

## KINETIC AND THERMODYNAMIC STUDIES FOR THE H<sub>2</sub>S ADSORPTION USING TiO<sub>2</sub> NANOMATERIALS

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This study is continuation of the studies carried out by our research group focusing on the catalytic and photocatalytic destruction of H<sub>2</sub>S gas using pure and doped TiO<sub>2</sub> nanomaterials. To further study the H<sub>2</sub>S adsorption mechanism, kinetic and thermodynamic studies were carried out, followed by adsorption isotherms like Langmuir and Freundlich isotherms. The reactions were assumed to be pseudo first order reactions. In agreement with our previous findings, lower activation energies were attained for 2% sulphur doped nanoparticles and nanofibers, the energy that of nanofibers being quite lower than the nanoparticles indicating the better destruction efficiency in case of nanofibers.

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### 1. Introduction

H<sub>2</sub>S gas is highly toxic in nature and has a very low odour threshold [1]. H<sub>2</sub>S is considered to be a broad spectrum toxicant because most of the human organs and tissues with mucous membrane exposed (eyes, nose) and organs having high oxygen demand (brain, lungs) are the main target of H<sub>2</sub>S gas [2]. This gas is also classed as a chemical asphyxiant, which is quite similar to cyanide gases and carbon monoxide. Many studies have been carried out for the destruction of this gas [3-5]. TiO<sub>2</sub> nanoparticles and nanofibers have also been used by us in our studies for evaluating their destruction potential using both catalytic and photocatalytic reactions [6-8]. TiO<sub>2</sub> nanoparticles were synthesized by using co-precipitation method at room temperature and atmospheric pressure [9]. The TiO<sub>2</sub> nanofibers were synthesized using electrospinning technique which is considered to be the most useful technique for synthesis of nanofibers in nanodomains [10, 11].

Besides other analyses carried out in our subsequent studies as described before, kinetics and thermodynamic studies were also carried out for catalytic reactions in order to understand the adsorption mechanism of H<sub>2</sub>S gas using pure and Sulphur doped TiO<sub>2</sub> nanoparticles and nanofibers. In order to further study the adsorption mechanism of H<sub>2</sub>S gas, the reaction data was also analysed using the Langmuir and Freundlich adsorption isotherms. The reactions were assumed to be the pseudo first order reactions. Since the nanofibers had comparatively significant H<sub>2</sub>S destruction efficiency as compared to nanoparticles [12], both the Langmuir and Freundlich isotherms were tested to fit the experimental data of H<sub>2</sub>S adsorption on the surface of the TiO<sub>2</sub> nanofibers.

### 2. Methodology

#### 2.1 Kinetic and Thermodynamic Studies

Keeping in view the comparatively significant H<sub>2</sub>S destruction efficiency of nanofibers, kinetic and thermodynamic studies were carried out using pure and doped TiO<sub>2</sub> nanofibers to

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understand the H<sub>2</sub>S adsorption and destruction mechanism. The reactions were assumed to be pseudo first order reactions and simplified kinetics equation after integrating the pseudo first order rate equation is as under:

$$t^*k_{ads} = \ln(C_o/C) \quad (1)$$

Where,

$$\begin{aligned} k &= \text{rate constant,} \\ C_o &= \text{Initial concentration,} \\ C &= \text{Concentration at time 't'} \end{aligned}$$

The kinetic and thermodynamic parameters were calculated using the famous Arrhenius Equation as under:

$$k = A * e^{(-E_a/RT)} \quad (2)$$

Where,

$$\begin{aligned} k &= \text{rate constant} \\ A &= \text{frequency factor} \\ E_a &= \text{activation energy} \\ R &= \text{gas constant (8.314 J mol}^{-1}\text{K}^{-1}) \\ T &= \text{temperature in K}^\circ \end{aligned}$$

This equation can be further simplified by taking the log natural, as:

$$\ln(k) = \ln(A) - E_a / RT \quad (3)$$

The other thermodynamic parameters were calculated using the following thermodynamic equations:

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

Where,

$$\begin{aligned} \Delta G &= \text{Gibbs free energy change} \\ R &= \text{Gas constant (8.314 J mol}^{-1}\text{K}^{-1}) \\ T &= \text{Temperature in K}^\circ \end{aligned}$$

## 2.2 Adsorption Isotherms

Both the Langmuir and Freundlich isotherms were tested to fit the experimental data of H<sub>2</sub>S adsorption on the surface of the TiO<sub>2</sub> nanofibers. Langmuir model describes the adsorption onto a surface where the monolayer coverage represents the maximum sorbate concentration ( $C_{max}$ ). The equation can be written as:

$$C_s = \frac{K_L C_{max} C_{eq}}{1 + K_L C_{eq}} \quad (5)$$

Inverting eq.5,

$$\begin{aligned} \frac{1}{C_s} &= \frac{1 + K_L C_{eq}}{K_L C_{max} C_{eq}} \\ \frac{1}{C_s} &= \frac{1}{K_L C_{max} C_{eq}} + \frac{K_L C_{eq}}{K_L C_{max} C_{eq}} \\ \frac{1}{C_s} &= \frac{1}{K_L C_{max} C_{eq}} + \frac{1}{C_{max}} \end{aligned} \quad (6)$$

Where,

$$\begin{aligned} C_s &= \text{Sorbate (H}_2\text{S) concentration} \\ C_{eq} &= \text{H}_2\text{S concentration at equilibrium} \\ C_{max} &= \text{Maximum H}_2\text{S concentration adsorbed} \end{aligned}$$

$K_L$  = Langmuir sorption constant

Freundlich model can be expressed mathematically as:

$$C_{ads} = K_f C_e^{1/n} \quad (7)$$

Rearranging eq. 7,

$$\ln C_{ads} = \frac{1}{n} \ln C_e + \ln K_f \quad (8)$$

Where,

$C_{ads}$  = Amount of  $H_2S$  adsorbed  
 $C_e$  =  $H_2S$  concentration at equilibrium  
 $K_f$  = Freundlich adsorption constant  
 $n$  = Empirical constant that varies with degree of heterogeneity

### 2.3 Sample IDs

The samples were named as per the sulphur doping concentrations and 0, 1, 1.5, 2, 2.5 and 3% sulphur doped nanoparticles were coded as 0P, 1P, 1.5P, 2P, 2.5P and 3P, respectively. The 0, 1, 2, 3, 4 and 5% nanofibers were coded as 0F, 1F, 2F, 3F, 4F and 5F, respectively.

## 3. Kinetics and Thermodynamics Studies

### 3.1 Results

The reaction constant ' $k_{ads}$ ' was calculated by plotting a graph between  $\ln(C_o/C)$  and time ' $t$ '. Different values of  $k_{ads}$  have been listed in Tables 1 and 2 for nanofibers and nanoparticles, respectively. It was observed in our previous studies that highest efficiencies were achieved using 2% S-doped nanofibers [12]. Therefore, only the graph obtained for 2% S-doped nanofibers (2F) showing a relationship between time and  $H_2S$  concentration at different temperatures of 450, 350, 250, 150 and 50  $^{\circ}C$  are shown in Fig.1.

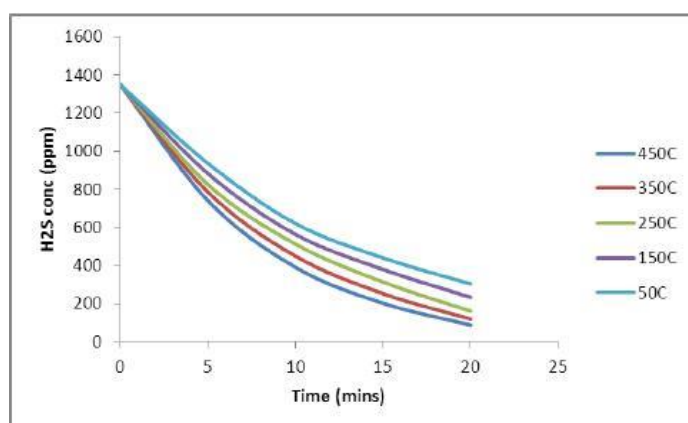


Fig.1. Catalytic  $H_2S$  destruction using 2F at different temperatures

The values of  $A$  and  $E_a$  for 2% S-doped nanofibers were calculated by plotting a graph between  $\ln(k)$  and  $1/T(K^{\circ})$ , which is as shown in Fig. 2.

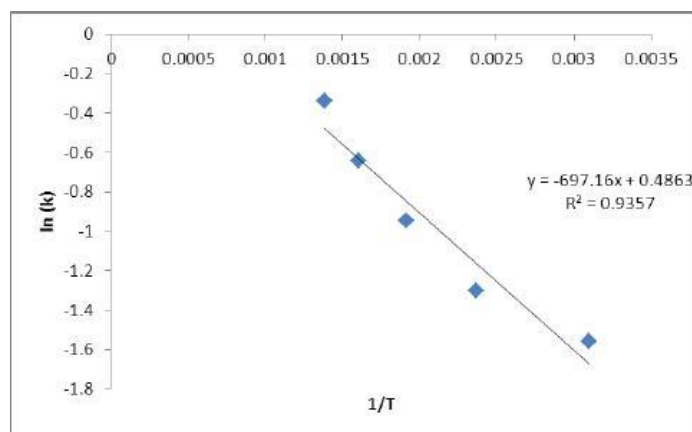


Fig.2. Graph plotted between  $\ln(k)$  and  $1/T$  for 2F nanofibers

Different thermodynamic parameters calculated using the above mentioned graph and equations for the nanofibers have been shown in Table 1.

Table 1. Values of thermodynamic parameters  $E_a$  and  $G$  calculated for  $\text{TiO}_2$  nanofibers

Sample ID	$k_{\text{ads}} (\text{s}^{-1})$	$E_a (\text{kJ/mole})$	$G (\text{kJ})$	A
0F	0.4839	6.721	-4363.26	1.274686
1F	0.6534	6.103	-2558.09	1.578697
2F	0.7124	5.796	-2038.43	1.626287
3F	0.6619	6.059	-2480.39	1.588039
4F	0.5754	6.42	-3322.23	1.452084
5F	0.6684	5.96	-2421.65	1.55566

Using the average values of the frequency factor 'A' found for the nanofibers, the thermodynamic parameters for the nanoparticles were calculated as both the experiments were performed under same experimental conditions. The thermodynamic parameters have been tabulated in Table 2.

### 3.2 Discussions

#### 3.2.1 Nanoparticles

The values of thermodynamic parameters,  $k_{\text{ads}}$ ,  $E_a$  and  $G$  calculated for all catalytic reactions using nanoparticles are presented in the Table 2. It can be seen from that as observed in all the cases, the  $k_{\text{ads}}$  for the 2P nanoparticles (2P) is the highest and consequently its  $E_a$  is lowest showing that it requires the lowest activation barrier for the destruction of  $\text{H}_2\text{S}$  gas as compared with the other nanoparticles. The calculated value of Gibbs free energy change ' $\Delta G$ ' as a result is also found to be lowest for the 2P nanoparticles. Negative values of the Gibbs energy change show the spontaneity of all the reactions.

Table 2. Values of thermodynamic parameters  $E_a$  and  $G$  calculated for  $\text{TiO}_2$  nanoparticles

Sample ID	$k_{\text{ads}} (\text{s}^{-1})$	$E_a (\text{kJ/mole})$	$G (\text{kJ})$
0P	0.1624	12.38507	-10926.2
1P	0.1569	13.87793	-11133.3
1.5P	0.2254	11.79025	-8955.69
2P	0.2744	10.69642	-7773.26
2.5P	0.2592	10.96787	-8115.81
3P	0.159	13.83347	-11053.4

### 3.2.2 Nanofibers

Similar to the findings of the nanoparticles, the value of  $k_{\text{ads}}$  was found to be highest for 2% S-doped nanofibers and the activation energy was the lowest. This shows that these nanofibers have the highest adsorption capacity as compared with the other nanofibers. It was also noted that the  $E_a$  for 2% S-doped nanofibers was higher than the  $E_a$  for the 2% S-doped nanoparticles once again showing that the efficiency of the nanofibers is higher than the nanoparticles. Moreover these findings can also be correlated to the pore volume and pore diameter of the nanomaterials. As discussed in our previous studies, pore volume and pore diameter of 2% S-doped nanofibers was greater than those of other  $\text{TiO}_2$  nanoparticles and nanofibers. Therefore the large pore volume and pore diameter facilitate the mass transfer of reactants [13] resulting into highest destruction efficiency.

It is worth mentioning that the  $\text{H}_2\text{S}$  activation energies of 10.69 and 5.79 kJ/mole for 2% S-doped nanofibers and nanoparticles, respectively were quite lower to the activation energies reported in quite a number of studies [14]. Brink and co authors reported that activation energy of  $\text{H}_2\text{S}$  varied from 10-60 kJ/moles in different studies. A summary of the studies which have explored the activation energies of  $\text{H}_2\text{S}$  on different catalysts is presented in Table 3.

Table 3: Studies conducted for calculation of  $E_a$  for the  $\text{H}_2\text{S}$  adsorption on different catalysts

$\text{H}_2\text{S}$ Activation Energies (kJ/mole)	Catalyst	Reference
72.4	Low pressure flame analysis	[15]
16.3	Carbon	[16]
76.1	Lime Particles	[17]
31-53	Vanadium Sulphide	[18]
163.24	Uncalcined Limestone	[19]
$30.1 \pm 4.9$	Fe (VI)	[20]
16.8	Activated Carbon	[21]
26.6-29.3	Activated Carbon	[22]
30-36	Direct oxidation in fluidized bed reactor	[23]

It can therefore be inferred from the low activation energies calculated from the experiments in this study that the 2% S-doped  $\text{TiO}_2$  nanoparticles and nanofibers are highly

favourable catalysts for the H<sub>2</sub>S destruction. The negative values of the free energy change explain the spontaneity of these reactions.

## 4. H<sub>2</sub>S Adsorption Isotherms

### 4.1 Results

Both the Langmuir and Freundlich isotherms were tested to fit the experimental data of H<sub>2</sub>S adsorption on the surface of the TiO<sub>2</sub> nanofibers.

#### 4.1.1 Langmuir Isotherm

From the equation 6,  $C_{max}$  and  $K_L$  were calculated by plotting the graphs between  $1/C_s$  and  $1/C_{eq}$  for all the nanofibers. From the  $C_{max}$ , maximum number of molecules adsorbed on TiO<sub>2</sub> surface ( $\eta_{max}$ ) was also calculated [24]. The values of  $C_{max}$  and  $K_L$  and  $\eta_{ads}$  have been tabulated in Table 4.

Table 4: Values of  $C_{max}$ ,  $K_L$  and  $\eta_{ads}$  for TiO<sub>2</sub> nanofibers

Sample ID	$C_{max}$	$K_L$	$R^2$	$\eta_{max}$
0F	313	0.0249	0.99	0.00816
1F	357	0.0172	0.76	0.0104
2F	588	0.0075	0.76	0.0173
3F	250	0.0116	0.41	0.0073
4F	345	0.0046	0.58	0.0101
5F	238	0.0127	0.81	0.0069

#### 4.1.2 Freundlich Isotherm

A plot between ' $\ln C_{ads}$ ' and ' $\ln C_e$ ' gave the parameters ' $K_f$ ' and ' $n$ ' for Freundlich isotherm which have been summarized in Table 5.

## 4.2 Discussions

As the noxious gases like H<sub>2</sub>S, follow the Langmuir adsorption behavior [25], Langmuir and Freundlich adsorption isotherms were tested to fit the experimental data for the moles adsorbed on the surface of the TiO<sub>2</sub> nanofibers.  $K_L$  and  $K_f$  are the functions of the capacity of adsorbent to adsorb a specific adsorbate. Constant ' $1/n$ ' is also termed as the intensity of adsorption. The values of ' $n$ ' were all found to be below or equal to 10, which shows favourable adsorption ability [26]. The number of molecules adsorbed ( $\eta_{ads}$ ) on the surface of the TiO<sub>2</sub> nanofibers were calculated by using the Langmuir isotherm. The number of molecules adsorbed were found to be highest for the 2F nanofibers which showed the highest photocatalytic efficiency for the H<sub>2</sub>S gas destruction. The  $R^2$  value for this data was 76% which shows a relatively good fit.

Table 5: Values of ' $K_f$ ' and ' $n$ ' calculated for  $TiO_2$  nanofibers

Sample ID	$K_f$	$n$	$R^2$
0F	105.8	6.1	0.99
1F	26.0	2.3	0.94
2F	198.0	6.7	0.82
3F	63.7	5.1	0.68
4F	61.1	4.7	0.53
5F	123.6	10.8	0.84

## 5. Conclusions

As found in our previous studies [12], the highest  $H_2S$  destruction efficiency was achieved in the case of 2% Sulphur doped nanofibers samples, and 2% sulphur doped particles. But the destruction efficiency found in the case of nanofibers was quite higher as compared to that of nanoparticles which is in good agreement with the previous studies [26, 27]. This was also reflected in the kinetic and thermodynamic studies where the  $k_{ads}$  values were higher and  $E_a$  was lower in the case of 2F nanofibers. The same trend was also observed in the adsorption isotherms where the number of moles adsorbed was found to be highest for these samples. It can therefore be concluded that the best  $H_2S$  destruction efficiency could be achieved by using 2% S-doped nanofibers in photocatalytic experiments.

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