

# PREPARATION OF ACTIVATED CARBON FROM TIRE DERIVED PYROLYTIC CHAR FOR ADSORPTION OF TETRACYCLINE HYDROCHLORIDE

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## Graphical abstract



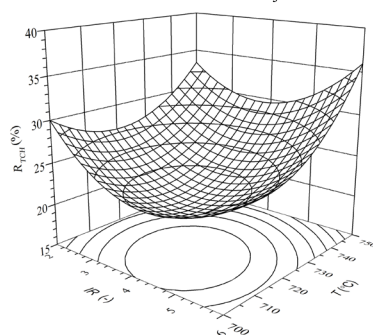
Tire Pyrolytic Char



Tetracycline removal by activated carbon

Effect of activation parameters

$$Y_k = a + \sum_{i=1}^3 b_i x_i + \sum_{ii=1}^3 c_{ii} x_{ii}^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 d_{ij} x_i x_j$$



## Abstract

Effects of activation variables on performance of the obtained activated carbon (AC) were investigated for removal of tetracycline hydrochloride (TCH). Pyrolytic char derived from waste tire was chemically activated via two-step of KOH impregnation following by thermal treatment. According to regression analysis and fitting with second-degree polynomial equation, empirical models were developed to correlate performance of AC in TCH adsorption (percentage removal and adsorption capacity at equilibrium) with three activation variables: impregnation ratio (*IR*), activation temperature (*T*) and holding time of thermal treatment (*t*). The analysis of variance indicated that only *T*, *T*<sup>2</sup> and *IR*<sup>2</sup> were significant to the prediction of both percentage removal and adsorption capacity. According to the developed models, it is suggested that the pyrolytic char should be activated at *IR* = 6, *T* = 750 °C and *t* = 2 h to obtain the highest efficiency of TCH removal in the tested range of activation condition.

**Keywords:** Activated carbon, Adsorption, Empirical model, Tetracycline, Waste tire

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## 1.0 INTRODUCTION

Tetracycline family drug (TCs) has been widely used as an effective ingredient of antibiotics for treatment of infections in humans and livestock [1, 2]. Recently, the accumulation of TCs in aquatic systems has been frequently reported. This contamination should be considered as serious environmental problem because longtime uptake of trace TCs may gradually develop antibiotic resistance [3]. As an effective method to prevent contamination of TCs in water resources, a wastewater

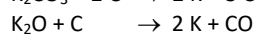
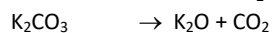
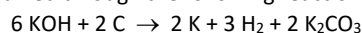
treatment unit should be installed. In the literature, several techniques, including membrane filtration, photocatalytic degradation, catalytic oxidation, biodegradation, adsorption, have been investigated to reduce TCs in wastewater [2, 4, 5, 6, 7, 8]. Among the reported techniques, adsorption is an attractive method because of its simplicity and low operation cost. It is, therefore, necessary to find cheap and highly efficient adsorbents for TCs adsorption.

Since large demand of tires has led to difficulty of dealing with end-of-life tires, several technologies have been proposed

for utilization of waste tires [9, 10, 11]. Among the proposed alternatives, pyrolysis of scrap tire has been mainly focused as a promised technology for management of such large volume of waste tires because the process can effectively break out the structure, which are difficult to degrade, of the waste tires and the obtained product containing smaller molecules could be recovered and further utilized. Liquid and gas products can be used as an energy resource of the pyrolyzer itself or additionally processed and utilized as chemical resources while the pyrolytic char can be recycled as raw material to produce valuable synthesis gas, carbon black and other functional carbonaceous materials. Activated carbons (AC) from waste tire pyrolytic char were also reported as effective adsorbent in treatment of many chemicals such as rhodamine B, methylene blue, phenol and heavy metals in wastewater [10, 11, 12, 13].

To utilize pyrolytic chars originated from agricultural wastes and end-of-life tires as effective adsorbents, it is crucial to improve porous property and to enlarge internal surface area of the chars by physical or chemical activation [10, 11, 12]. It is widely known that chemical activation consisting of mixing of an activating reagent with precursor and consecutive thermal treatment is more suitable for preparation of AC than physical activation in both aspects of properties and efficiency of the obtained AC as well as energy consumption. As reported in the aforementioned reviews, many chemicals such as KOH, NaOH, NaCl, ZnCl<sub>2</sub>, BaCl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub>, have been used in chemical activation of high carbon content materials including agricultural wastes, sludges, and tire-derived char. Among these chemicals, KOH has been mainly focused as the most effective activating reagent to prepare effective adsorbents for treatment of large organic molecules. This is because using KOH could develop both meso- and micropores while others could develop only micropores or macropores [13, 14, 15, 16, 17, 18].

Mechanism of pore formation during KOH activation can be explained through the following reactions:



where carbon is removed in the forms of CO or CO<sub>2</sub> and pore expansion occurs through intercalation of potassium in carbon lattice [11, 12, 19]. Mixing of KOH with AC precursor before activation at high temperature is important and can be performed in aqueous phase (wet method) or solid phase (dry method). The wet method is generally considered as the more effective method to have uniform distribution of penetrated activating reagent in the particles of precursors. Furthermore, porous structure, porosity and surface area of the prepared AC strongly depend on concentration of KOH, distribution of KOH in precursors, activation temperature and activation time, as well as the type of carbon precursor.

To prepare highly efficient AC from pyrolytic char of waste tire, effect of activation variables and interactions of these variables on adsorption performance of the obtained AC must be investigated and the optimized activation condition must be identified. Applying regression analysis and analysis of variance (ANOVA) is a simple statistical approach that could provide empirical model that can be used to describe this important information with less effort on experimental works.

In this study, the waste tire derived pyrolytic char was chemically activated using KOH as activating reagent and adsorption performance of AC was measured using model solution of tetracycline hydrochloride (TCH). Since relative amount of KOH and char (impregnation ratio, *IR*), activation temperature (*T*), and holding time in thermal treatment step (*t*) are important variables in the chemical activation, influence of these variables on performance of the obtained ACs was experimentally investigated. Based on regression analysis, an empirical model was then developed to relate the adsorption efficiency, evaluated as percentage removal of TCH (*R*<sub>TCH</sub>) and adsorption capacity at equilibrium (*q*<sub>e</sub>), with the activation variables. In addition, the optimized activation condition was also predicted based on the obtained regression model.

## 2.0 METHODOLOGY

### Materials and Chemicals

Pyrolytic char derived from waste tire supplied from Bangkok Tire Refinery (Chonburi, Thailand) was sieved to size of 300 to 430 mesh and used as precursor of activated carbon.

Potassium hydroxide (KOH, AR grade, 85%, Univar) was used as activating reagent.

Tetracycline hydrochloride (TCH, AR grade, 99%, Vesco Pharmaceutical Co., Ltd.) was used to prepare a model solution of wastewater containing low concentration TCs.

Deionized water was used in preparation of all aqueous solutions.

### Activated Carbon Preparation

Activation of pyrolytic char consisted of impregnation in KOH and thermal treatment in nitrogen stream.

In the first step, the sieved char was mixed with KOH aqueous solution (11.3 M) in a closed glass vessel (120 ml) at specific impregnation ratio (*IR*: ratio of KOH weight to char weight, g-g). The mixture was shaken at 140 rpm and 60 °C for 2 h in an orbital shaker (4000ic, IKA) and then dried in an oven 110 °C for 1 h.

In the second step, the dried impregnated char was thermally treated under nitrogen atmosphere in a vertical stainless-steel reactor (diameter of 0.5 in, 30 cm in length). Flow rate of N<sub>2</sub> was constant at 100 ml/min. The sample was heated from room temperature to 600 °C with heating rate of 20 °C/min, then to activation temperature (*T*, °C) with heating rate of 5 °C/min and maintained constant at *T* for the required holding time (*t*, h).

After the activation was completed, the sample was naturally cooled under nitrogen atmosphere and washed several times by the deionized water until pH of the washed water was neutral. After washing, the obtained activated carbon was dried in the oven at 110 °C for 6 h and kept dried in a desiccator before being used in adsorption experiment.

To investigate effects of activation variables (*IR*, *T*, and *t*) on efficiency of the obtained activated carbon, three levels of the variables were selected: *IR* = 2, 4, and 6; *T* = 700, 725, and 750 °C; *t* = 0.5, 1, and 2 h. As listed in Table 1, the three levels of these variables were combined for 13 activation conditions and only the condition at 4, 725 °C, and 1 h had triplicate experimental runs to show the experimental error and the reproducibility of the data. It should be noted that the

sequence of run was randomized in order to avoid effects of uncontrolled factors in doing experiments.

### Adsorption Experiment

To compare performance of ACs prepared from various activated conditions (13 conditions), batch adsorption experiment was isothermally performed at the same adsorption condition.

The activated carbon (0.03 g) was mixed with TCH solution (50 mg/l, 40 ml) in a closed glass vessel (120 ml) at the required  $IR$  and then shaken in the orbital shaker at room temperature (around 26 °C), 190 rpm for 6 h. It should be noted that preliminary experiments, separately done, showed that the time required to reach adsorption equilibrium was shorter than 6 h. Liquid samples (1 ml) were taken before and after the adsorption treatment for quantification of TCH using a UV-visible spectrophotometer (Evolution 210, Thermo Fischer Scientific). A syringe filter, 0.45  $\mu$ m in pore diameter, was used to remove the contaminated ACs powder from the samples before TCH quantification. Absorbance of the sample was measured at wavelength of 355 nm. Calibration curve was constructed in range of 1–30 mg/l with  $R^2$  of 0.999.

Efficiency of adsorbent in TCH removal was evaluated according to percentage removal,  $R_{TCH}$  (%), and adsorption capacity at equilibrium,  $q_e$  (mg/g), using Eqs. (1) and (2), respectively.

$$R_{TCH} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)$$

$$q_e = \left( \frac{V(C_0 - C_e)}{m_c} \right) \quad (2)$$

$C_0$  and  $C_e$  are concentrations of TCH at initial time and at equilibrium (mg/l), respectively,  $V$  is volume of TCH solution (l) and  $m_c$  is mass of activated carbon (g).

### Empirical Model Development

To develop empirical models, which can be used to describe effects of three activation variables ( $IR$ ,  $T$ , and  $t$ ) and their interactions ( $IR$ - $T$ ,  $IR$ - $t$  and  $T$ - $t$ ) on  $R_{TCH}$  and  $q_e$ , a second-degree polynomial equation, as written in Eq. (3), was considered.

$$Y_k = a + \sum_{i=1}^3 b_i x_i + \sum_{ii=1}^3 c_{ii} x_{ii}^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 d_{ij} x_i x_j \quad (3)$$

$Y_k$  is response of the model ( $R_{TCH}$  and  $q_e$ );  $a$ ,  $b_i$ ,  $c_{ii}$ , and  $d_{ij}$  are constant, coefficients of linear terms, coefficients of quadratic terms, and coefficients of interaction terms, respectively;  $x_1$ ,  $x_2$  and  $x_3$  are  $IR$ ,  $T$ , and  $t$ , respectively.

Experimental data were analyzed by using regression tool in the Analysis ToolPak add-in program of Excel for estimation of the coefficients in the model and also for evaluation of the statistical significance of the obtained model. The analysis was done at confident level of 95%.

## 3.0 RESULTS AND DISCUSSION

### Regression Model

Table 1 summarizes the experimental values of  $R_{TCH}$  and  $q_e$  together with their corresponding preparation conditions. In the tested range of activation variables ( $IR = 2 - 6$ ,  $T = 700 - 750$  °C, and  $t = 0.5 - 2$  h),  $R_{TCH}$  and  $q_e$  were in ranges from 21.20 to 35.29% and from 13.83 to 22.95 mg/g, respectively. It should be reasonably noted that in this adsorption experiment, there was no limitation in TCH adsorption resulted from both inadequacy of adsorbent dosage and saturation of adsorbent capacity.

According to the regression analysis, Eqs. (4) and (5) were obtained for  $R_{TCH}$  and  $q_e$ , respectively.

$$R_{TCH} = 3828.369 - 35.018 IR - 10.480 T + 25.837 t + 1.273 IR^2 + 0.007 T^2 - 2.462 t^2 + 0.032 IR \cdot T + 1.116 IR \cdot t - 0.029 T \cdot t \quad (R^2 = 0.9298) \quad (4)$$

$$q_e = 2505.017 - 22.939 IR - 6.856 T + 16.661 t + 0.832 IR^2 + 0.005 T^2 - 1.584 t^2 + 0.021 IR \cdot T + 0.715 IR \cdot t - 0.019 T \cdot t \quad (R^2 = 0.9343) \quad (5)$$

The results indicated that the variables studied in this work account for 92.98 and 93.43% of the total variations in  $R_{TCH}$  and  $q_e$ , respectively. According to the high  $R^2$  values, these models seem to give well prediction of both  $R_{TCH}$  and  $q_e$ . Furthermore,  $p$ -values of the overall models for  $R_{TCH}$  and  $q_e$  were 0.0204 and 0.0174, respectively, indicating that the overall regression models predict significant amounts of variances in  $R_{TCH}$  and  $q_e$ .

**Table 1** Activation conditions and corresponding experimental results

Run	Activation Condition			Adsorption Performance	
	$IR$ (-)	$T$ (°C)	$t$ (h)	$R_{TCH}$ (%)	$q_e$ (mg/g)
1	2	700	1	30.90	20.16
2	2	750	1	35.29	22.95
3	6	700	1	24.15	15.81
4	6	750	1	35.05	22.87
5	2	725	0.5	22.85	14.96
6	2	725	2	26.51	17.36
7	6	725	0.5	23.84	15.50
8	6	725	2	32.28	20.99
9	4	700	0.5	21.20	13.83
10	4	700	2	25.28	16.49
11	4	750	0.5	27.07	17.66
12	4	750	2	29.69	19.37
13	4	725	1	21.97	14.34
14	4	725	1	21.79	14.17
15	4	725	1	21.41	13.97

Significance of each term in the model was evaluated through analysis of variance (ANOVA). For the model to predict  $R_{TCH}$ , as listed in Table 2,  $p$ -values of only three terms ( $T$ ,  $IR^2$  and  $T^2$ ) were less than 0.05, implying that  $T$ ,  $IR^2$  and  $T^2$  were significant whereas  $IR$ ,  $t$ ,  $t^2$  and all interactions were insignificant to the prediction of  $R_{TCH}$ . Parabolic responses of  $R_{TCH}$  on  $IR$  and  $T$  should be, therefore, expected from the regression model. Moreover, based on the relative  $p$ -values of  $T$ ,  $IR^2$  and  $T^2$ , it was found that influences of the terms on the predicted  $R_{TCH}$  were in the order of  $T > T^2 > IR^2$ .

Result from ANOVA for  $q_e$  model, as summarized in Table 3, implied that significance of the terms in  $q_e$  model was similar to  $R_{TCH}$  model: only  $T$ ,  $IR^2$  and  $T^2$  were significant whereas  $IR$ ,  $t$ ,  $t^2$  and all interactions were insignificant to the prediction of  $q_e$ . Therefore, parabolic responses of  $q_e$  on  $IR$  and  $T$  should be expected from the regression model, as well. Furthermore, influences of the terms on the predicted  $q_e$  were also in the same order with the order in  $R_{TCH}$  model ( $T > T^2 > IR^2$ ).

Similar results have been reported in the recent review [11], the activation temperature and impregnation ratio are the important factors affecting specific surface area which directly corresponds to performance of AC prepared from tire pyrolysis char using KOH as an activating reagent.

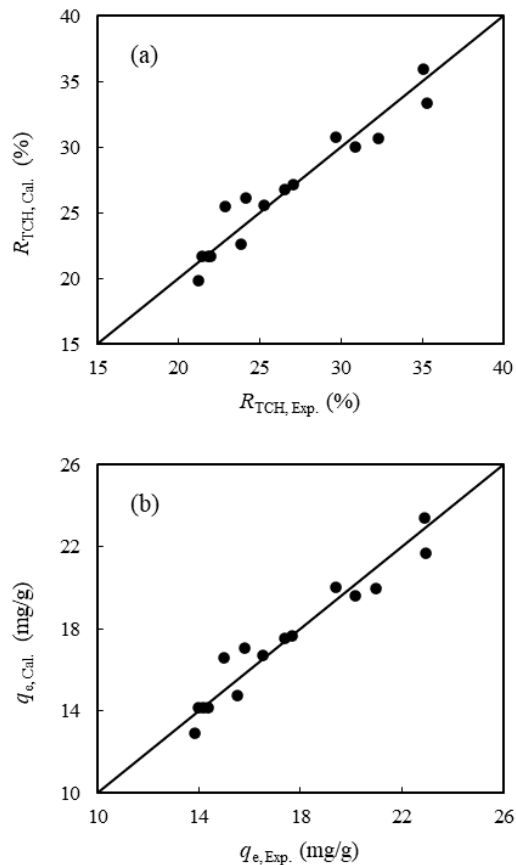
**Table 2** Estimated coefficient of each factor and statistic results for percentage removal of TCH

	Coefficient	Standard Error	P-Value
Intercept	3828.3694	956.3533	0.0103
$IR$	-35.0178	15.9720	0.0798
$T$	-10.4802	2.6312	0.0105
$t$	25.8368	41.5230	0.5611
$IR^2$	1.2732	0.2833	0.0064
$T^2$	0.0072	0.0018	0.0103
$t^2$	-2.4622	2.3236	0.3378
$IR \cdot T$	0.0325	0.0218	0.1958
$IR \cdot t$	1.1162	0.7064	0.1749
$T \cdot t$	-0.0290	0.0565	0.6299

**Table 3** Estimated coefficient of each factor and statistic results for adsorption capacity at equilibrium

	Coefficient	Standard Error	P-Value
Intercept	2505.0174	600.7566	0.0087
$IR$	-22.9394	10.0332	0.0710
$T$	-6.8562	1.6529	0.0089
$t$	16.6614	26.0837	0.5511
$IR^2$	0.8318	0.1779	0.0055
$T^2$	0.0047	0.0011	0.0088
$t^2$	-1.5844	1.4596	0.3272
$IR \cdot T$	0.0213	0.0137	0.1796
$IR \cdot t$	0.7149	0.4438	0.1681
$T \cdot t$	-0.0186	0.0355	0.6219

Parity plots, as shown in Figure 1, reveal that both  $R_{TCH}$  and  $q_e$  calculated using the regression models were reasonably closed to the experimental values. In other words, the developed regression models gave good correlation between the performance of the prepared activated carbons ( $R_{TCH}$  and  $q_e$ ) and the studied activation variables ( $IR$ ,  $T$ , and  $t$ ).



**Figure 1** Parity plot of regression models: (a) percentage of TCH removal ( $R_{TCH}$ ), (b) adsorption capacity at equilibrium ( $q_e$ )

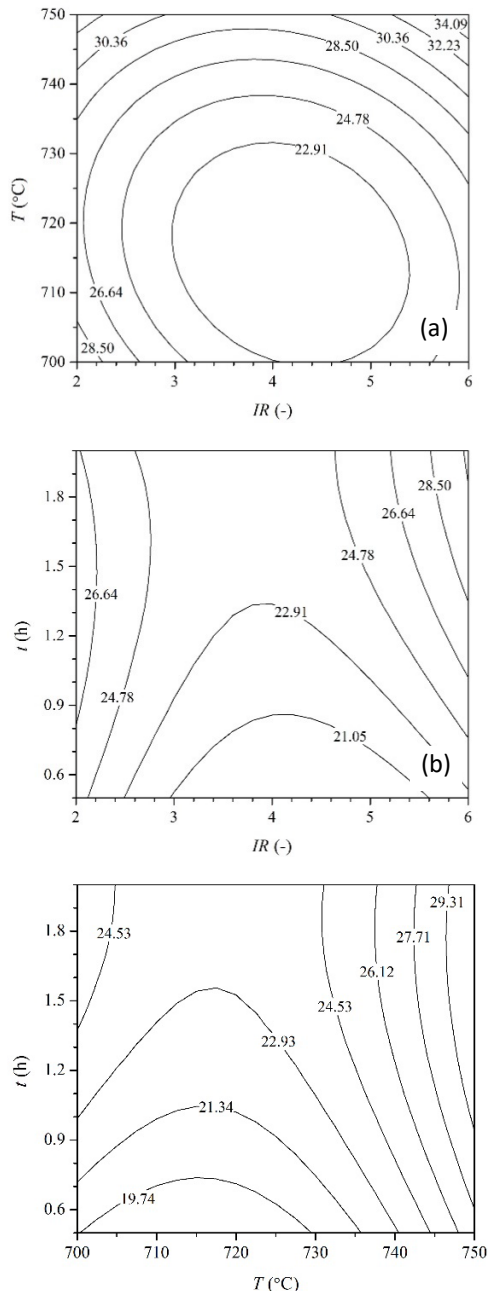
### Influence of Activation Variables on TCH Adsorption

Contour plots of the predicted response calculated using the developed regression model for  $R_{TCH}$ , in Figure 2, show effects of activation variables on  $R_{TCH}$  in range of  $IR = 2 - 6$ ,  $T = 700 - 750$  °C and  $t = 0.5 - 2$  h.

Figure 2(a) shows that the  $R_{TCH}$  model gave an oval shaped contour, which is reasonably expected because of the parabolic responses on  $IR$  and  $T$  as reported in Regression Model section, with the minimal value of 21.09 % around  $T = 716$  °C and  $IR = 4.2$ . As seen from the plot, the radius of curvature for the change of  $T$  was shorter than that for the change of  $IR$ , meaning that  $R_{TCH}$  is more sensitively changed with  $T$  than  $IR$ . Figures 2(b) and 2(c) confirm the weak influence of  $t$  on  $R_{TCH}$ , as found in Regression Model section.

Similar contours between the predicted  $q_e$  and activation variables were also plotted, but not shown here because the response of  $q_e$  was analogous to that of  $R_{TCH}$ . From the contour plots of  $R_{TCH}$ ,  $q_e$  can be approximated by division the value of  $R_{TCH}$  by 1.5. Additionally, the highest predicted value of  $q_e$  in

this activation range was 23.43 mg/g and found at  $IR = 6$ ,  $T = 750$  °C and  $t = 1$  h.



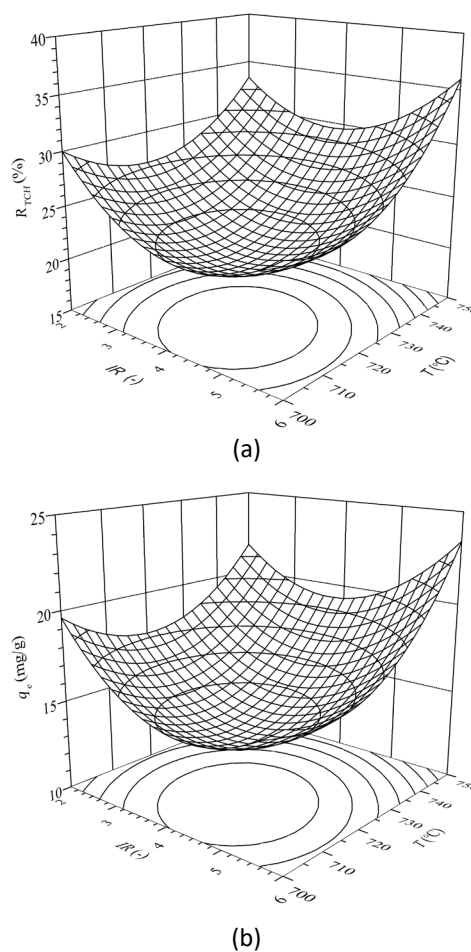
**Figure 2** Contour plots of  $R_{TCH}$  of activated carbons prepared various activation conditions: effects of (a)  $IR$  and  $T$  at  $t = 1$  h, (b)  $IR$  and  $t$  at  $T = 725$  °C, (c)  $T$  and  $t$  at  $IR = 4$

Figure 3 shows the response surface for  $R_{TCH}$  and  $q_e$  at  $t = 1$  h. The responses at other levels of  $t$  (0.5 and 2 h) were also plotted, but not shown here. It was found that all the responses had the same shape as the responses shown in Figure 3 and the longer  $t$  resulted in slightly higher  $R_{TCH}$  and  $q_e$ .

Based on the models, in the range investigated, the optimized activation condition for preparation of AC from pyrolytic char was found at  $IR = 6$ ,  $T = 750$  °C and  $t = 2$  h and using this AC should remove 39.36% of TCH with  $q_e$  of 25.64

mg/g. Additionally, it was experimentally found that this nonactivated pyrolytic char had extremely low efficiency in TCH adsorption, undetectable difference of  $C_0$  and  $C_e$ .

The large enhancement of tetracycline removal efficiency of tire pyrolytic char by chemical activation using KOH was also reported in literature [20]. Although the precursor and KOH mixing method were different from this present work, AC with the highest total surface area was obtained at the same temperature and impregnation ratio (750 °C and 6).



**Figure 3** Response surface of the predicted (a)  $R_{TCH}$  and (b)  $q_e$  on significant activation variables ( $T$  and  $IR$ ) at  $t = 1$  h

#### 4.0 CONCLUSION

Empirical models to predict percentage removal of tetracycline hydrochloride ( $R_{TCH}$ ) and adsorption capacity at equilibrium ( $q_e$ ) of activated carbon prepared from tire derived char were successfully developed through regression analysis. Analysis of variance for  $R_{TCH}$  and  $q_e$  models revealed that activation temperature and quadratic terms of impregnation ratio and activation temperature were significant to the prediction of both  $R_{TCH}$  and  $q_e$ . In ranges of impregnation ratio from 2 to 6, activation temperature from 700 to 750 °C and thermal treatment holding time from 0.5 to 2 h, it was found that the

optimized condition for preparation of activated carbon was at 6, 750 °C and 2 h.

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