Supplementary Material: Process optimization and modelling of methylene blue adsorption using zero-valent iron nanoparticle synthesized from the sweet lime pulp

Naincy Sahu[1], Shalu Rawat [1], Jiwan Singh [1,*], Rama Rao Karri[2,*], Suhyun Lee [3], Jong-Soo Choi [3], Janardhan Reddy Koduru [3,*]

[1]Department of Environmental Science, Babasaheb Bhimrao Ambedkar University, Lucknow-226025, India;
[2]Faculty of Engineering, Universiti Teknologi Brunei, Brunei Darussalam;
[3]Department of Environmental Engineering, Kwangwoon University, Seoul 139-701, Republic of Korea;
*Corresponding authors: kramarao.iitd@gmail.com (R. R. K.); jiwansingh95@gmail.com (J. S.); reddyjchem@gmail.com; Tel: +82-02-940-5496 (J.R.K.).

Sections as per the manuscript

2.5.1. Equilibrium isotherm models

In this research study, various well known adsorption equilibrium isotherms as shown in *Table S1* are investigated to elucidate the methylene blue adsorption onto nZVISLP in a batch system. The underlying thermodynamic principles of these adsorption equilibrium isotherm models usually provide some insight into the affinities of the adsorbent and adsorption mechanisms.

Table S1. Various forms of isotherm models for single component expressed in linear and non-linear forms.

Type of Isotherm	Non-linear expression	Linear expression	Plot	Parameters
Two parameters isotherm models				
Freundlich model	$q_e = K_F C_e^{1/n}$	$ln(q_e) = ln(K_F) + \dfrac{1}{n} ln(C_e)$	$ln(q_e)$ vs $ln(C_e)$	K_F and n
Langmuir (Type 1)	$q_e = \left(\dfrac{K_L b C_e}{1 + b C_e}\right)$	$\dfrac{1}{q_e} = \dfrac{1}{K_L} + \left(\dfrac{1}{K_L b}\right)\dfrac{1}{C_e}$	$1/q_e$ vs $1/C_e$	K_L and b
Langmuir (Type 2)		$\dfrac{C_e}{q_e} = \dfrac{1}{K_L} C_e + \dfrac{1}{K_L b}$	C_e/q_e vs. C_e	K_L and b
Langmuir (Type 3)		$q_e = K_L - \dfrac{1}{b}\dfrac{q_e}{C_e}$	q_e vs. q_e/C_e	K_L and b
Langmuir (Type 4)		$\dfrac{q_e}{C_e} = K_L b - b q_e$	q_e/C_e vs. q_e	K_L and b
Three parameters isotherm models				
Redlich - Peterson	$q_e = \left(\dfrac{K_R C_e}{1 + a_R C_e^{\alpha}}\right)$	$log\left(K_R \dfrac{C_e}{q_e} - 1\right) = log(a_R) + \alpha\, log(C_e)$	Thru trial and approximation method	K_R, a_R, and α
Sips	$q_e = \left(\dfrac{K_S b_S C_e^{1/n_S}}{1 + b_S C_e^{1/n_S}}\right)$	$\dfrac{1}{q_e} = \dfrac{1}{K_S} + \left(\dfrac{1}{K_S b_S}\right)\dfrac{1}{C_e^{1/n_S}}$	Thru trial and approximation method	K_S, b_S, and n_S
Toth	$q_e = \dfrac{K_{th} C_e}{(b_{th} + C_e^{n})^{1/n}}$	$\dfrac{1}{q_e^{n}} = \dfrac{1}{K_{th}} + \left(\dfrac{b_{th}}{K_{th}}\right)\dfrac{1}{C_e^{n}}$	Thru trial and approximation method	K_{th}, b_{th} and n_{th}
Fritz Schlunder	$q_e = \left(\dfrac{K_{FS} b_{FS} C_e}{1 + b_{FS} C_e^{1/n_{FS}}}\right)$	$\dfrac{C_e}{q_e} = \dfrac{1}{K_{FS}} C_e^{1/n_{FS}} + \left(\dfrac{1}{K_{FS} b_{FS}}\right)$	Thru trial and approximation method	K_{FS}, b_{FS} and n_{FS}

2.5.2. Optimization technique

Optimization is an art of science which investigates the best estimation of the parameters (decision variables) of a complex problem that may originated under definite conditions. This framework aims to identify the relevant parameter values that enable an objective (cost) function to generate the maximum or minimum value depending on the requirements. Implementation of optimization to real time problems is very challenging to solve, and often these applications need to be dealt with non-deterministic issues. In these circumstances, hybrid evolutionary techniques like differential evolution optimization (DEO) approach found to be best optimization technique (Karri et al., 2017a; Karri et al., 2017b). This optimization technique is a metaheuristics search algorithm which utilizes the framework of genetic algorithm, approach of evolutionary strategies and computationally intensive for programming. The advantage of DEO is it can be applied to find the best possible estimates of process variables to minimize/maximum the identified objective function under the given set of constraints. DEO is a conventionally population based search technique that commonly uses population of *NP* factors with a dimensional parameter (D) vector for every generation. This concept facilitates to generate trial parameter vectors for initialization. Then, DE creates an arrangement to produce a set of new augmented parameter vectors by appending the third population member with the weighted difference vector between two existing members. The newly generated vector replaces the vector with which it was analyzed, if the subsequent vector produces a lower objective function value than a predetermined member. This process is continued till the best optimal parameter set is determined for each generation. DE algorithm uses typical evolutionary scheme and works through four phases:

$$\text{Initialization} \rightarrow \text{Mutation} \rightarrow \text{Recombination} \rightarrow \text{Selection} \qquad \text{(a.1)}$$

Performance of DE mainly lies on the last three phase; wherein it uses *mutation* concept as a search mechanism, *recombination* augments the successful members from previous generation and *selection* technique to forward the direction of search method towards the probable regions in the feasible region. Mutation expands the search space of present generation, while recombination reuses the earlier successful population members and selection concept identifies the survival of the fittest. The effectiveness of DE solely depends on the implementation, manipulation and efficacy of three key operators namely mutation, recombination and selection. DE initiates with a NP, population size with members represented as Y_i, where *i* represents the population member *i = 1, 2,…, NP;* Procedure and implementation of the three key operators are discussed as follows:

Mutation: This operator is the significant process (operator) in DE algorithm and implementation methodology makes DE significantly differs from other evolutionary algorithms. The mutation procedure augments the weighted difference vector between the existing population members to explore the search space. This framework determine both the degree and direction of perturbation. The different mutation approaches that are employed in the differential evolution algorithm are shown below.

rand / 1: $V_i = Y_i + F_1 * (Y_{r2} - Y_{r3})$ (a.2)

best / 1: $V_i = Y_{best} + F_1 * (Y_{r2} - Y_{r3})$ (a.3)

rand to best / 1: $V_i = Y_{r1} + F_1 * (Y_{r2} - Y_{r3}) + F_2 * (Y_{best} - Y_{r1})$ (a.4)

curr to best / 1: $V_i = Y_i + F_1 * (Y_{r2} - Y_{r3}) + F_2 * (Y_{best} - Y_i)$ (a.5)

rand / 2: $V_i = Y_{r1} + F_1 * (Y_{r2} - Y_{r3} + Y_{r4} - Y_{r5})$ (a.6)

best /2 : $V_i = Y_{best} + F_1 * (Y_{r2} - Y_{r3} + Y_{r4} - Y_{r5})$ (a.7)

Where $r_1, r_2,… r_5$ are uncorrelated randomly selected population members

Recombination: In this phase, successful members from the previous generation are augmented with current members. The perturbed individual vector, $V_{i+1} = (v^1_{i+1}, v^2_{i+1}, \ldots, v^n_{i+1})$, and the recent population member, $Y_i = (Y^1_i, Y^2_i, \ldots, Y^n_i)$, are subject to the crossover (recombination) operation which thus generates a new set of population vectors, termed as "trial" vectors, $U_{i+1} = (u^1_{i+1}, u^2_{i+1}, \ldots, u^n_{i+1})$, as follows:

$$u^j_{i+1} = \begin{cases} v^j_{i+1} & \text{if } rand_j \leq C_r \\ Y^j_i & \text{otherwise} \end{cases} \quad \text{(a.8)}$$

Where, j=1, 2, …, n; and the crossover rate, C_r chosen in the range of 0 ~ 1.

Selection: This implementation scheme also differs from that of other evolutionary algorithms thus making a popular global optimization technique. This approach is termed as greedy scheme which is the key for fast convergence of DE algorithm. The set of population members for the next generation are chosen from the current generation members and its resultant vector is evaluated as:

$$Y^k_{i+1} = \begin{cases} u^k_{i+1} & \text{if } f(u^k_i) \angle f(Y^k_i) \\ Y^k_i & \text{otherwise} \end{cases} \quad \text{(a.9)}$$

Therefore, each distinct member of the temporary population vector is compared with its corresponding member in the current population vector. The member which results in producing least objective function value will be identified for selection to proceed into the next new generation.

2.5.3. Equilibrium kinetic models

Kinetic modelling is an approach to estimate the sorption rate as well as to find the best suitable adsorption rate expressions that represent possible mechanisms. In general, the overall rate of adsorption is assumed to be due to the adsorption rate of the solute on the surface of the adsorbent and due to intraparticle diffusion. The mechanism of adsorption process is influenced by the chemical and/or physical characteristics of the adsorbent. Prominent kinetic models are pseudo 1st order, 2nd order and intraparticle diffusion models namely Weber – Morris, and Boyd kinetic models are investigated in this study. The four kinetics models (both conventional (non-linear) form and linear form are shown in Table S2 are evaluated to understand the mechanics in adsorption process taking place in a batch process. The parameters evaluated from these kinetic models provide the characteristics of surface properties, sorption mechanisms and affinities of the adsorbents.

Table S1. Summary of different conventional type of kinetics both in linear and non-linear forms generally used to estimate the adsorption rate along with corresponding plot to estimate the parameters

Type of kinetics	Non-linear form	Linear form	Plot	Parameters
Pseudo 1st order	$q = q_e(1 - e^{-k_1 t})$	$ln(1 - \frac{q}{q_e}) = -k_1 t$	$ln(1-q/q_e)$ vs. t	k_{ad} = -slope
Pseudo 2nd order (Type 1)		$\frac{t}{q} = \frac{1}{k_{2,1}q_e^2} + \frac{1}{q_e}t$	t/q vs. t	q_e = 1/slope, $k_{2,1}$=slope^2/intercept h = 1/intercept
Pseudo 2nd order (Type 2)		$\frac{1}{t} = k_{2,2}q_e^2\left(\frac{1}{q}\right) - k_{2,2}q_e$	1/t vs.1/q	q_e = -slope/intercept, $k_{2,2}$= intercept^2/slope h = -slope * intercept
Pseudo 2nd order (Type 3)	$q = \left(\frac{K_2 q_e^2}{1 + t K_2 q_e}\right)t$	$\frac{1}{q} = \left(\frac{1}{k_{2,3}q_e^2}\right)\frac{1}{t} + \frac{1}{q_e}$	1/q vs.1/t	q_e = 1/intercept, $k_{2,3}$= intercept^2/slope h = 1/slope
Pseudo 2nd order (Type 4)		$\frac{1}{q_e - q} = \frac{1}{q_e} + k_{2,4}t$	1/(q$_e$-q) vs. t	q_e = 1/intercept, $k_{2,4}$=slope h = slope/intercept^2
Pseudo 2nd order (Type 5)		$\frac{q}{t} = -k_{2,5}q_e * q + k_{2,5}q_e^2$	q/t vs. q	q_e = - intercept/slope, $k_{2,5}$=slope^2/intercept h = intercept
Pseudo 2nd order (Type 6)		$q = q_e - \left(\frac{1}{k_{2,6}q_e}\right)\frac{q}{t}$	q vs. q/t	q_e = intercept, $k_{2,6}$=-1/slope*intercept h = -intercept/slope
Weber - Morris model	$q = k_{id}\sqrt{t}$		log(q) vs. 0.5log(t)	k_{id} = exp (intercept)
Boyd model	$\frac{q}{q_e} = 1 - \frac{6}{\pi^2}exp(-Bt)$	$Bt = -0.4977 - ln(1 - F)$ for $F (= q/q_e) > 0.85$ $B = \frac{\pi^2 D_i}{r^2}$	Bt vs t	D_i

3

3.1.3 Zero-point charge
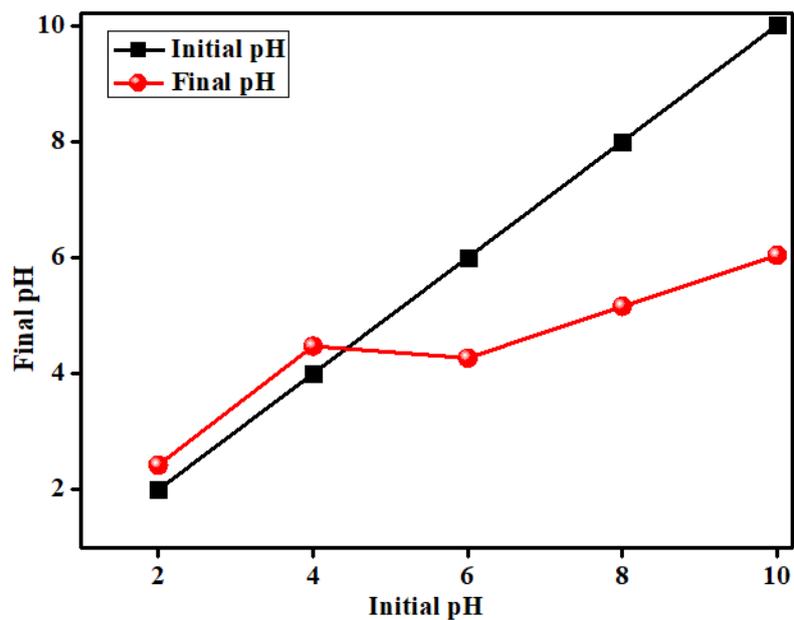
Figure S1. pHzpc of synthesized SLP-IPs

3.1.5 Determination of porosity and internal structure
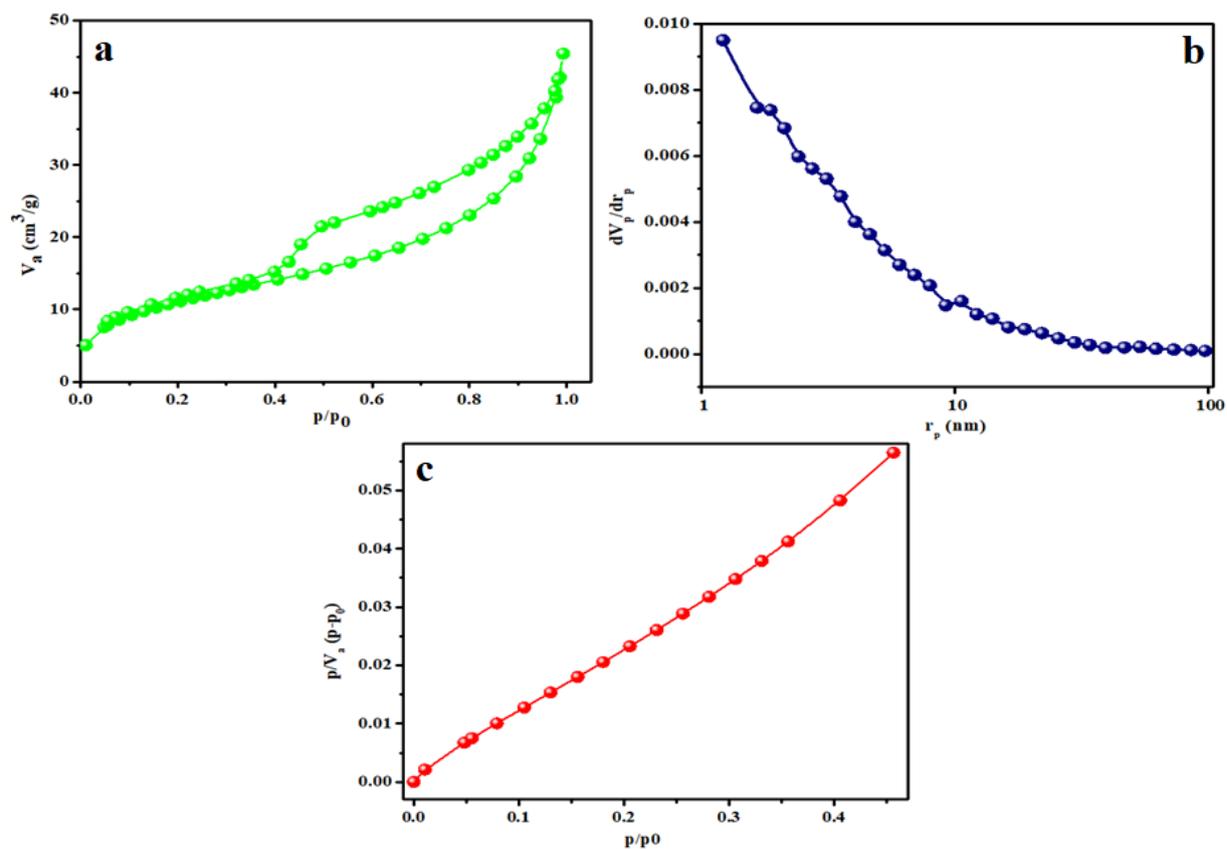
Figure S2. (a) Pressure variation on adsorption/desorption of N_2 (b) variation in dV_P/dr_P (c) BET plot.

3.1.6 X-ray diffraction (XRD)
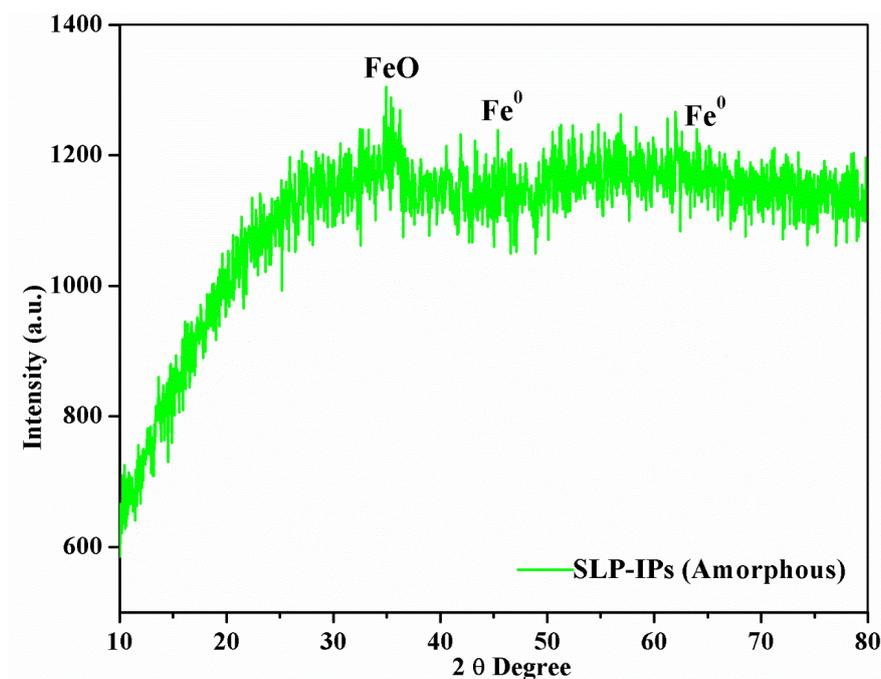
Figure S3. XRD pattern of prepared nZVISLP to identify crystallinity of particles and confirmation of zero valent iron.

3.4 Evaluation of intrinsic parameters in kinetic models

The linear plots of pseudo 1st order, pseudo 2nd order and Weber - Morris kinetic model for other initial dye concentrations (C_0) of 10, 20, 30 and 40 mg/L are shown in *Figure S4* and *Figure S5.* The characteristics constants along with R^2 for the pseudo 1st order and pseudo 2nd order are given in *Table S3*.
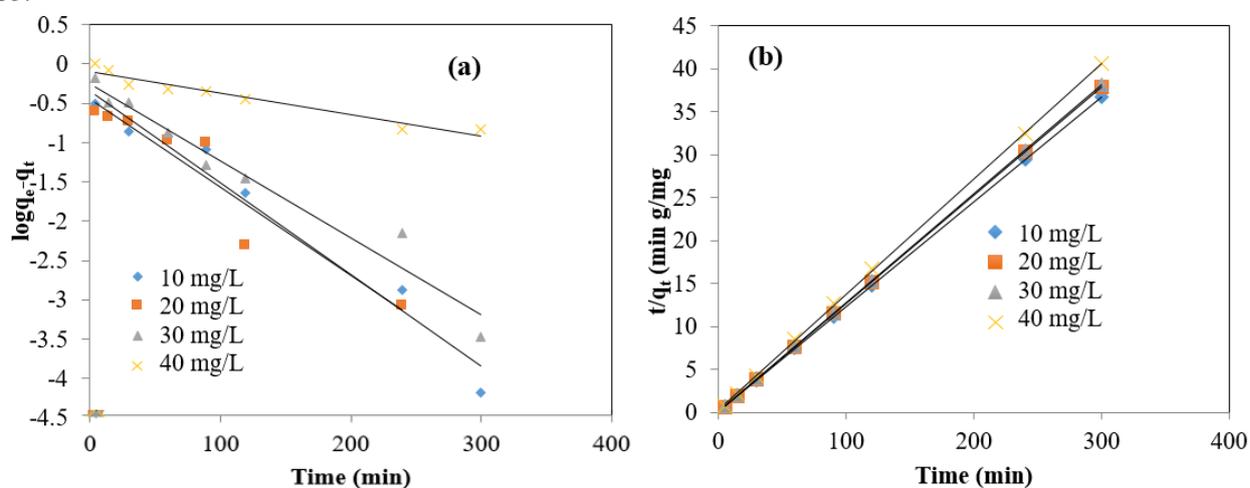
Figure S4. The pseudo 1st order and pseudo 2nd order kinetics study for the adsorption of MB onto nZVISLP at different initial dye concentrations (C_0 = 10, 20, 30 and 40 mg/L; T = 293 K; adsorbent concentration=1.2g/L; initial pH 8.0).
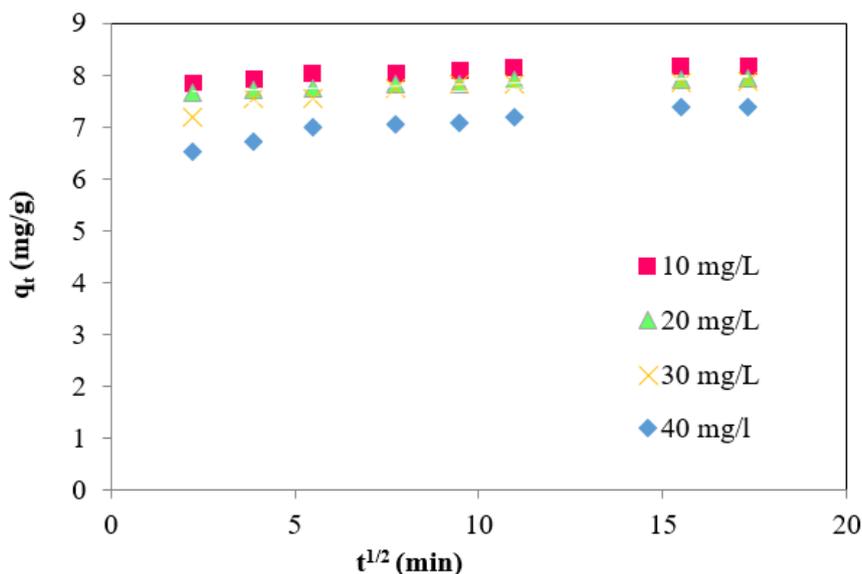
Figure S5. Intraparticle diffusion model for the adsorption of MB on to nZVISLP with different initial dye concentrations (C_0 = 10, 20, 30 and 40 mg/L; T = 293 K; adsorbent concentration=1.2g/L; initial pH 8.0).

Table S3. Pseudo first order and second order kinetics for the removal of MB by nZVISLP

MB conc. (mg/L)	Pseudo-first-order			Pseudo-second-order		
	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g/mg-min)	q_e (mg/g)	R^2
10	0.0938	8.023	0.922	0.017	8.84	0.9362
20	0.0814	7.925	0.878	0.022	8.85	0.9824
30	0.0785	9.105	0.862	0.020	8.83	0.9875
40	0.0951	7.818	0.968	0.021	8.83	0.9831

3.5 Thermodynamic parameters

Thermodynamic parameters were also evaluated from the concepts of Gibbs free energy (ΔG^o: kJ/mol), enthalpy (ΔH^o: kJ/mol) and entropy (ΔS^o: kJ/mol K):

$$K_c = (q_e/C_e) \tag{10}$$
$$\ln K_c = (\Delta S/R) - (\Delta H/RT) \tag{11}$$
$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{12}$$

here R (=8.314 J/mol K), T (K), q_e, C_e and K_c (L/g) are gas constants, absolute temperature, amount of MB adsorbed on nZVISLP at equilibrium (mg/g), equilibrium concentration of MB in solution (mg/L), and the standard thermodynamic equilibrium constant, respectively. Values ΔH^o and ΔS^o may be calculated from slopes and intercepts, respectively, by plotting a graph of ln K_c versus 1/T (Figure S6).
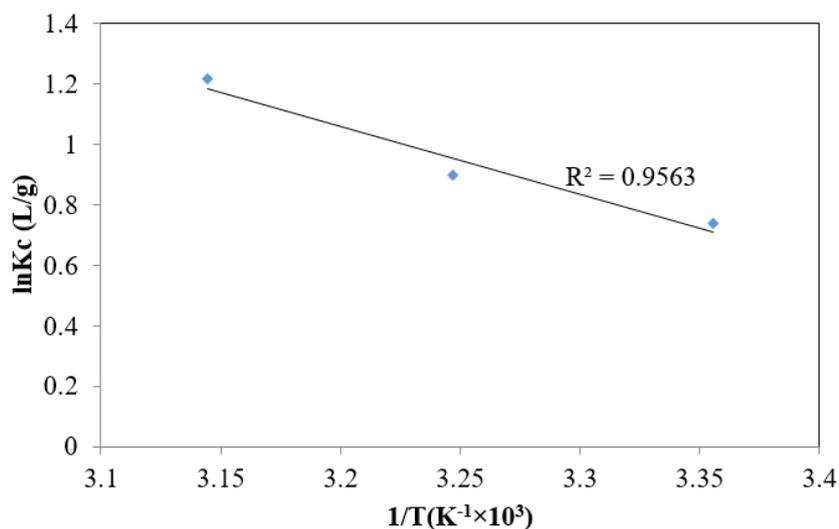
Figure S6: Plots of lnKC versus 1/T of the adsorption of MB onto the nZVISLP.

Table S4: Thermodynamic parameters of MB adsorption onto the nZVISLP

Temperature (°C)	Thermodynamic parameters		
	ΔG^o (kJ/mol)	ΔH^o (J/mol)	ΔS^o (J/mol K)
25	-20.5	18.7	68.67
35	-21.1		
45	-21.8		

References:

Karri, R.R., Jayakumar, N.S., Sahu, J.N., 2017a. Modelling of fluidised-bed reactor by differential evolution optimization for phenol removal using coconut shells based activated carbon. J. Mol. Liq. 231, 249-262.

Karri, R.R., Sahu, J.N., Jayakumar, N.S., 2017b. Optimal isotherm parameters for phenol adsorption from aqueous solutions onto coconut shell based activated carbon: Error analysis of linear and non-linear methods. J. Taiwan Inst. Chem. Eng, .