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## Thermodynamics of carbofuran adsorption on pyrite

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## 1. Introduction

Pesticides have immensely contributed to enhance crop productivity and to control the insect borne diseases [1]. The high temperature and humidity conditions persistent in the tropical world provide a favourable environment for rapid multiplication of pests. Therefore, the application of pesticides on crops is required to combat pests and vector borne diseases [2]. Carbofuran (2. 3-dihvdro-2. 2-dimethvlbenzofuran-7-vl-methvlcarbamate). a carbamate group pesticide, is widely used as an insecticidenyameticide through the inhibition of acetyl-cholinesterase (AChE) activity in insects and mammals [2,3]. The ubiquitous presence of carbofuran in the environment has received a great concern not only due to its heavy usage but also due to its high oral toxicity  $(LD_{50} \sim 11 \text{ mg} \cdot \text{kg}^{-1} \text{ body weight in rats})$  [4]. The half lives of carbofuran in water is a variable which ranged from 690 days at pH 5 to 7 days at pH 9 [4,5]. To control this hazard, the European Union (EU) has promulgated standards for drinking water at a maximum permissible level for any particular pesticide to be at 0.1  $\mu g \cdot dm^{-3}$ and for the sum of all pesticides including their degradation products, to be at 0.5  $\mu$ g  $\cdot$  dm<sup>-3</sup> [6].

Carbofuran resists biodegradation; hence, abiotic treatment methods such as UV radiation [7], Fenton's process [8], direct photolysis [7,9],  $UV/O_3$  process [10] or photo-degradation [7,10] showed a great promise for its control. In the aforementioned process, the OH radical is the key to destroy refractory micro

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#### ABSTRACT

Thermodynamic parameters of carbofuran adsorption on pyrite were determined from experimental data. In order to minimize the dissolution of pyrite as well the degradation of carbofuran, all experiments were restricted to (15 to 20) min. The maximum adsorption capacity of carbofuran varied with both pH and temperature in the order:  $[\Gamma_{\text{carb}}^{\text{max}}]_{pH\,177} > [\Gamma_{\text{carb}}^{\text{max}}]_{pH\,270} > [\Gamma_{\text{carb}}^{\text{max}}]_{pH\,401}$ . The Dubinin–Radushkevick (D–R) model was used to assess the degree of site heterogeneity. The interactions between carbofuran and surface sites can largely be ascribed to specific chemical interactions.

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pollutants. However, these treatment methods require costly chemicals (FeSO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>) and skilled training. The final motivation of this research is to propose a novel methodology for the in situ production of OH utilizing redox sensitive minerals. Pyrite is a redox sensitive mineral that provides additional advantages due to its dual behaviour in aqueous phase: namely the hydrophobicity and hydrophilicity [11]. Pyrite (FeS<sub>2</sub>) is ubiquitous and occurs in different geologic environments, viz. mineralized zones, vein graphite, igneous bodies, peat, coal, sediments and soils [12]. Pyrite is an intrinsic d band semiconductor that exhibits both n and ptypes of conductivity [13]. The Fe(II) on pyrite is low spin  $(d^6 t_{2g}^6)$ . The  $S_2^{2-}$  ions have a series of molecular orbitals that are the key in understanding electron transfer processes (oxidation or reduction) of pyrite. The sulphide sites has a lone pair of electrons (from a  $\pi^*$  HOMO) that are available for donation to a vacant orbital of a Lewis acid. These electrons are important for the attachment of reactants to the pyrite surface [14]. It was also shown that a reaction between H<sub>2</sub>O and  $\equiv$ Fe(III) at defect sites on the pyrite can generate surface bound OH radicals (i.e. OH ad) [15]:

 $\equiv Fe(III) + H_2O \rightarrow \equiv Fe(II) + OH_{ad} + H^+.$ 

The OH radical is non-specific in that it destroys most of the organic pollutants. Thus pyrite-assisted catalysis is considered as being surface mediated. Presently, we examined the thermodynamics parameters of carbofuran adsorption by pyrite. The pyrite used for this work has previously been characterized for its surface reactivity [11]. However, the thermodynamic data for carbofuran and pyrite or allied sulphide minerals are scanty to date. The thermodynamic data presented here will be used to calibrate the molecular dynamic simulations of carbofuran–pyrite complexes to elucidate



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interfacial processes at the molecular level. Further, the thermodynamic data shown here will also be useful in determining the fate of carbofuran in environmental systems.

## 2. Materials and methods

Pyrite samples were hand-picked from a vein graphite deposit in Sri Lanka (Bogala Graphite Mine, Sri Lanka). As shown in table 1, the chemical composition of Sri Lankan and commercial pyrite (Peru) samples showed a similarity particularly with respect to  $\binom{|s|}{|fe|}$  mole ratio. Although the thermodynamic data of the carbofuran-pyrite system are scarce in the literature, the  $\Delta G_f^0$ ,  $\Delta H_f^0$  and  $\Delta S_f^0$ values of synthetic pyrite were given as (-160.2, 171.5 and 52.9) J · K<sup>-1</sup> · mol<sup>-1</sup>, respectively [16].

The XRD data confirmed the pyrite phase. All chemicals were from Sigma-Aldrich (USA), Fluka (Switzerland) or BDH (UK). In order to minimize  $CO_2$  and  $O_2$  contamination, the distilled water was boiled for 3 h and cooled in a glass vessel leaving no headspace and kept inside a glove box filled with nitrogen (mass fraction purity 0.9995). Control experiments were carried out using (1 and 5)  $\mu$ M carbofuran in 0.01M NaClO<sub>4</sub> to assess any losses to container walls and filtration apparatus. Within 20 min of the reaction period, the spike recoveries of the (1 and 5)  $\mu$ M carbofuran solutions were 95.5% to 97.8% respectively. The physico-chemical parameters used in pyrite and carbofuran in this work are given in table 2.

Preparation of  $20 \text{ g} \cdot \text{dm}^{-3}$  pyrite slurry was carried out according to the following method. A known quantity of pyrite was homogenized with a minimum quantity of water. The pyrite paste prepared was transferred to a water-jacketed vessel which contained 0.01M NaClO<sub>4</sub>. The tightly capped reaction vessel had a provision for gas outlets, sampling, and pH and temperature probes. Unless otherwise indicated, the temperature of the reaction system was always at *T* = 298 K. The pyrite-solution suspension was stirred continuously. Whenever required, the pH adjustments were made with 0.887M HClO<sub>4</sub> or 0.787M NaOH. Reaction solutions were always purged with N<sub>2</sub> to ensure inert conditions.

Time dependence experiments by pyrite were carried out to examine equilibration time,  $t_c$  for optimal adsorption of 20  $\mu$ M carbofuran. Relevant experimental details are well documented [17]; hence, only a brief account was given. A 0.5 dm<sup>3</sup> of 20 g  $\cdot$  m<sup>-3</sup> pyrite suspension in 0.01M NaClO<sub>4</sub> was prepared and the pH was adjusted to 1.77, 2.70 or 4.01. At a given time, the solution was spiked with carbofuran to reach a final concentration 20  $\mu$ M. At pre-defined time intervals, 0.005 dm<sup>3</sup> aliquots of the suspension were pipette out; solid/solution separation was done by filtration into glass vials using 0.45  $\mu$ m filter cartridges (Millipore USA). The filtrates were stored at 4 °C for carbofuran analysis.

The adsorption isotherms of carbofuran were constructed in 0.01M NaClO<sub>4</sub> at pH 1.77, 2.70 and 4.01. The system pH was regulated by the addition of 0.887 HClO<sub>4</sub>/0.787M NaOH. Generally the adjustment of pH was minimal at pH 1.77 or 2.70. The initial loading of carbofuran was varied between (0.05 to 20)  $\mu$ M. After the hydroxylation, 0.01 dm<sup>3</sup> aliquots of the suspension were transferred into glass vials, and they were equilibrated for 15 min at 100 rpm in a temperature regulated water bath shaker (EYELA, Japan); the final pH was measured after adjustments, if needed. The temperature of the water bath was adjusted at (313 and 333) K. The ambient temperature of the laboratory was 298 K.

#### TABLE 2

Physico-chemical parameters of pyrite and cabofuran.

Parameter	Value	Source
Pyrite (Sri Lanka)/Pyrite (Peru)		
Specific surface area/ $(m^2 \cdot g^{-1})$	1/0.50	[11,29]
Site density/(sites · nm <sup>-2</sup> )	12	[11]
Carbofuran, $C_{12}H_{15}NO_3$		
Formula mass	221.26	[30]
Density/(g · cm <sup>−3</sup> )	1.18	do
Boiling point /°C	313	do
Vapour pressure/Torr	0.005	do
Solubility/(g per100 cm <sup>3</sup> H <sub>2</sub> O)	0.07	do
pK <sub>a</sub>	11.9	do
Kow	2.32	do

Most of the isotherm experiments were conducted in three replicates and the arithmetic average was used in the calculation of errors as shown in figure 2(a to c). The pH of the sample was determined with Auto Chemistry Analyzer (Orion 960, USA) using a pH electrode (Orion 81038N) and double junction reference electrode (Orion 100057) after calibrating at pH 2.15 and 4.11 and 7.00 at a given temperature. The outer sheath of the double junction electrode was filled with 0.01M NaClO<sub>4</sub> to minimize diffusion. Analysis of carbofuran was carried out by reversed phase HPLC with RP-18 column in 50% methanol, 50% water and 0.01M Na<sub>2</sub>HPO<sub>4</sub>/NaH<sub>2</sub>-PO<sub>4</sub> mobile phase at  $\lambda = 282$  nm under isocratic conditions. The degradation products were observed after a 15 min period of equilibration and no detailed discussion into this direction is given.

## 3. Results and discussion

Pyrite decomposed rapidly when exposed to oxygenated H<sub>2</sub>O for a long contact time ( $t_c$ ). The pyrite dissolution rate was dependent on pH, pO<sub>2</sub>,  $t_c$ , oxidant concentration and defects density [18]. Particular attention was paid to maintain anaerobic environment. The initial pH of the system was restricted to pH 1.77 to 4.01; unless otherwise mentioned, the contact time was 15 min. When these stringent conditions were satisfied, the production of Fe<sup>2+</sup> was accounted for by a surface mediated process as shown [17–19]:

$$>$$
 FeS<sub>2</sub> + H<sup>+</sup>  $\rightarrow$  > FeSH2  $\rightarrow$  Fe<sup>2+</sup> + > HS<sub>2</sub>

As shown in figure 1a the adsorption density of carbofuran as a function of  $t_c$ , pH and equilibration temperature is shown in 0.01M NaClO<sub>4</sub>. The NaClO<sub>4</sub> was chosen to regulate the ionic strength of the solution due to its inertness towards pyrite. The NO<sub>3</sub><sup>-</sup> showed a slow reduction in the presence of pyrite [20]:  $2FeS_2 + 6NO_3^- + 2H_2O \rightarrow 3N_2 + 2FeOOH + 4SO_4^{2-} + 2H^+$ ;  $\Delta G_f^0 = -415.84$ kJ · mol<sup>-1</sup> hence, we avoided NaNO<sub>3</sub> use to regulate the background electrolyte concentration.

In all time dependence experiments, the initial concentration of carbofuran was kept at 20  $\mu$ M. As shown in figure 1a at a given pH, the carbofuran sorption first increased and then reached a plateau which was followed by a data scatter due to gradual degradation of carbofuran (the scattered data are not given). Always  $\frac{[pyrite sites]}{[initial carbo furan]} \gg 25$ , therefore, the chemical rates of carbofuran sorption can thus be treated as pseudo-first order kinetics. Carbofuran is a weak monoprotic acid, *i.e.*  $pK_a = 11.90$ ; therefore when pH < 10 virtually 99.98% of carbofuran was not dissociated. As

#### TABLE 1

Chemical composition of pyrite samples from different localities.

Pyrite Elemental Composition /(%)	Fe	S	S/Fe	С	Ca	Si	Cu	Pb	Zn	Со	Mn
Peru [28]	42	49.6	2.05	>0.01	0.03	<0.01	2.67	0.12	0.06	ND	ND
Sri Lanka [this work]	41.7	46.5	2.01	ND	0.05	0.20	ND	ND	0.02	0.01	0.01



**FIGURE 1.** (a) Variation of carbofuran adsorption density on pyrite as a function of equilibration time and pH at T = 298 K in 0.01M NaClO<sub>4</sub>. Similar curves were received for other temperatures and pH values (data not given). Arrows indicate the data points used for rate calculations. Initial [carbofuran] = 20  $\mu$ M, pyrite = 20 g · dm<sup>-3</sup>. Apparent scatter of data points after  $t_c > 15$  min. is attributed to slow dissolution of the solid and subsequent degradation of carbofuran. (b) Variation of ln{ $(\Gamma_{carb}^{max} - \Gamma_{carb})/(\mu mol \cdot m^{-2})$ } as a function of time for carbofuran adsorption on pyrite at and T = 298 K.

shown in figure 1a, the adsorption density of carbofuran on pyrite, *i.e.*  $\Gamma_{carb}$  was highest when pH 1.77. The  $\Gamma_{carb}$  values do not change with the stirring rate of the reaction mixture. Variation of the stirring rate varies the thickness of the stationary layer through which the molecules diffuse from the bulk solution to the mineral phase. If the rate is independent of the stirring rate, it is likely that the reaction rate is surface controlled [21]. For the carbofuran and pyrite system the observed variations of adsorption may be explained due to two reasons; first, the pyrite showed a slow dissolution around ~15 min and as time proceeds, the pyrite-mediated degradation of carbofuran is evidenced. When  $t_C < 15$  min. the kinetics of carbofuran adsorption showed similar trends at all pH and temperatures examined. The rate of carbofuran adsorption was modelled by the following equation;

$$\frac{d\Gamma}{dt} = k_{\text{carb}} (\Gamma_{\text{carb}}^{\text{max}} - \Gamma_{\text{carb}}) \tag{1}$$

which leads to the relation  $-\ln(\Gamma_{carb}^{max} - \Gamma_{carb}) = k_{carb}t + lnA_{carb}$  where  $k_{carb}$  is the 1st order rate constant for carbofuran and pyrite interactions,  $\Gamma_{carb}$  is the extent of adsorption at time t,  $\Gamma_{carb}^{max}$  is the extent of sorption when the equilibrium was reached, and  $A_{carb}$  was a constant of integration. Due to the data scatter, the  $\Gamma_{carb}$  values correspond to  $t_c \sim 15$  min is taken as  $\Gamma_{carb}^{max}$  (refer to figure 1(a,b) for details). Based on these arguments, as shown in figure 1b, the  $k_{carb}$  values were estimated from the slope of the  $\ln(\Gamma_{carb}^{max} - \Gamma_{carb})vs.t$  plots. Previously the same method was used to quantify protein and phenol adsorption processes on silica and pyrite surfaces respectively [17,22,23]. In the case of protein adsorption on silica,



**FIGURE 2.** (a to c): Variations of  $\Gamma_{carbofuran}$  as a function of pH and system temperature. Initial conditions used: pyrite 20 g · dm<sup>-3</sup>; [carbofuran] = (0.05 to 20)  $\mu$ M; 0.01M NaClO<sub>4</sub>. The experimental data are limited to *T* = (313 and 333) K. Therefore the  $\Gamma_{carb}^{max}$  values were obtained by modelled calculations.

TABLE 3

Observed rate constants, maximum adsorption densities and D–R free energies of pyrite–carbofuran interactions as a function of pH and temperature. The maximum adsorption densities were calculated by fitting the experimental data to Langmuir equation. Refer to the text for details.

рН	T/K	k <sub>carb</sub> rate const./min <sup>-1</sup>	$K_{\text{Langmuir}}/(\text{m}^3 \cdot \text{mol}^{-1})$	$\begin{array}{l} 10^{-6} \ \varGamma_{\max} \\ (\text{mol} \cdot \text{m}^{-2}) \end{array}$	D-R free energy/ $(kJ \cdot mol^{-1})$
1.77	298	0.184	317	3.68	
	313	0.250	410	3.90	22.4
	333	0.300	511	4.20	26.9
2.70	298	0.114	189	2.20	
	313	0.189	194	2.36	3.95
	333	0.263	220	2.53	3.67
4.01	298	0.045	78	1.05	
	313	0.150	87	1.35	12.0
	333	0.282	92	1.50	12.5

this model was successfully used to quantify multi-step reaction processes. However in the present case multi-steps of carbofuran adsorption on pyrite (if any) are masked with the slow carbofuran degradation [24]. As shown in table 3 the  $k_{carb}$  values were decreased from two to five fold when the system pH was varied from 1.77 to 4.01 whereas the value of  $\Gamma_{carb}^{max}$  was lowest at pH 4.01.

The adsorption isotherms of carbofuran were measured in 0.01M NaClO<sub>4</sub> at pH 1.77, 2.70, and 4.01 (figure 2a to c). The system temperature was varied at (298, 313, and 333) K and the initial carbofuran concentrations were varied between (~0.03 and 2.0) · 10<sup>-6</sup> M at pH 1.77 and (~0.02 and 1.25) · 10<sup>-6</sup> M at both pH 2.70 and 4.01. Always the adsorption isotherms showed similar trends (figure 2a to c). As given in table 3, the order of maximum adsorption on pyrite was in accordance with  $[\Gamma_{carb}^{max}]_{pH 1.77} > [\Gamma_{carb}^{max}]_{pH 2.70} > [\Gamma_{carb}^{max}]_{pH 4.01}$ . When pH < 4.01, carbofuran is essentially not dissociated, however, the degree of surface speciation of pyrite is different, which seems to control the carbofuran retention. Previously, the possible surface species of the pyrite, *viz.*  $\equiv HSS^{-1/3}$ ,  $\equiv FeSS^{-1/3} \equiv SS^{-5/3}$ , and  $\equiv FeSSH^{2/3}$ , were quantified using the 1 - pK diffused layer model and the important results are shown below [11]. The  $\equiv FeSS^{-1/3}$ 

dominated over the entire pH range (1 to 5) examined. The occurrence of the *FeSSH*<sup>2/3</sup> species is low (compared to  $\equiv$ *FeSS*<sup>-1/3</sup>), which follows the opposite pattern to  $\equiv FeSS^{-1/3}$ . The proton saturation of surface sites is observed when pH < 4. This implies that in acid solution the surface is covered with  $\equiv HSS^{-1/3}$  groups. However, the activities of both  $\equiv FeSS^{-1/3}$  and  $\equiv FeSSH^{2/3}$  and the values of  $\Gamma_{carb}$ declined with the pH (<4.01). This implies that both  $\equiv$ SS<sup>-5/3</sup> and  $\equiv$ *FeSSH*<sup>2/3</sup> are active in carbofuran adsorption. Therefore, at the microscopic level, these sites should exhibit different adsorption affinities to carbofuran. However, the model constructs using Langmuir or Dubinin-Radushkevick (D-R) are not capable of characterizing such minor variations. Presently, we decided to apply these non-variable charge models to account for carbofuran adsorption on pyrite. The site heterogeneity of pyrite was assessed by the Dubinin-Radushkevick (D-R) model [25]. This model does not impose an *a priori* assumption of homogeneous surface sites or constant sorption potential. Therefore this model provides an independent way of checking the homogeneousness of sites. As shown in figure 3, the plots based on the D-R model as shown in equation (2) were chosen to estimate the apparent free energy of carbofuran adsorption on pyrite:

$$\ln(q_E) = \ln(q_m) - K_E \epsilon^2 \text{and} \epsilon = RT \ln\left(1 + \frac{1}{C_s}\right)$$
(2)

where  $q_E$  is the amount of carbofuran adsorbed per unit mass of pyrite (mol.g<sup>-1</sup>),  $C_s$  is the equilibrium concentration (mol  $\cdot$  dm<sup>-3</sup>), when pH and temperature are fixed, the  $K_E$  is a constant which is related to mean free energy of sorption (*i.e. E*),  $q_m$  is the monolayer capacity and  $\epsilon$  is the Polanyi potential. The D–R plots were constructed for carbofuran in NaClO<sub>4</sub> at T = (313 and 333) K and all pH values examined. Although the D–R model does not assume homogenous surface sites of adsorption, our experience showed that this approach yields poor fits with experimental results when binding sites are largely heterogeneous. The relative affinities of carbofuran on pyrite at different pH values were determined as given in table 4. The  $K_E$  values of carbofuran sorption ranged from



FIGURE 3. (a to c): Dubinin–Radushkevick (D–R) plots for pyrite-carbofuran interface as a function of pH and temperature in 0.01M NaClO<sub>4</sub>. Arrows indicate the data points utilized for calculations. Symbols: open T = 313 K, filled 333 K. A: pH 1.77; B: pH 2.70; C: pH 4.01.

TABLE	4
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Thermodynamics parameters for the adsorption of carbofuran adsorption on pyrite in 0.01M NaClO<sub>4</sub>. The thermodynamics parameters at activation state were calculated using Arrenhius and Erying models. Vant'Hoff equation was used to calculate the thermodynamics parameters of adsorption process.

pН	$E_a/(kJ \cdot mol^{-1})$	$\Delta H/(kJ \cdot mol^{-1})$	$\Delta H^{\#}/(kJ \cdot mol^{-1})$	$\Delta S/(J \cdot K^{-1} \cdot mol^{-1})$	$\Delta S^{\#}/(J \cdot K^{-1} \cdot mol^{-1})$	$\Delta G/(kJ \cdot mol^{-1})$	$\Delta G^{\#}/(kJ \cdot mol^{-1})$
1.77	22.5	31.5	22.4	0.15	0.195	-13.4	-15.4
2.70	40.1	21.3	40.1	0.11	0.193	-11.8	-11.8
4.01	59.2	7.62	59.2	0.19	0.187	-11.2	-11.2

 $(-6.19 \cdot 10^{-4} \text{ to } -3.72 \cdot 10^{-3}) \text{ mol}^2 \cdot \text{kJ}^{-2}$ . Based on  $K_E$  values the free energy of adsorption, E, was estimated by the following equation:

$$E = \sqrt{\left(\frac{1}{-2K_E}\right)} \tag{3}$$

As shown in table 1, the *E* is a function of pH and the temperature. In most cases the *E* values are highest when pH 1.77 (table 3). The magnitude of *E* gives information about the type of adsorption and if this value lies between (8 to 16) kJ  $\cdot$  mol<sup>-1</sup> the adsorption is ion exchange [25]. In the case of *E* < 8 kJ  $\cdot$  mol<sup>-1</sup>, adsorption is thought to occur by physical forces. As shown in table 1 for most of the time, the *E* values > 8 kJ  $\cdot$  mol<sup>-1</sup>. Further, based on IR spectroscopic measurements, a direct interaction between carbofuran and pyrite surface sites has been shown [24]. Therefore, at a given pH and temperature condition, the bonding between aforementioned species can be ascribed to specific chemical interactions.

Therefore, the carbofuran and pyrite interactions were modelled using the Langmuir equation assuming  $\equiv SH$  collective sites, where  $\Sigma[\equiv SH] = [\equiv HSS^{-5/3}] + [\equiv FeSS^{-1/3}] + [\equiv FeSSH^{2/3}]$  and un-dissociated carbofuran molecules according to following expression:

$$\Gamma_{\rm carb} = \frac{K_{\rm carb[carb]/r_{\rm carb}^{\rm max}}}{1 + k_{\rm carb}[{\rm carb}]} \tag{4}$$

where  $\Gamma_{\text{carb}}$  and [carb] are the concentration of adsorbate at the surface and in solution respectively;  $K_{\text{carb}}$  is the empirical constant for the sorption process,  $\Gamma_{\text{carb}}^{\text{max}}$  is the amount of adsorbate required to attain monolayer coverage. The  $K_{\text{carb}}$  is dependent on pH. As shown

in figure 2(a to c) the adsorption data are always in accordance with Langmuir model. The amount of carbofuran sorption is always less than 5% which results in a largely unsaturated pyrite surface with respect to carbofuran sorption density. The results are shown in figure 2(a to c). As shown in the data, both  $K_{carb}$  and  $\Gamma_{carb}^{max}$  values exert a marked effect on pH and temperature. The decrease of  $\Gamma_{carb}^{max}$  with pH is due to the decrease in the fraction of surface sites that exhibit carbofuran sorption.

#### 3.1. Thermodynamics of carbofuran sorption

The thermodynamics of carbofuran adsorption on pyrite is calculated in two modes; the first based on the chemical kinetics data in which the thermodynamics of the transition state conditions were calculated; the second in which the overall reaction is taken into account. The initial rates of carbofuran adsorption (*i.e.*  $k_{carb}$  values given in table 4 were used to determine the thermodynamics parameters of the activation state required for the carbofuran-pyrite system, activation energy ( $E_a$ ), activation enthalpy ( $\Delta H^{\#}$ ), and activation entropy ( $\Delta S^{\#}$ ) to define reaction coordinates. Accordingly, the carbofuran will adsorb on the pyrite surface to produce an adsorbed complex. Given sufficient energy this complex will reach an activation complex, and proceed to form products:

 $Carbofuran(Carb) + Pyrite(Py) \rightarrow (Carb - Py) \rightarrow [Carb - Py]^{\#} \rightarrow Products$ 

As shown in figure 4a, the Arrhenius plots, *i.e.*  $-\ln(k)$  vs.  $\frac{1}{7}$ , were constructed to calculate the activation energy of carbofuran sorption on



**FIGURE 4.** (a) Arrehenius plots of ln(*k*) *vs*.  $\frac{1}{T}$  for adsorption of carbofuran on pyrite as a function of pH. (b) Erying plots of ln(*k*) *vs*.  $\frac{1}{T}$  for carbofuran adsorption on pyrite as a function of pH.



**FIGURE 5.** (a) Van't Hoff plot for the adsorption of carbofuran on pyrite in 0.01M NaClO<sub>4</sub>. (b) Variation of  $\Delta H$  as a function of  $T_{av}$ .  $\Delta S$  in pH 1.77, 2.70 and 4.01 for pyrite–water interface. The  $T_{av}$  represents the arithmetic average of temperature.

pyrite. All such plots were approximately linear, thus justifying that at least the initial phase of carbofuran adsorption can be characterized by a single step reaction. The  $E_a$  values were estimated from the slope of the straight lines shown in figure 4a. As shown in table 4 the activation energy of carbofuran adsorption was the highest recorded when pH 4.01, hence, the formation of carbofuran –pyrite surface complex is kinetically hindered at T = 298 K in pH 4.01, which results in the lowest  $\Gamma_{carb}^{max}$  value. The surface mediated processes are often characterized by high activation energy. The activation energy for diffusion in aqueous media is around 20 kJ  $\cdot$  mol<sup>-1</sup> and when it is higher than this value, a surface controlled mechanism is dominant [26,27].

As shown in table 4, the  $E_a$  values increased with the temperature. The activation entropy ( $\Delta S^{\pm}$ ), and activation enthalpy ( $\Delta H^{\pm}$ ) were calculated from the same kinetic data using the Erying model,

$$ln\left(\frac{k}{t}\right) = ln\left(\frac{k_b}{h}\right) + \frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{RT}$$
(5)

Here  $k_b$ , h, and R are Boltzmann, Planck, and the universal gas constants, respectively. Figure 4b shows that the plots of  $ln(\frac{k}{t})$  vs.  $\frac{1}{T}$  are linear. The  $\Delta S^{\#}$  and  $\Delta H^{\#}$  values calculated, respectively from the slope and intercept of these graphs, are shown in table 4.

The thermodynamic parameters of adsorption viz.  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  were estimated using the Langmuir equilibrium constants as shown in figure 5a. In the derivation of the Langmuir model, the charge of the surface or solute species is neglected. Therefore it is important to note that the thermodynamic parameters derived are conditional to the specific solution conditions used. The K values shown in table 3 were used to calculate thermodynamic parameters from the Van'Hoff plots (figure 5a) based on

$$\ln(K) = \left(\frac{-\Delta H}{R}\right) \frac{1}{T} + \frac{\Delta S}{R}$$
(6)

The  $\Delta G^{\#}$  (or  $\Delta G$ ) values shown in the table were calculated from  $G^{\#} = H^{\#} - TS^{\#}$  at T = 300 K. Both  $\Delta H$  and  $\Delta H^{\#}$  values increased with the pH. Both the  $\Delta S$  and  $\Delta S^{\#}$  values are negative. The negative entropy is associated with a more solvated and highly ordered product (or activation complex) than the reactants. The positive  $\Delta H$  suggests the endothermic nature of sorption. Further, both values of  $T_{av} \Delta S^{\#}$  and were calculated from experimental data. In most cases,  $\Delta H^{\#} < T_{av} \Delta S^{\#}$  or  $\Delta H < T_{av} \Delta S$ . This means that the associated reac-

tions steps are largely entropy driven, although the contribution from  $\Delta H^{\#}$  is not negligible. As shown in figure 5b, the  $\Delta H^{\#}$  values vary linearly with  $T_{av.}\Delta S^{\#}$  because of the presence of entropy–enthalpy compensating effects.

#### 4. Conclusions

The thermodynamics data of adsorption and activation state of pyrite–carbofuran system are presented. Carbofuran adsorption by pyrite is best described by Langmuir and D–R isotherms. Mostly  $\Delta H^{\#} < T_{av}\Delta S^{\#}$  or  $\Delta H < T_{av}\Delta S$  conditions implied entropy driven reactions of carbofuran adsorption. When [Pyrite sites]  $\gg$  [Carbofuran], the carbofuran adsorption by pyrite is modelled by pseudo first order kinetics.

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