CHEMICAL KINETICS AND ADSORPTION ISOTHERMS OF PHOTOCATALYTIC DEGRADATION OF METHYL ORANGE USING BISMUTH FERRITE INCORPORATED REGENERATED CELLULOSE NANOCOMPOSITES

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The degradation of methyl orange (MO) as an anionic dye was evaluated with the aid of bismuth ferrite ($BiFeO_3$) impregnated regenerated cellulose (RC) nanocomposite films as a photocatalyst. Oil palm empty fruit bunch (OPEFB) based Microcrystalline cellulose (MCC) was used to obtain RC films using the solution casting method, wherein, $BiFeO_3$ (0-5 wt%) was added into the MCC dissolution ionic liquid 1-butyl,3-methylimidazolium chloride [BMIM]Cl system. The photocatalytic performance of the prepared films was evaluated by treating the catalyst dye mixture under direct sunlight until a significant colour removal of the dye was observed. The dye concentration at each time interval of 30 minutes was determined with the aid of UV-visible spectroscopy. The photocatalyst shows a 90% degradation of 10 ppm MO as maximum with 3 wt% of $BiFeO_3$ loading at pH 2 and the catalytic performance was stabled for 4 cycles. The concentration reduction pattern of MO follows pseudo-second-order kinetic model, and the adsorption of MO onto the prepared photocatalyst is physisorption.

Keywords: Bismuth ferrite, nanocomposite, photocatalytic performance, reusability, pseudo-second-order, physisorption

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INTRODUCTION

This article is a subsequent showcase and a supplementary output to our previous article available in the journal of Polymer International (Hassan et al., 2023). The previous article discussed the physical experimental analysis of methyl orange (MO) degradation using the bismuth ferrite ($BiFeO_3$; BFO) incorporated regenerated cellulose (RC) nanocomposites. This secondary article elaborates on the chemical kinetics, adsorption isotherms and thermodynamics of that practical observation. The degradation kinetics and thermodynamics were evaluated using the measured dye concentrations at maximum degradation under the best process conditions such as 10 ppm of MO concentration, and 3 wt% of $BiFeO_3$. Also, the adsorption isotherm modelling was conducted using all concentrations at the best process conditions.

METHODOLOGY

Materials and Sample Preparation

The materials and Sample preparation procedure is the same as the methodology explained in the previous article (Hassan et al., 2023).

Chemical kinetics, adsorption isotherms and thermodynamics

The kinetic study of the photocatalytic colour removal process was examined concerning four kinetic models such as Langmuir Hinshelwood (LH), Pseudo first order (PFO), Pseudo second order (PSO) and Intraparticle diffusion (IPD) models. Table 1 describes the model equations and the results obtained at the maximum photocatalytic degradation conditions that were applied to the above four models. The most appropriate model with the practical data was considered the approximate kinetic model which obeys the actual colour removal process of MO. The colour removal at equilibrium; q_e (mg/g) and at time t ; q_t (mg/g) were determined by using Equation 1 and 2 respectively (Liu et al., 2015; Zaahari et al., 2019).

$$q_e = (C_o - C_e)\, V/m \qquad (1)$$

$$q_t = (C_o - C_t)\, V/m \qquad (2)$$

where, C_o, C_e, C_t, V and m are the initial dye (adsorbate) concentration (ppm), dye concentration at equilibrium (ppm), dye concentration at time t (ppm), amount of dye volume (litres) and mass of the catalyst (g) respectively (Liu et al., 2015).

Table 1

The selected different kinetic models to study the photocatalytic degradation of MO (Liu et al., 2015; Zaahari et al., 2019)

Model name	Equation	Notation
Langmuir Hinshelwood	$\ln \frac{C_0}{C_t} = kt$	k = Rate constant
Pseudo first order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	K_1 = Rate constant
Pseudo second order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$	K_2 = Rate constant
Intraparticle diffusion	$q_t = K_p(t^{1/2})$	K_p = Intraparticle diffusion rate constant

Adsorption of MO onto RC/BFO film was studied by using five different isotherm models such as Freundlich, Langmuir, Temkin, Dubinin-Radushkevich (D-R) and Elovich isotherms (Liu et al., 2015; Zulfiqar et al., 2019). Table 2 describes the model equations and the results obtained at the maximum photocatalytic degradation conditions were applied to the above five models. The most appropriate model with the practical data was considered the approximate adsorption isotherm model.

Table 2

The selected different adsorption isotherm models to study the adsorption of MO onto photocatalyst

Isotherm model name	Equation	Notation
Freundlich	$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e$	n = A constant indicating the favourableness of the adsorption process, K_F = A constant indicating the removal capacity of the adsorbent
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_{max}}$	K_L = Langmuir constant, q_m = Maximum removal capacity
Temkin	$q_e = B \ln K_T + B \ln C_e$	B and K_T are Temkin constants
Dubinin-Radushkevich (D–R)	$\ln q_e = \ln q_m - K_{DR} \varepsilon^2$ $\varepsilon = RT \ln (1+\frac{1}{C_e})$ $E = 1/\sqrt{2 K_{DR}}$	q_m = Maximum removal capacity, K_{DR} = D-R isotherm constant, R = Universal gas constant, T = Absolute temperature
Elovich	$\ln (\frac{q_e}{C_e}) = \ln (K_E q_m) - \frac{1}{q_m} q_e$	K_E = Elovich constant

The influence of temperature on photocatalytic degradation was evaluated by treating the catalyst dye mixture at five different temperatures (30 – 70 ^{o}C within 10 ^{o}C intervals) under the identified best process conditions (3 wt% of $BiFeO_3$ at pH2 with 10 ppm MO). Thermodynamic stability was determined using Equation 3, 4 and 5 (Liu et al., 2015)

$$\ln(K_d) = \frac{\Delta G}{R} - \frac{\Delta H}{RT} \quad (3)$$

$$\Delta G = -RT.\ln(K_d) \quad (4)$$

$$K_d = \frac{(C_o - C_e)}{C_e}\frac{V}{W} \quad (5)$$

Where K_d, ΔS, ΔH, ΔG and W are the distribution coefficient of the adsorption process, change in entropy, change in enthalpy, change in free energy, and weight of the solid adsorbent respectively.

RESULTS AND DISCUSSION

Chemical Kinetics

It is interesting to determine the rate of pollutant uptakes onto the photocatalyst to accomplish the redox reactions (Zulfiqar et al., 2019). Therefore 4 different kinetic models including Langmuir Hinshelwood, Pseudo first order, Pseudo second order and Intraparticle diffusion models were considered in this study to define the most appropriate degradation process. The concentration values obtained with 3 wt% of $BiFeO_3$ loading at pH2 for 10 ppm MO were considered in all kinetic model calculations. Figure. 1 displays the data points and linear fitting curves of the 4 models while Table 4 demonstrates the parameters calculated with the aid of each plot and respective equations. According to the obtained parameters using the linear plots of the above 4 models, R^2 value was considered as a primary parameter to determine the most appropriate kinetic model that is obeyed by the colour removal process of MO. The R^2 values of all conditions in each model are greater than 0.9 and therefore it is a good agreement of every model. Therefore, as secondary parameters, the agreement of linear plots with the mathematical form was taken into account. In that scenario, if the colour removal process follows either the LH or IPD model, the linear plot should pass through zero and the intercept should not have a value since their simplified mathematical formulae is y=mx. But in both of the models, there are positive values for intercept in all concentrations. Therefore, it can be confirmed that LH and IPD models do not best fit with the actual colour removal process. Then, the simplified mathematical formula of PFO and PSO models are y=-mx+c and y=mx+c respectively. Hence, there should be a positive intercept value if the process obeys one of these models. According to the intercept values of the results of both models, it is acceptable and afterwards, other parameters were calculated with the aid of intercept and slope using the relevant equations. Then, the calculated q_e values were compared with the experimental q_e values. As per the q_e values, the PFO model is more appropriate with the experimental results. However, according to the plots (Figure. 1(b) and Figure. 1(c)) and R^2 values PSO model is more appropriate with linear fit compared with PFO. In these results, except in the IPD model, every model shows a decrease of rate constant with the increase of concentration indicating reduced efficiency. It may be due to the long degradation affected by the high concentration of MO (Zulfiqar et al., 2019). However, in IPD, the rate constant is increased with the increase of concentration by denoting the enhanced degradation. This may be due to the increase in mass transfer as a result of increased driving force at high concentrations (Zulfiqar et al., 2019). According to the overall analysis, PSO can be confirmed as the most appropriate model to describe the degradation of MO using 3 wt% of $BiFeO_3$ loading in the RC matrix at pH2.

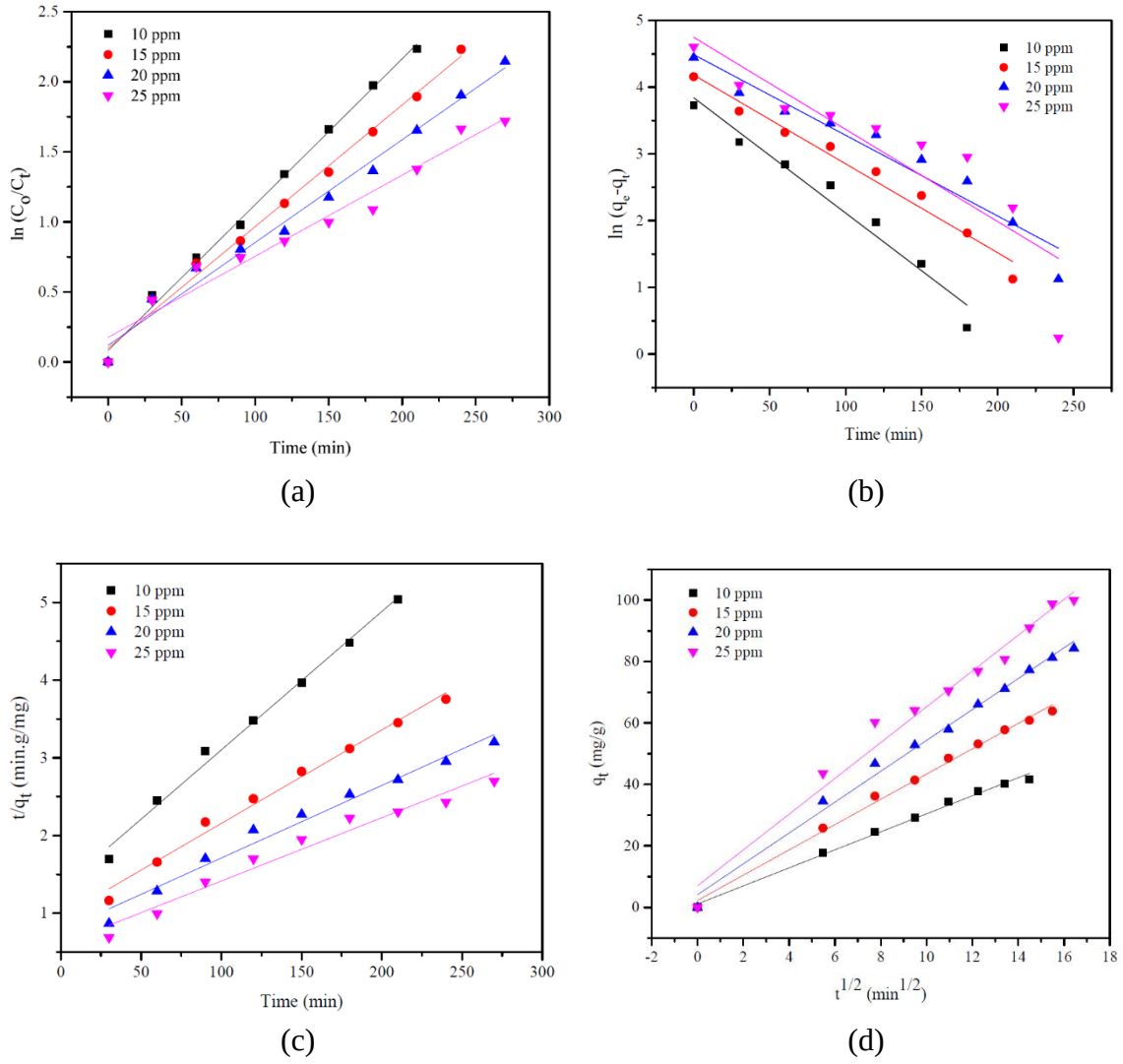


Figure. 1. The linear fitting plots of Langmuir Hinshelwood (a), Pseudo first order (b), Pseudo second order (c) and Intraparticle diffusion (d) models as per the degradation of 10 ppm MO at pH2 with 3 wt% $BiFeO_3$ loading in RC

Table 4

Parameters obtained for the linear plots of Langmuir Hinshelwood (LH), Pseudo first order (PFO), Pseudo second order (PSO) and Intraparticle diffusion (IPD) models

Model	Parameters	MO concentration			
		10 ppm	15 ppm	20 ppm	25 ppm
	$q_{e\ exp}$ (mg/g)	41.67	63.85	85.13	100
	R^2	0.996	0.993	0.987	0.963
LH	Slope ; K_{LH} (min^{-1})	0.010	0.009	0.007	0.006
	Intercept	0.083	0.099	0.120	0.177

PFO	R^2	0.967	0.975	0.943	0.806
	Slope ; K_1 (min^{-1})	0.017	0.013	0.012	0.014
	Intercept (ln q_e)	3.841	4.183	4.488	4.747
	q_e cal (mg/g)	46.59	65.56	88.96	115.25
PSO	R^2	0.993	0.989	0.978	0.967
	Slope ($1/q_e$)	0.018	0.012	0.009	0.008
	q_e cal (mg/g)	56.12	83.19	106.95	122.70
	Intercept ($1/k_2q_e^2$)	1.320	0.954	0.775	0.599
	K_2 (g/mg.min)	0.000241	0.000152	0.000113	0.000111
IPD	R^2	0.994	0.995	0.992	0.979
	K_p ($mg/g.min^{1/2}$)	2.94	4.12	5.03	5.83
	Intercept	1.808	2.214	4.064	6.996

Adsorption isotherms

It is important to determine the mechanism of pollutant adsorption onto the photocatalyst. Physical adsorption happens when the attractive intermolecular forces between the catalyst and dye are greater than the intramolecular attractive forces within dye molecules. In chemical adsorption, chemical bonds are created between the dye and catalyst molecules (Liu et al., 2015). In this study, the interaction between the adsorbate and the adsorbent for efficient photocatalytic degradation was studied with the aid of five adsorption isotherm models such as Freundich, Langmuir, Temkin, Dubinin-Radushkevich (D–R) and Elovich isotherms. The adsorption was evaluated for the identified maximum MO degradation conditions such as 3 wt% of $BiFeO_3$ and pH 2 with the selected different concentrations of MO; 10 ppm, 15 ppm, 20 ppm and 25 ppm at ambient temperature 30^{o}C. According to the model curves shown in Figure. 2(a-e) and their linear fitting, the parameters were calculated as displayed in Table 5.

According to Figure. 2 and Table 5, the Elovich isotherm model does not fit the experimental results since R^2 is very low (0.2426). In the Freundich model, the n value is 1.8 which indicates the significance of MO degradation via selected concentrations over the surface of RC/BFO film since n is greater than 1 (Zulfiqar et al., 2019). Further, the n value is between 1 and 10 which indicates the feasible photocatalytic degradation of MO under the selected process conditions (Zulfiqar et al., 2019). However, the calculated parameters in Table 5 and Figure 2 confirm that the D-R model is the most appropriate isotherm to describe the MO adsorption on RC/BFO thin film since the R^2 is higher (0.9963) than Freundich, Langmuir, and Temkin isotherm models. In general, mean free energy of adsorption (E) is used to determine the type of adsorption such as physical or chemical. A particular adsorption process is physical if the E value is less than 8 kJ/mol and the process is chemical if the E value is between 8 kJ/mol and 16 kJ/mol (Amin et al., 2015). According to the obtained E value in the D-R isotherm model, MO adsorption onto RC/BFO film is physisorption since E (1.31 kJ/mol) is less than 8 kJ/mol (Amin et al., 2015).

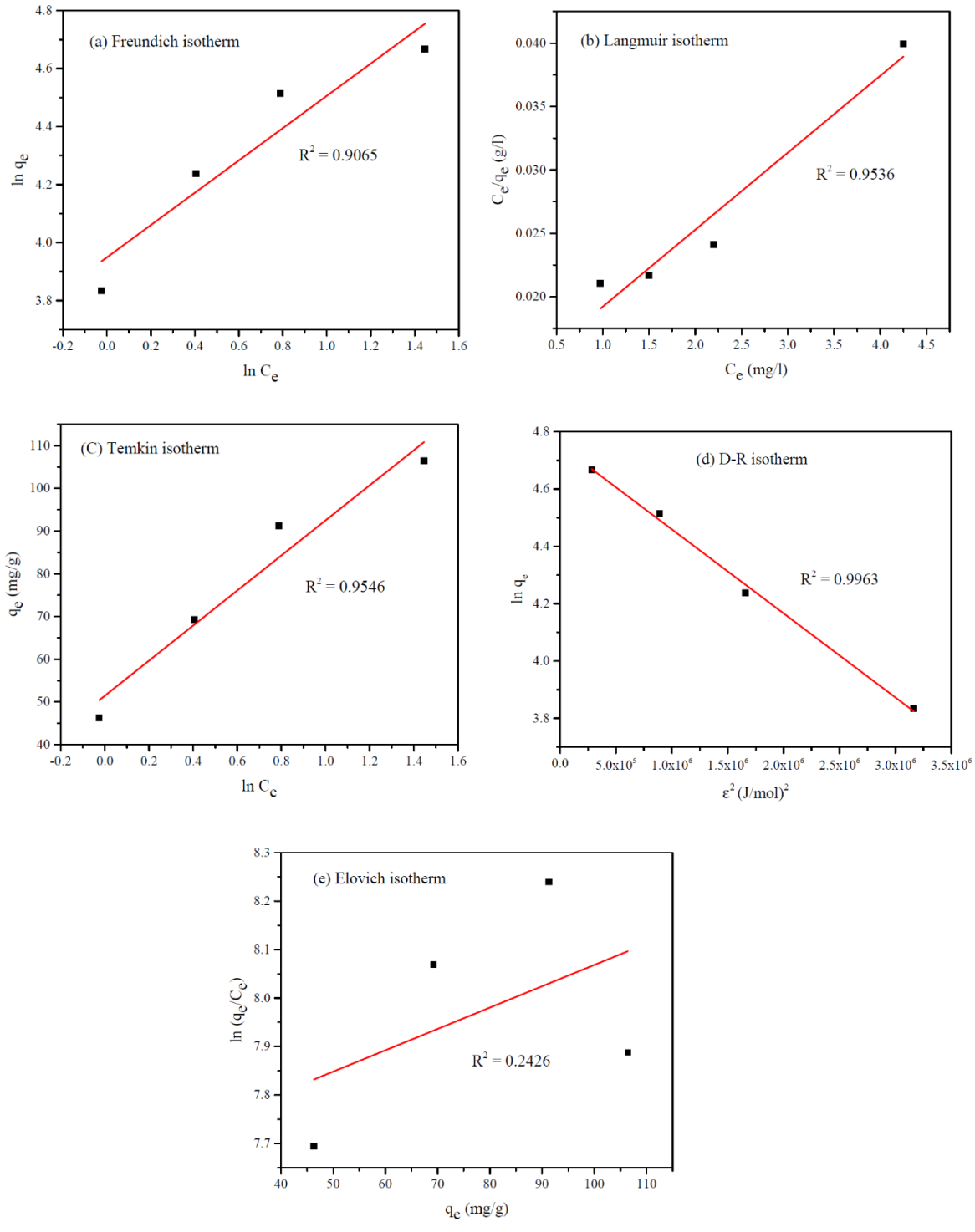


Figure. 2 (a-e) Freundich, Langmuir, Temkin, D-R and Elovich isotherms for MO degradation with 3 wt% of $BiFeO_3$ and pH 2 with 10 ppm, 15 ppm, 20 ppm and 25 ppm MO concentrations at 30°C

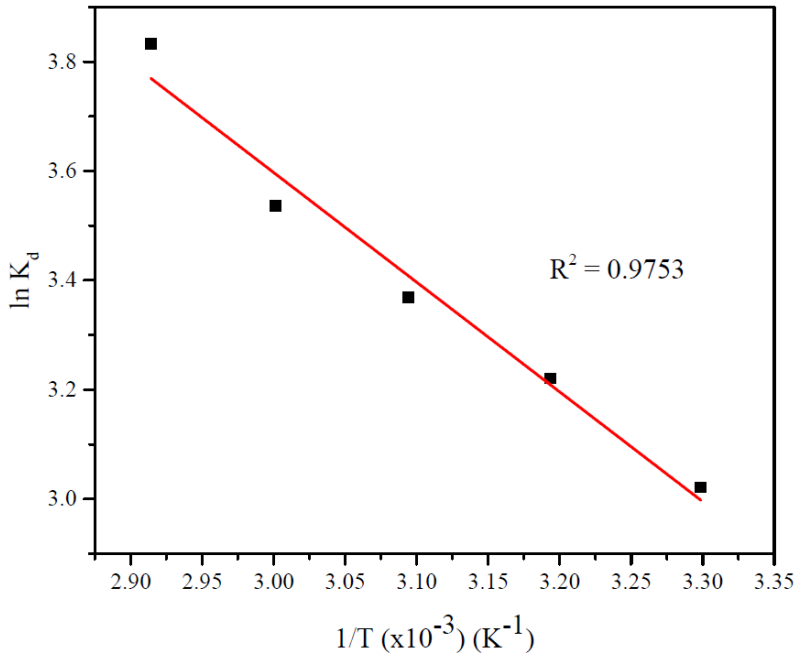
Table 5
Calculated parameters of adsorption isotherm models for MO adsorption on RC/BFO film

Isotherm model	Parameters	Values
Freundich	R^2	0.9065
	slope (1/n)	0.557
	n	1.80
	Intercept (ln K_F)	3.95
	K_F (mg/g)	51.89
Langmuir	R^2	0.9536
	slope ($1/q_{max}$)	0.006
	q_{max} (mg/g)	164.74
	Intercept ($1/(q_{max}.K_L)$)	0.013
	K_L (l/mg)	0.462
Temkin	R^2	0.9546
	slope (B)	41.06
	Intercept (B.ln K_T)	51.45
	K_T (l/g)	3.50
D-R	R^2	0.9963
	Slope; K_{DR} (mol^2/J^2)	2.93×10^{-7}
	Intercept; ln q_m	4.75
	q_m (mg/g)	115.90
	E (kJ/mol)	1.31
Elovich	R^2	0.2426
	slope ($1/q_m$)	0.004
	q_m (mg/g)	227.27
	Intercept ; ln ($K_E.q_m$)	7.63
	K_E (l/mg)	9.04

Thermodynamic behaviour of the system

In terms of entropy and energy of a particular process, the spontaneous nature can be estimated. Thermodynamic parameters such as enthalpy, entropy and change of free energy are vital in photocatalytic degradation to define the colour removal mechanism through the photocatalyst at variable temperatures. Thermodynamics of MO adsorption onto RC/BFO film was studied by conducting the photocatalytic degradation at 5 different temperatures (30°C, 40°C, 50°C, 60°C and 70°C) using the maximum degradation conditions (10 ppm MO with pH 2 and 3 wt% of $BiFeO_3$

loading). According to the experimental results, ln (k_d) vs 1/T was drawn as shown in Figure. 3 and the thermodynamic parameters were calculated using the slope and intercept of the plot as shown in Table 6. The negative ΔG values denote that the photocatalytic degradation is feasible and spontaneous in nature throughout the experimental conditions. Further the increase of ΔG with temperature confirms the more favourable and spontaneous nature of the reaction at high temperatures. An adsorption process is physical if ΔG lies between 0 to -20 kJ/mol while the process is chemical if ΔG exists between -80 kJ/mol to -400 kJ/mol. According to Table 6, the ΔG values lie between 0 to -20 kJ/mol (-7.62, -8.38, -9.05, -9.8 and -10.93 kJ/mol) at all temperatures and that further proves the physisorption of MO onto RC/BFO (Liu et al., 2015). The positive ΔH value indicates the endothermic process that may happen due to the increase of inner pores of the photocatalytic film as a result of increased heat rate of MO over the exterior boundary layer (Zulfiqar et al., 2019). Theoretically, an adsorption process is physical when ΔH is between 2.1 and 20.9 kJ/mol, whereas it is chemical when ΔH is between 80 and 200 kJ/mol. According to Table 6, the obtained ΔH value is 16.69 kJ/mol which further proves the physisorption of MO onto photocatalytic film. The positive value of entropy change (ΔS=79.97 J/mol.K) shows the increased randomness of



The system over the catalyst dye interface throughout the operated conditions (Zulfiqar et al., 2019).

Figure. 3. Plot of ln (K_d) vs 1/T for the adsorption of MO onto RC/BFO film

Table 6
Thermodynamics adsorption parameters of MO adsorption onto RC/BFO at different temperatures

Temperature (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)
303.15	-7.61	16.69	79.97
313.15	-8.38		
323.15	-9.05		
333.15	-9.79		
343.15	-10.93		

CONCLUSIONS/RECOMMENDATIONS

According to our first article, the synthesis of $BiFeO_3$ incorporated RC film was successful according to the confirmation made by XPS and SEM analysis. The incorporation of $BiFeO_3$ inside RC matrix is a physical blending as per the FTIR and XRD analysis. Based on the E_g value, BET surface area and cross-sectional morphology 3 wt% of $BiFeO_3$ with respect to MCC weight was confirmed as the best loading. According to the irradiation experiment, 3 wt% of $BiFeO_3$ loading, pH 2 and 10 ppm concentration were identified as the best process conditions to obtain a maximum degradation of MO dye. The colour removal of MO in front of the best process conditions follows pseudo-second-order kinetic model. The reusability study showed that photocatalyst can be reused until 4 cycles without destroying the film. The adsorption of MO molecules onto photocatalyst obeys D-R isotherm model. According to the D-R isotherm model and thermodynamic parameters, the adsorption of MO onto RC/BFO film is physical adsorption. Hence, the new photocatalyst RC/BFO can be suggested as a feasible nanocomposite to utilize in polluted water purification systems in the future.

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