Adsorptive and photocatalytic removal of carcinogenic methylene blue dye by SnO₂ nanorods: an equilibrium, kinetic and thermodynamics exploration

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Abstract

The present study reports a simple co-precipitation approach for the synthesis of SnO₂ nanorods. The SnO₂ nanorods were characterized by XRD, SEM, TEM, EDAX, SAED, and FTIR techniques, to examine their structural, morphological, functional group, and elemental properties. The findings of the SEM and TEM reveal the nanorod like morphology. For the adsorptive and photocatalytic removal of methylene blue dye from their aqueous solution the synthesized SnO₂ nanorods have been used. The effect on adsorptive and the photocatalytic removal capability of SnO₂ nanorods was examined by optimizing the various parameters such as pH, initial dye concentration, contact time and catalyst dose. The maximum adsorptive and photocatalytic removal of MB up to the 66% and 94% were obtained at pH = 7 and pH = 2, respectively. Besides, experimental adsorption results were used for the exploration of kinetics and adsorption isotherm (Langmuir and Freundlich), which shows that methylene blue adsorption over SnO₂ nanorods follows the pseudo-second-order kinetics with the rate constant K_2 is 1.1×10^{-1} (g/mg/min) and obeys the Langmuir isotherm. However, the thermodynamic parameters were studied, indicating that adsorption is spontaneous and favorable. The adsorptive removal is an endothermic process and pointing towards the chemisorptions nature of the process.

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Graphic abstract

Keywords SnO_2 · Nanorods · Langmuir isotherm · Freundlich isotherm · Kinetics · Thermodynamics · Endothermic

1 Introduction

The enormous efforts are currently being made in order to develop and modify the nanocrystalline semiconducting materials. The semiconducting materials are designed for a range of applications in the optoelectronics fields, solar cells, catalysis, drug design sensors, etc. [1–5]. The SnO_2 nanoparticle with a rutile structure is the most widest studied metal oxide among the different nanocrystalline semiconducting materials. The SnO_2 nanoparticles are a semiconductor of the n-type with a 3.6 eV bandgap that makes them a flexible metal oxide [6]. In the area of the catalyst [7], solar cell [8], transistor [9], gas sensing [10] and photovoltaic energy conversion [11], the SnO_2 has been used extensively.

The rapid industrialization and population flare-up have resulted in the incredible demand of freshwater for both domestic and industrial purposes. This leads to water contamination consisting primarily of dyes with a number of other organic contaminants. Such dyes contribute to a number of environmental problems by potentially introducing cancer-causing toxins into the water systems. Therefore, the presence of such harmful dyes in the

water bodies is a significant problem for the remediation of the environment [12–17]. Recently, the use of nanoscale materials for environmental compensation has been the most remarkable area of research in the field of advanced oxidation processes (AOP's) [18]. AOP's were assessed as an effective tool for treating organic dyes in wastewater. AOP's combine many processes that focused on the development of extraordinarily sensitive hydroxyl radicals. AOP's have emerged as a possible destructive technology leading to the degradation of organic contaminants [19].

Photocatalysis is a fast-growing, powerful AOP's to remove chemical and bacterial contaminants from the wastewater by means of semiconducting nanoscale materials. Nonetheless, semiconducting photocatalysis facilitates the process of electron transfer more efficiently and results in electrons and positive hole production respectively within the conduction and valence band. The oxygen adsorbed over the photocatalyst surface reduces into the superoxide radicals (O_2^-) while the positive holes either directly or indirectly oxidize organic pollutants from wastewater to produce hydroxyl free radicals ($\text{HO}^\bullet$) [20]. Hydroxyl radicals speed up the chain reactions that eventually destroy the organic pollutants [21–23].

The synthesis of SnO_2 nanorods is reported in the present study using a simple chemical co-precipitation method [24, 25]. The resulting SnO_2 nanorods have been used to remove methylene blue dye adsorptively and photocatalytically by varying parameters such as pH, initial dye concentration, contact time and catalyst dose, etc. Many researchers have used the SnO_2 nanoparticles for the degradation methylene blue dye [26, 27], but according to the literature survey, only a few studies have been reported on the comparative study of adsorptive and photocatalytic removal of methylene blue dye by SnO_2 nanoparticles. Whereas we have systematically investigated the adsorptive and photocatalytic efficiency of SnO_2 nanorods for the removal of methylene blue dye. The uniqueness of this study is that the adsorptive and photocatalytic efficiency of the catalyst has been scientifically studied along with the kinetic, thermodynamic and equilibrium analysis for the removal of methylene blue dye using SnO_2 nanorods.

2 Experimental

2.1 Materials and methods

All the chemicals, stannous chloride dehydrates ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), concentrated ammonia solution (25%, NH_3) and methylene blue (MB) were of analytical grade and bought from S. D. Fine chemical, Ltd., Mumbai, India. The stock solution of dye 100 mg/L of MB was prepared in distilled water and required concentrations of dye solution (10, 15 and 20 mg/L) were prepared by diluting the stock solution with distilled water.

2.2 Synthesis of SnO_2 nanorods

Tin oxide nanorods have been prepared by a co-precipitation method using 0.1 M of stannous chloride dehydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 100 ml double distilled water under the constant stirring still it becomes homogeneous. Add the ammonia solution dropwise into the above solution under the constant stirring to obtained the precipitates (i.e. pH ~ 8–9). In order to remove water molecules, the resulting gels were filtered and dried at 80 °C for 8 h. The SnO_2 nanorods were obtained after the calcination at 450 °C for 2 h.

2.3 Characterizations

X-ray Diffraction [XRD- Bruker D 8 Advance X-ray Diffractometer Germany, using a CuK_α ($\lambda = 1.54 \text{ \AA}$) and scanning angle 2θ range from 10° to 80°] study was used to investigate the crystalline nature of the synthesized SnO_2 nanorods. To analyze the morphology of synthesized nanorods, the Scanning Electron Microscopy (SEM-Hitachi S-4800 Japan) and Transmission Electron Microscopy (TEM-200 kV TECNAI G² 20 microscope equipped with a LaB_6 filament) was used. The FTIR spectrum was recorded in (Shimadzu FTIR-8400, wavelength range—400 cm^{-1} –4000 cm^{-1}) instrument and the electron dispersive X-ray spectroscopy (EDAX- Nova NanoSEM 450) was used for elemental analysis. The UV–Visible double beam spectrophotometer (Systronic 2203) was used for the photocatalytic degradation experiment.

2.4 Adsorptive and photocatalytic study

The photocatalytic degradation of MB dye has been carried out in a photocatalytic reactor with a 160 W mercury

Fig. 1 Schematic of photocatalytic reactor used in the present study reprinted from (Ref. [55]) copyright 2018, Iranian Journal of Catalysis

Fig. 2 **a** XRD pattern of SnO₂ nanorods and **b** particle size distribution

lamp (Lelesil Innovative Systems, Ltd. Mumbai). The reactor temperature was controlled by circulating water. Appropriate quantities of synthesized SnO₂ nanorods were added to the 50 ml dye solution and kept inside the reactor. After the specified time intervals, an appropriate amount of dye solution was collected and centrifuged so that the suspended catalyst particles were removed. Afterward, a UV–visible, double beam spectrophotometer at λ_{max} 664 nm examined the changes in the concentration of dye. The same procedure was adopted in the absence of light for the adsorptive removal of MB dye (Fig. 1). The percentage degradation and amount of MB adsorbed were estimated by the following equations (Eq. 1 and 2).

$$\% \text{ Degradation} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

where C_0 and C_t are the initial concentration and concentration of dye at time t in mg/L; q_t (mg/g) is the adsorption capacity; V (l) is the initial volume of the dye and W (g) is the amount of catalyst dose.

3 Results and discussion

3.1 X-ray diffraction analysis

The XRD has explored the phase identification of synthesized SnO₂ nanorods. Figure 2a. Show the SnO₂ nanorods XRD pattern synthesized by a simple method of co-precipitation. All the diffraction peaks obtained at 2θ values of 18.29°, 20.06°, 21.47°, 25.67°, 33.83°, 46.01°, 51.74° and 65.42° which corresponds to the (111), (110), (101), (200), (101), (210), (211), and (310) crystalline planes respectively. The peaks at different 2θ values correspond very well to SnO₂ nanorods (JCPDS no. 41-1455) tetragonal rutile structure [28, 29].

Table 1 The lattice parameters of SnO₂ nanorods

Sr.	Catalyst	2θ degree	(hkl) planes	FWHM(β)	Crystallite size (nm)
1	SnO ₂ nanorods	18.29	111	0.4510	18.65
		20.06	110	0.7856	10.73
		21.47	101	0.4679	18.06
		25.67	200	0.3848	22.13
		33.83	101	0.3288	26.39
		46.01	210	0.4248	21.24
		51.74	211	0.3640	25.35
		65.42	310	0.6707	14.71
		Average crystallite size			19.65

Therefore, it is confirmed from the above XRD data that the SnO₂ nanorods with a tetragonal rutile structure are derived from a simple co-precipitation method. In addition, all SnO₂ nanorods XRD peaks are sharper due to the reduction in the half-width full maximum (FWHM) (inset Fig. 2a). This results in an increase of SnO₂ nanorods crystallite size. The average size of SnO₂ nanorods has been determined from XRD data using the Debye–Scherrer equation (Eq. 3).

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (3)$$

where D is the average crystalline size, λ is a wavelength in Å, β is the FWHM in radian and θ is diffraction angle in degree. The SnO₂ nanorods average crystallite size was approximately 19.65 nm (Table 1) and confirmed by the particle size distribution from SEM image using image J software (Fig. 2b).

Fig. 3 SEM images of SnO_2 nanorods (**a**, **b**); TEM images (**c**, **d**); SAED pattern of SnO_2 nanorods (**e**); 3D view of SnO_2 nanorods (**f**)

Fig. 4 EDAX spectrum of SnO_2 nanorods

3.2 Morphology

The SEM technique has been used to examine the morphology of synthesized SnO_2 nanoparticles, and the findings are shown in Fig. 3a, b. The SnO_2 reveals a smooth surface with a nanorod like morphology. The SnO_2 nanorods were bound to each other and densely arranged. Further confirmation of nanorods like morphology, the synthesized SnO_2 nanoparticles has been subjected to TEM analysis and the findings are as shown in Fig. 3c, d. It also reveals the polycrystalline structure and preferential orientation along the planes (111) and (110) of SnO_2 crystals. The shape and size of synthesized SnO_2 nanorods were non-uniform due to the varying drying and calcination temperature. The 3D view of SnO_2 nanorods derived from the SEM image is shown in Fig. 3f. To find out the diffraction

Fig. 5 FTIR spectra of SnO_2 nanorods

patterns of synthesized SnO_2 nanorods, which results from the electron beam scattered by the SnO_2 crystal lattice, the SnO_2 nanorods were subjected to the SAED analysis as shown in Fig. 3e. The SAED analysis of SnO_2 nanorods (Fig. 3e) clearly shows the continuous ring diffraction pattern due to the SnO_2 containing a large number of smalls randomly distributed crystallites [30].

3.3 Energy-dispersive X-ray spectroscopy

Based on the energy-dispersive x-ray spectroscopy (EDAX) study as shown in Fig. 4, the examination of the elemental composition of synthesized SnO_2 nanorods was explored. The EDAX study confirmed the successful synthesis of SnO_2 nanorods with elements composition 15.93 and 84.03% of tin and oxygen respectively. There is also no additional peak observed confirming the purity of synthesized SnO_2 nanorods.

Fig. 6 Effect of pH on adsorptive and photocatalytic removal of MB (conditions: pH=2–10, dye concentration. 10 mg/L and catalyst dose 1 g/L for the time 90 min)

3.4 FTIR analysis

As shown in Fig. 5, FTIR was used to analyze the precise relationship between SnO_2 and the exact functional group. The absorption bands at 785.5 cm^{-1} represent the Sn–O bond stretching frequency and confirmed the presence of SnO_2 nanorods. The absorption band at 2338.7 , 1895.1 and 1320 cm^{-1} is due to the symmetrical and asymmetrical stretching frequency of CO_2 absorbed from the air [29, 31–34]. Also, the IR band at 2925 cm^{-1} is due to the –OH group of water molecule absorbed from air during the sample preparation for the IR analysis.

3.5 Adsorption versus photocatalytic removal study

3.5.1 Effect of pH of solution

The solution's pH is one of the most critical factors influencing the degree of adsorption and photocatalytic degradation substantially. Besides, the charge on the catalyst surface is considered to have a dominant factor in the determination of overall adsorption and photocatalytic efficiency of the catalyst. Therefore, the point of zero charge (pH_{ZPC}) of synthesized SnO_2 nanorods needs to be investigated. So it is possible to predict the nature of a charge on the SnO_2 surface at a specified pH. SnO_2 nanorods' pH_{ZPC} has been observed to be 5.4 using the reported method [35], which is in good agreement with those reported for SnO_2 [33]. The surface would, therefore have a net-zero charge at pH_{ZPC} and will be charged either positively or negatively at $\text{pH} < \text{pH}_{\text{ZPC}}$ or $\text{pH} > \text{pH}_{\text{ZPC}}$.

The effect of pH of the solution on the adsorptive and photocatalytic removal efficiency for MB was explored in this study by varying the pH of the solution from 2 to 10 pH in the presence of 1 g/L of SnO_2 nanorods an initial dye concentration of 10 mg/L for 90 min. Figure 6, shows the effect of pH on adsorptive and photocatalytic removal of

Fig. 7 Effect of initial dye concentration and contact time. **a** Photocatalytic removal of MB, conditions pH=2, dye concentration 10, 15, 20 mg/L and catalyst dose 1 g/L for irradiation time 90 min. **b** Adsorptive removal of MB, conditions: pH=7 dye concentration 10, 15, 20 mg/L and catalyst dose 1 g/L kept in dark for 90 min

MB by SnO₂ nanorods. The adsorption curve in the figure shows that the percentage of adsorptive removal of MB increases slowly as the pH of the solution increases. The maximum MB adsorption on SnO₂ surface was achieved around 66% at pH = 7. Furthermore, increased pH does not result in maximum removal. At pH = 7, the SnO₂ has a negative charge ($pH > pH_{ZPC}$) surface which electrostatically attracts the cationic MB dye over its surface into a greater extent and gives a maximum removal. Nevertheless, as the solution pH increases ($7 < pH$), the larger number of MB molecules is adsorbed and agglomeration occurs which minimizes the percentage of adsorption over the SnO₂ surface [36].

For photocatalytic removal of MB, maximum removal of around 94% was obtained at pH = 2. The surface of SnO₂ is positively charged and protonated at pH = 2 ($pH < pH_{ZPC}$). The positive holes are an excellent oxidizing species at low pH and the catalyst is also acting as a photosensitizer [37]. Hydroxyl radicals ($\cdot OH$) are generated by the photo-generated valence band hole. In addition, the positive holes

trap the MB molecule, leading to the direct oxidation of MB [38].

3.5.2 Effect of initial dye concentration and contact time

The effect of initial dye concentration and contact time was investigated at optimized pH for adsorptive (at pH = 7) and photocatalytic (pH = 2) removal of MB dye by varying the initial concentration 10, 15 and 20 mg/L for 90 min at a fixed amount of catalyst (1 g/L). Fig. 7b shows the effect of initial dye concentration and contact time over the rate of adsorption. Adsorption of MB on the SnO₂ catalyst surface is improved with an initial concentration from 10 to 20 mg/L. The adsorption rate is also higher for the first 60 min after it has reached equilibrium. This is because in the first 60 min, there were more active sites for adsorption on SnO₂ surface. The repulsion between the solute and the solvent phase takes place after the first 60 min. This causes adsorption difficulties over the SnO₂ surface and eventually decreases adsorption efficiency. Thus, only 64.05% of MB dye molecules were adsorbed over the surface of the SnO₂ nanorods [36, 39].

On the other hand, the photocatalytic degradation of MB by SnO₂ nanorods is shown in Fig. 7a. The photocatalytic degradation efficiency of SnO₂ nanorods decreases as the initial dye concentration of MB solution increases from 10 to 20 mg/L and increases with contact time. The explanation is that excess MB molecule is adsorbed over the catalyst surface resulting in a reduction in the number of active sites. Therefore, reactive species formation ($\cdot OH$ and O^{2-}) will be reduced, and the degradation efficiency of SnO₂ will effectively be decreased. Total degradation was achieved for the initial concentration of 10 mg/L in 90 min at around 94%. In the first 60 min, the rate of photocatalytic degradation MB was faster and then the equilibrium was achieved [40–43].

Fig. 8 Effect of catalyst dose on adsorptive and photocatalytic removal of MB at optimized condition (for adsorption at pH = 7, Contact time = 60 and initial concentration = 20 mg/L) and (for photocatalytic at pH = 2, Contact time = 90 and initial concentration = 10 mg/L) by varying catalyst dose 0.2–1 g/L

3.5.3 Effect of catalyst dose

The effect of catalyst dose was studied by varying the catalyst dose from 0.2 to 1 g/L at optimized conditions

Table 2 Comparison of adsorptive and photocatalytic removal of MB results with reported literature

Sr. No.	Material	Reaction time (min)		% Removal		Reference
		Photocatalytic	Adsorption	Photocatalytic	Adsorption	
1	Ag/SnO ₂	120	120	90	48	33
2	SnO ₂	180	–	79	–	35
3	SnO/SnO ₂	180	–	90.28	–	36
4	SnO ₂	120	–	90	–	37
5	SnO ₂	240	–	96	–	38
6	ZnO-SnO ₂	90	–	75	–	39
7	SnO ₂	90	90	94.33	64.05	Present study

for adsorption (at pH=7, Contact time=60 and initial concentration = 20 mg/L) and photocatalytic degradation (at pH=2, Contact time=90 and initial concentration = 10 mg/L). The obtained results were shown in Fig. 8, It showed an increase in the rate of adsorption and photocatalytic removal as the catalyst dose increased by 0.2–1 g/L. The overall adsorption and photocatalytic removal were achieved at about 62.66 and 93.77% for the catalyst dose 1 g/L, due to increased active sites [44, 45]. The results show that the synthesized SnO₂ nanorods demonstrate outstanding photocatalytic and adsorption efficiency in 90 min for removing MB dye from their aqueous solution. The findings obtained are compared to the literature (Table 2), which indicates that the present study shows better efficiency of adsorption and photocatalytic removal with fewer contact times.

3.6 Adsorption isotherm

Langmuir and Freundlich are the most commonly used adsorption isothermal models that provide information concerning the affinity of the adsorbent, surface features and adsorption mechanisms. These also offer some insight into how the molecules are adsorbed in equilibrium between solid and liquid phases. The Langmuir, as well as the Freundlich isotherm, has therefore been used for MB adsorption results. Equations 4 and 5, reflects the linear forms of the Langmuir and Freundlich isotherm [34, 46].

$$\frac{C_e}{q_e} = \frac{1}{ab} + \frac{C_e}{a} \quad (4)$$

$$\log q_e = \log K_f + \frac{1}{n} \log c_e \quad (5)$$

where q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/g), C_e is the concentration of dye at equilibrium, 'a' is monolayer coverage capacity (mg/g), 'b' is Langmuir isotherm constant, K_f is Freundlich isotherm constant and $1/n$ is a surface heterogeneity.

The linear plot of C_e / q_e Vs C_e , gives a straight line as shown in Fig. 9a, from which the constant 'a' and 'b' could be evaluated. Figure 9a shows the applicability of the Langmuir isotherm for monolayer coverage of MB on SnO₂ nanorods. All MB isotherm parameters of MB adsorption over SnO₂ are described in Table 3. The adsorption nature can be predicted from the RL (dimensionless) separation factor values according to the Langmuir model. In general, the adsorption is favorable (if $0 < R_L < 1$), unfavorable (if $R_L > 1$), Linear (if $R_L = 1$) and irreversible (if $R_L = 0$). In the present study, the R_L values are lower ($0 < R_L < 1$) which indicates the adsorption of MB by SnO₂ nanorods was favorable [47].

Figure 9b shows the linear plot of $\log q_e$ Vs $\log C_e$ i.e. Freundlich isotherm for adsorption of MB on SnO₂ surface. According to the Freundlich isotherm model, the value of 'n' (dimensionless) indicated the favorability of the adsorption process if the values of 'n' are greater than one ($n > 1$). Table 3 shows all the values of 'n' are greater than one ($n > 1$), that is the adsorption is highly favorable. Also, when the values of the slope are $1/n < 1$, it shows the chemisorptions; $1/n > 1$ then co-operative adsorption while $1/n$ equal to zero indicates the heterogeneity [48]. In the present study, the $1/n$ values are less than one; it

Fig. 9 Adsorption plots of MB by SnO₂ nanorods. **a** Langmuir plot. **b** Freundlich plot

Table 3 Freundlich and Langmuir isotherm constants for adsorption of MB over SnO₂ nanorods for different initial dye concentration

Dye concentration (mg/L)	Freundlich coefficient				Langmuir coefficient			
	K_f (L/g)	n	$1/n$	r^2	a (mg/g)	b (g/L)	R_L	r^2
10	1.050	6.995	0.142	0.969	7.352	0.3002	0.249	0.983
15	1.141	6.718	0.148	0.981	1.285	1.238	0.051	0.996
20	1.147	10.681	0.093	0.991	2.020	0.773	0.060	0.992

Fig. 10 **a** Pseudo-first order kinetics of photocatalytic removal of MB (at pH=2, Contact time=90 and initial concentration = 10 mg/L); **b** pseudo-second order kinetics of adsorptive removal of MB (at pH=7, Contact time=60 and initial concentration = 20 mg/L)

clearly shows the adsorption of MB on the SnO₂ surface is chemisorptions. However, the Langmuir isotherm has a greater linear regression coefficient (R^2) values as compared to the Freundlich isotherm values (Table 3). Hence, the Langmuir isotherm model is the most appropriate isotherm for the adsorption of MB over the SnO₂ nanorods.

3.7 Kinetics study

The kinetics of adsorption and photocatalytic removal of MB by SnO₂ nanorods give information about the mechanism of the reaction. The pseudo-first-order and pseudo-second-order model has therefore been used. The pseudo-first-order kinetic model for the photocatalytic removal of MB is given as in Eq. 6 [49, 50].

$$\ln \frac{C_0}{C_t} = kt \quad (6)$$

The rate constant for the photocatalytic removal of MB by SnO₂ nanorods was calculated from the slope of the straight line obtained from the linear plot of $\ln C_0/C_t$ versus time (t) (Fig. 10a). The rate constant k for MB photocatalytic removal K_1 is $9.16 \times 10^{-1} \text{ min}^{-1}$ with a linear regression coefficient (R^2) near to unity.

Adsorption is a critical process involving the mass transfer of a substance from the liquid phase to the surface of the catalyst. Also, the rate of pseudo-second-order reaction depends on the quantity of solute adsorbed on the catalyst surface and at equilibrium. The pseudo-second-order kinetic model is represented as in Eq. 7, [46].

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Fig. 11 Van't Hoff plot

Table 4 Thermodynamic parameters of MB adsorption on SnO₂ nanorods

Dye Concentration (mg/L)	Temperature (K)	K_d (L/g)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/Kmol)
10	303	2.91	-2.646	0.87	11.93
15	303	4.08	-3.423	1.48	16.50
20	303	3.39	-3.014	1.06	13.65

where K_2 is second-order rate constant (g/mg/min), q_e is the amount of dye adsorbed (mg/g) and q_t is the amount of dye adsorbed at time t . The linear plot of t/q_t versus time as shown in Fig. 10b, gives the values of the rate constant K_2 is $1.1 \times 10^{-1} \text{ (g/mg/min)}$ and the linear regression coefficient i.e. R^2 is 0.997. From both kinetic model studies, it indicates the photocatalytic removal follows the pseudo-first-order kinetics while adsorptive removal follows the pseudo-second-order kinetics [51].

3.8 Thermodynamics of adsorption

The variation of adsorption data with an initial dye concentration of MB solution was utilized to evaluate the thermodynamic parameters like change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) using the following equations (Eq. 8 and 9) [52].

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

where R is a gas constant, T is the absolute temperature and K_d is the equilibrium constant. The changes in thermodynamic parameters are obtained from the slope and intercept of the Van't Hoff plot of $\ln K_d$ versus the $1/T$ graph as shown in Fig. 11. Table 4 shows the values of all thermodynamic parameters. The negative value of ΔG° indicates the adsorption is spontaneous and favorable. The positive values of ΔH° evidencing the endothermic process and indicating the chemisorptions occurred, while the physisorption is always exothermic. Moreover, the positive value of ΔS° indicates the increases in randomness during the adsorption [53, 54].

4 Conclusions

The SnO_2 nanorods are synthesized with a simple coprecipitation method and are characterized by XRD, SEM, TEM, SAED, EDAX, and FTIR techniques. It is clear from XRD's diffraction pattern that the SnO_2 nanorods have a tetragonal rutile structure. The SEM and TEM patterns reveal the nano-rods of SnO_2 with polycrystalline structure. The SnO_2 nanorods were used successfully to remove MB dye from its aqueous solution by means of the adsorptive and photocatalytic mechanisms. Total adsorptive and photocatalytic removal of MB was achieved within 90 min by approximately 64.05 and 94% for the initial 20 and 10 mg/L concentration of dye. The Langmuir isotherm (R^2 similar to unity) best describes the adsorption activity of SnO_2 nanorods. The Freundlich isotherm reveals the chemisorptions nature of the adsorption process. Adsorptive removal of MB follows pseudo-second-order kinetics while photocatalytic removal follows pseudo-first-order kinetics. Also, a thermodynamic study suggests spontaneous and endothermic adsorption of MB on the SnO_2 surface, indicating that chemisorptions occur during adsorption. The results reveal that SnO_2 nanorods are an outstanding catalyst for the photocatalytic removal of carcinogenic MB from its aqueous solution in comparison with the adsorptive removal.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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