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Supplementary materials

Supplementary discussion sections

Discussion section S1: Point of zero charge and Zeta potential

The point of zero charge is defined as the pH value at which a sorbent surface has a net zero or neutral charge (pHPZC). Studying pHPZC for any sorbent is important because it shows if a surface has the ability to draw in cationic or anionic adsorbates. If a particular sorbent surface has a positive charge in a solution with a pH lower than pHPZC, or if an adsorbent surface is positively charged, then the adsorbent surface will absorb anionic adsorbates. Similar to this, an adsorbent will absorb cationic adsorbate if its surface is negatively charged in a solution with a pH higher than pHPZC [32]. To determine the SLS-AC zero point of charge, seven flasks containing 50 mL of distilled water were set at various initial pH values (pHi) (2-9). SLS-AC in the dosage of 50 mg was added to each flask and shaken for 24 hours. To determine the final pH values of the aqueous solutions, the material was taken out of the solution mixture (pHf). The pH difference was calculated using the formula pH = pHi - pHf. At the point where the curve intersects the X-axis, the pH plots versus pHi and pHPZC were evaluated.

The primary determinant of the stability of colloidal dispersions is the zeta potential. The value of zeta potential indicates the strength of electrostatic attraction between close particles and those in a dispersion that have similar charges. High zeta potential will show that the solution is resistant to aggregation and that the tiny particles are stable. Forces of attraction may overwhelm forces of repulsiveness in the presence of low potential, leading to fragmentation and flocculation of the dissipation. Electrically stable colloids are those that have a high zeta potential capacity (positive or negative), whereas colloids with a low zeta potential coagulate or flocculate. The zeta potential for SLS-AC in a suspension of liquid was examined using the Zetasizer Nano ZS (Malvern Instruments) at 25 °C. The light source was a 633 nm He-Ne laser, and the detector was an avalanche photodiode (APD). The electrophoretic light scattering mechanism was used to detect the zeta potential. A dip cell with two parallel Pd electrodes (zen1002, Malvern Instruments) was used to provide electrical support for the ionised surface of the adsorbent. Zetasizer Software was used to analyse the data after noting the signals at a temperature of 12.8°. The Smoluchowski model was applied for the interpretation of the SLS-AC zeta potential in solution in accordance with ISO13099 [33, 34]. Using a surface zeta potential cell made by Malvern Instrument and bearing the model number zen1020, the surface zeta potential was measured in accordance with Malvern Instruments' methodology [35]. The main distinction between zeta potential and point of zero charge is that the former refers to the difference between the stationary layer and the dispersion medium of a solution containing colloidal dispersion, whereas the latter refers to the average charge of the colloidal particles when it reaches zero.

Discussion section S2: Analysis of Error Function

A vast amount of data from the investigation of dye adsorption by surfactant modified AC (SLS-AC) was evaluated on multiple linearized models for finding the best fit model. But due to the linearization inherent bias resulted and sets of different isotherm parameters were established using non-linear regression equations. This gives a mathematical procedure to find out the parameters of isotherm using the actual isotherm equation. So, the optimization approach requires an error function to match the isotherm data to the experimental equilibrium data. Because the error function chosen has an impact on the parameters of the derived-error function, which is mostly based on absolute deviation bias, the data fits into a zone of high concentration. This weighting is increased even more when extreme errors are penalized by the square of the deviation. The bias can be counterbalanced by dividing the deviation with the help of a computed value to demonstrate the relevance of fractional deviation. By the use of Solver add-in with Microsoft Excel, isotherm parameters were discovered during the analysis of error function isotherms by minimizing the respective error functions over the concentration range. This program's initialization is based on a clever guessparameter. In Microsoft Excel, an iterative procedure was started using the numbers obtained from the linearized version of the model. The following sections detail the various error functions.

The sum of the absolute errors (SAEs)

The summation of the method of absolute errors can be given by the following equation:

$$SAE = i = 1 \left| q_{e,exp} - q_{e,cal} \right|$$
(26)

Where $q_{e,exp}$ is the adsorbate concentration that was adsorbed during the experiment, which was calculated from the concentration of equilibrium sorbate liquid phase, Ce was achieved experimentally, and $q_{e,cal}$ is the concentration of theoretical solid phase of sorbate that was adsorbed onto the sorbent, which was calculated using one of the isotherm equations. The data

of the error function is raised by biassing the fit towards the zone of high concentration, which is done by using error functions to determine isotherm parameters.

The Sum of the square of the errors (SSEs)

The summation of the squares of the error's method can be written as follows:

$$SSE = i = 1 \left(q_{e,cal} - q_{e,exp} \right)_{i}^{2}$$
(27)

The isotherm parameters that are computed using this error function provide a better fit as the error value, hence the biassing of fit towards data acquired at the high end of the concentration range increases as the square of the magnitude of error increases. Despite being the most often used error function, the error function has a number of drawbacks.

The hybrid fractional error function (HYBRID)

The sum of the square of the error is divided by the measured value to best suit the sum of the square of the error at a very low concentration. Porter et al. created an error function to achieve this better match. It also uses the number of data points minus the number of parameters (n-p) and the number of degrees of freedom of the system as a divisor in the isotherm equation. It is written as follows:

$$HYBRID = \frac{100}{n-p} \sum_{i=1}^{n} \left[\frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right]_{i}$$
(28)

Marquardt's percent standard deviation (MPSD)

It is represented as:

$$MPSD = 100\sqrt{\left(\frac{1}{n-p\left(\sum_{i=1}^{n}\left(\frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}}\right)_{i}^{2}\right)\right)}\right)}$$

(29)

This error function is used by different researcher in this subject in the past. It sometimes resembles the geometric mean error distribution, which improves with the number of degrees of freedom of the system [47].

Average Relative Error (ARE)

The average relative error function [48] is:

$$ARE = \frac{100}{n} \sum_{i=1}^{n} \left[\frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right]_{i}$$
(30)

This error function tries to keep the fractional error distribution as small as possible throughout the whole concentration range

Chi-square $(\chi 2)$ test

$$\chi 2 = \frac{\left(q_{e,exp} - q_{e,cal}\right)^2}{q_{e,cal}}$$
(31)

The sum of square of difference between actual experimental data and theoretical data predicted from using various models is defined as Chi-square with all the individual difference of square being divided from each respective data produced from models. When comparing the fitness of isotherms, the lowest values of χ^2 are used in error analysis and the greatest values of R² are used when evaluating the fitness of isotherms. Study of error analysis revealed that among all the models, hybrid fractional error study explores lowest error distribution of the experimental data.

Discussion section S3: Discussion on four models

The Thomas model is a generic model for describing column performance when external and internal diffusion resistances are exceptionally low. The adsorption behaviour is generally assumed to suit with second order kinetics and a Langmuir model without axial dispersion in this model.

Linear form:

$$\ln \left(C_{e}/C_{0} - 1 \right) = k_{TH} q_{0} m/Q - k_{TH} C_{0} t$$
(39)

Yoon and Nelson devised a simpler model that requires no precise information on the adsorbate's characteristics, the adsorption bed's parameters, or the kind of adsorbent. In this model, the rate of fall in the likelihood of an adsorbate molecule is proportional to the feasibility of adsorbate adsorption and the feasibility of an adsorbate breakthrough on the adsorbent. Linear form:

$$\ln \left[\frac{C_e}{C_0 - C_e} \right] = k_{YN} t - k_{YN} \tau$$
(40)

The equilibrium, according to Bohart-Adams, is not immediate. The adsorption potential depends on the adsorbing species and adsorbent concentrations are proportional to adsorption rate.

Linear Form:

$$\ln\left(C_{e}/C_{0} = k_{AB}C_{0}t - \left[\frac{kN_{0}H}{v}\right]\right)$$
(41)

The Clark model is based on the usage of the Freundlich isotherm in conjunction with a masstransfer notion. The Clark model implies that the mass transfer zone's shape remains fixed and total adsorbate quantity is eliminated at the column's end.

Linear form:

$$\ln \left({^{\mathcal{C}}_{0}} / {^{\mathcal{C}}_{e}} \right)^{n-1} - 1 = A \times e^{-rt}$$
(42)

 $A = \exp (K_c N_0 Z/\nu)$ $r = K_c C_0$

Supplementary figures



Fig. S1. MG sorption onto different AC's (Dye conc.= 50 mg/L, pH = 6.0, T = 303K, adsorbent dose = 0.15 g/L)



Fig. S2. Chemical phenomenon for MG sorption onto SLS-AC surface



Fig. S3. Plot for *q vs. t* $\frac{1}{2}$ consisting of multiple straight line for MG adsorption onto SLS-AC (T= 293K, MG concentration = 25 mg/L, pH = 6.0)



Fig. S4. Film diffusion model for MG adsorption onto SLS-AC (MG dye concentration = 25 mg/L, pH= 6.0, Time = 60 min,



Fig. S5. Plot between ΔH_X vs. Temperature (K) for sorption of MG onto SLS-AC



Fig. S6a Break through curves at different flow rates (bed depth = 10 cm, MG dye conc. = 25 mg/L)



Fig. S6b. Breakthrough curves at different MG concentrations (Flow rate = 0.5 ml/min, bed depth = 10 cm.



Fig. S6c. Breakthrough curves for variation in bed depths (flow rate = 0.5 ml/min, MG conc. = 25 mg/L)



Fig. S7. (a) Adsorption-regeneration cycle (b) Regeneration of SLS-AC with HCl and NaOH

Supplementary tables

Parameters Adsorbent (SLS-AC)		nt (SLS-AC)
	Before adsorption	After adsorption
Area of surface (m^2/g)	188.57	198.56
Volume of pore (cm^3/g)	28.45	18.29
Average pore size (nm)	34.67	24.78

Table S1: BET analysis parameters

Parameters	Operati	Adsorbent	(SLS-AC)
	on	Before adsorption	After adsorption
Volume of pore (BJH) (cc/g)	А	0.249	19.472
	D	31.756	20.279
Pore radius (BJH) (Å)	А	20.478	23.627
	D	341.475	296.145
Area of surface (BJH) (m^2/g)	А	101.124	101.278
	D	1857.894	1443.543

Table S2. BJH analysis parameters

Table S3: Error Functions for MG sorption onto SLS-AC

Isotherm	Error Functions		Temperature	
		293	303	313
Langmuir	SAE	0.293	0.252	0.241
	SSE	0.018	0.015	0.013
	HYBRID	1.381	0.891	0.887
	MPSD	3.424	3.746	3.587
	ARE	3.642	2.879	2.471
	χ2	0.002	0.003	0.003
Freundlich	SAE	0.248	0.347	0.378
	SSE	0.054	0.035	0.047
	HYBRID	1.675	0.008	-0.024
	MPSD	4.781	6.645	6.742
	ARE	2.997	3.745	4.014
	χ2	0.017	0.024	0.075
Temkin	SAE	0.247	0.279	0.279
	SSE	0.017	0.026	0.028
	HYBRID	-0.245	-0.324	-0.279
	MPSD	4.371	5.472	5.875
	ARE	2.745	2.579	3.478
	χ2	0.008	0.014	0.017

Redlich- Peterson	SAE	0.245	0.257	0.278
	SSE	0.012	0.014	0.013
	HYBRID	-0.214	-0.113	-0.152
	MPSD	3.984	4.254	3.124
	ARE	2.278	2.314	2.007
	χ2	0.007	0.006	0.006
Toth	SAE	0.234	0.245	0.241
	SSE	0.013	0.014	0.012
	HYBRID	-0.124	-0.134	-0.213
	MPSD	4.523	4.278	3.124
	ARE	2.642	2.548	2.354
	χ2	0.012	0.019	0.014
Radke-Prausnitz	SAE	0.254	0.423	0.246
	SSE	0.014	0.086	0.024
	HYBRID	-3.245	-3.423	-0.247
	MPSD	4.785	6.245	5.247
	ARE	3.124	5.247	2.578
	χ2	0.014	0.024	0.013
D-R	SAE	0.124	0.243	0.238
	SSE	0.011	0.013	0.012
	HYBRID	-0.217	-0.115	0.175
	MPSD	4.017	4.245	3.241
	ARE	2.195	2.297	2.010
	χ2	0.005	0.004	0.005

Table S4: Linear equations for Break through models

Model	Linear Equation
Thomas	$\ln \left(\mathcal{C}_{e} / \mathcal{C}_{0} - 1 \right) = k_{TH} \times q_{0} \times m / Q - k_{TH} \times \mathcal{C}_{0} \times t$
Yoon Nelson	$\ln \left[\frac{C_e}{C_0} - C_e \right] = k_{YN} \times t - k_{YN} \tau$
Bohart- Adam	$\ln \left({^{C}}_{e} / {^{C}}_{0} \right) = k_{AB} \times C_{i} \times t - \left[\frac{k N o H}{\nu} \right]$
Clark	$\ln \left(\mathcal{C}_0 / \mathcal{C}_e \right)^{n-1} - 1 = A \times e^{-rt}$

Table S5: Parameters for different column study models for different flow rates

Column	Constants	Flow rate, Q (mL/min)		/min)
analysis Model		0.5	1.0	1.5
Thomas	q (mg/g)	91.2	85.4	79.4
	k_{TH}	0.001	0.002	0.003
	R ²	0.988	0.999	0.997

	Slope	0.01	0.02	0.01
	Intercept	3.721	3.431	3.124
Yoon-Nelson	k_{YN}	3.71	3.42	3.13
	τ	3.42×10 ⁻³	3.25×10 ⁻³	3.37×10 ⁻³
	R ²	0.978	0.979	0.978
	Slope	-3.62	-3.34	-3.18
	Intercept	0.012	0.008	0.009
Bohart-Adam	N	3.6×10 ³	3.7×10 ³	3.5×10 ³
	k_{AB}	0.0008	0.0007	0.0005
	R ²	0.967	0.968	0.965
	Slope	0.007	0.006	0.006
	Intercept	2.419	1.972	1.859
Clark	K_C	8.1×10 ⁻⁴	7.8×10 ⁻⁴	7.6×10 ⁻⁴
	R	8.1×10 ⁻⁴	7.8×10 ⁻⁴	7.6×10 ⁻⁴
	A	8.57	6.71	5.62
	R^2	0.948	0.957	0.956
	Slope	0.007	0.006	0.006
	Intercept	2.42	1.97	1.86

 Table S6: SLS-AC recycle-regeneration data using 1.0M NaOH

No. of Cycles	Residual concentration (mg/L)	MG removal %
1 st	0.14	94.6
2 nd	0.85	89.9
3 rd	1.96	80.1
4 th	2.73	70.2
5 th	3.58	62.1
6 th	4.98	49.8

 Table S7. Adsorption capacity and % adsorption by using different conc. of NaOH and HCl for SLS-AC regeneration

Eluent	Concentration [M]	C _e (mg/L)	% Adsorption	q _e (mg/g)
HC1	0.2	4.89	49.4	1.32

	0.4	4.04	56.1	1.54
	0.6	3.12	70.3	1.67
	0.8	2.49	72.5	1.85
	1.0	1.51	81.7	1.97
	0.2	3.57	64.1	1.67
NaOH	0.4	3.01	70.3	1.81
	0.6	2.27	75.8	1.92
	0.8	1.93	80.2	2.21
	1.0	0.14	94.6	2.46

Table S8: MG adsorption onto SLS-AC in real water samples

Water Sample	MG concentration (mg/L)	MG removal %
	25	94.6
Tap water	50	81.2
	75	54.7
	25	94.5
Raw water	50	81.8
	75	55.4
	25	94.5
Distilled water	50	79.6
	75	53.8
	25	94.5
Waste water	50	81.6
	75	55.8