute adsorbed on adsorbent at equilibrium and at agitation time t (min), respectively and k_1 (mg g^{-1}) the rate constant for pseudo-first order adsorption.

Pseudo second order equation [2] is based on the assumption that adsorption capacity is proportionate on the active sites on the adsorbent surface. The pseudo second order [2,3] model is represented by the equation:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad \text{(S8)}$$

Here, k_2 is the adsorption rate constant. Elovich adsorption kinetics model [3] is represented by

$$q_t = \frac{1}{\beta}\ln(\beta\alpha) + \frac{1}{\beta}\ln(t) \quad \text{(S9)}$$

α and β are the initial adsorption rate (mg g^{-1} min) and the desorption constant (g mg^{-1}), respectively.

Intraparticle diffusion model,[3] follows the equation:

$$q_t = k_{\text{int}} t^{0.5} + C \quad \text{(S10)}$$

Where, k_{int} is the rate constant of intra-particle diffusion model and C is related to the thickness of the boundary layer.

Table S7 Adsorption kinetics fitting parameters and correlation coefficient for BPA adsorption on MIL 53 (Al)@SiO_2

Adsorption Kinetic Model	Parameters	Values		
		30 mg/l	80 mg/l	110 mg/l
Pseudo-first order model	k_1(min^{-1})	0.020	0.081	0.287
	q_e(mg g^{-1})	22.110	38.007	68.560
	R^2	0.990	0.860	0.952
Pseudo-second order model	k_2(g mg^{-1} min^{-1})	0.0005	0.003	0.007
	q_e(mgg^{-1})	32.360	42.760	72.410
	R^2	0.991	0.931	0.985

Elovich kinetic model	β (mgg^{-1}min^{-1})	0.157	0.138	0.164
	α (mg g^{-1}min^{-1})	1.190	21.644	1139.100
	R^2	0.973	0.970	0.996
Intra particle diffusion model	k_{int}(mg g^{-1} min$^{-0.5}$)	2.355	2.710	2.412
	C	-3.014	16.53	49.30
	R^2	0.973	0.924	0.911

Thermodynamic parameters

The values of ΔH^0, ΔS^0 and ΔG^0 can be calculated from the following equations:

$$\Delta G = -RT \ln K_d \quad \text{(S11)}$$

$$K_d = \frac{q_e}{C_e} \quad \text{(S12)}$$

$$\ln K_d = \left(\frac{-\Delta H}{RT}\right) + \left(\frac{\Delta S}{R}\right) \quad \text{(S13)}$$

$$\Delta S = \left(\frac{\Delta H - \Delta G}{T}\right) \quad \text{(S14)}$$

Here R is the universal gas constant with the value of 8.314 J mol^{-1} K^{-1} and T is the temperature in K [2].

Table S8 Thermodynamic parameters for BPA adsorption on MIL 53 (Al)@SiO_2

K_d (L mol^{-1})			ΔG^0 (kJ mol^{-1})			ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1})
283(K)	303(K)	318(K)	283(K)	303(K)	318(K)		
1.0436	0.918	0.4657	-0.1004	0.208	1.990	-20.53	-0.072

Reference

[1] S. Deng, Y.P. Ting, Fungal Biomass with Grafted Poly(acrylic acid) for Enhancement of Cu(II) and Cd(II) Biosorption, Langmuir. 21 (2005) 5940–5948. doi:10.1021/la047349a.

[2] N.M. Mahmoodi, B. Hayati, M. Arami, Textile dye removal from single and ternary systems using date stones: Kinetic, isotherm, and thermodynamic studies, J. Chem. Eng. Data. 55 (2010) 4638–4649. doi:10.1021/je1002384.

[3] H. Mazaheri, M. Ghaedi, A. Asfaram, S. Hajati, Performance of CuS nanoparticle loaded on activated carbon in the adsorption of methylene blue and bromophenol blue dyes in binary aqueous solutions : Using ultrasound power and optimization by central composite design, J. Mol. Liq. 219 (2016) 667–676. doi:10.1016/j.molliq.2016.03.050.