

CHAPTER 4

RESULTS AND DISCUSSION



4.1 Adsorption and desorption of 4-nitrophenol by GAC

4.1.1 Adsorption Isotherm

The equilibrium time for the adsorption of 4-NP was examined in the beginning. The study was performed by shaking 150 ml 4-NP solution of 1 mM with 0.01 g, 0.1 g and 0.4 g of activated carbons and sample was collected at each the interval of time within 72 hours. It was observed that the adsorption process reached equilibrium within 48 hours for the 3 types of activated carbon. Among various amounts of GAC mass, the dosage of 0.4 g result in the slowest adsorption equilibrium. Therefore, the experiment time of 48 hours was applied for all subsequent experiments. Figure 4.1 shows the equilibrium time profiles for 4-NP adsorbed onto 3 types of GAC.

The equilibrium data were interpreted by adsorption isotherm model and both Freundlich and Langmuir were applied. The equation parameters of both models are presented in Table 4.1. A linear regression analysis on the Freundlich and Langmuir parameters resulted in the correlation coefficients of 0.99 and 0.94 for bituminous coal, 0.99 and 0.96 in palm shell ,and 0.99 and 0.96 in coconut shell, respectively. The linearized form of the Freundlich's equation: $\log X/M = \log K + 1/n \log C_e$ was applied to the data of figure A-1 (see Appendix A). And, the Langmuir equation was applied to the data of figure A-2 (see Appendix A) with the linear form: $1/(X/M) = 1/a + 1/[(ab)xC_e]$.

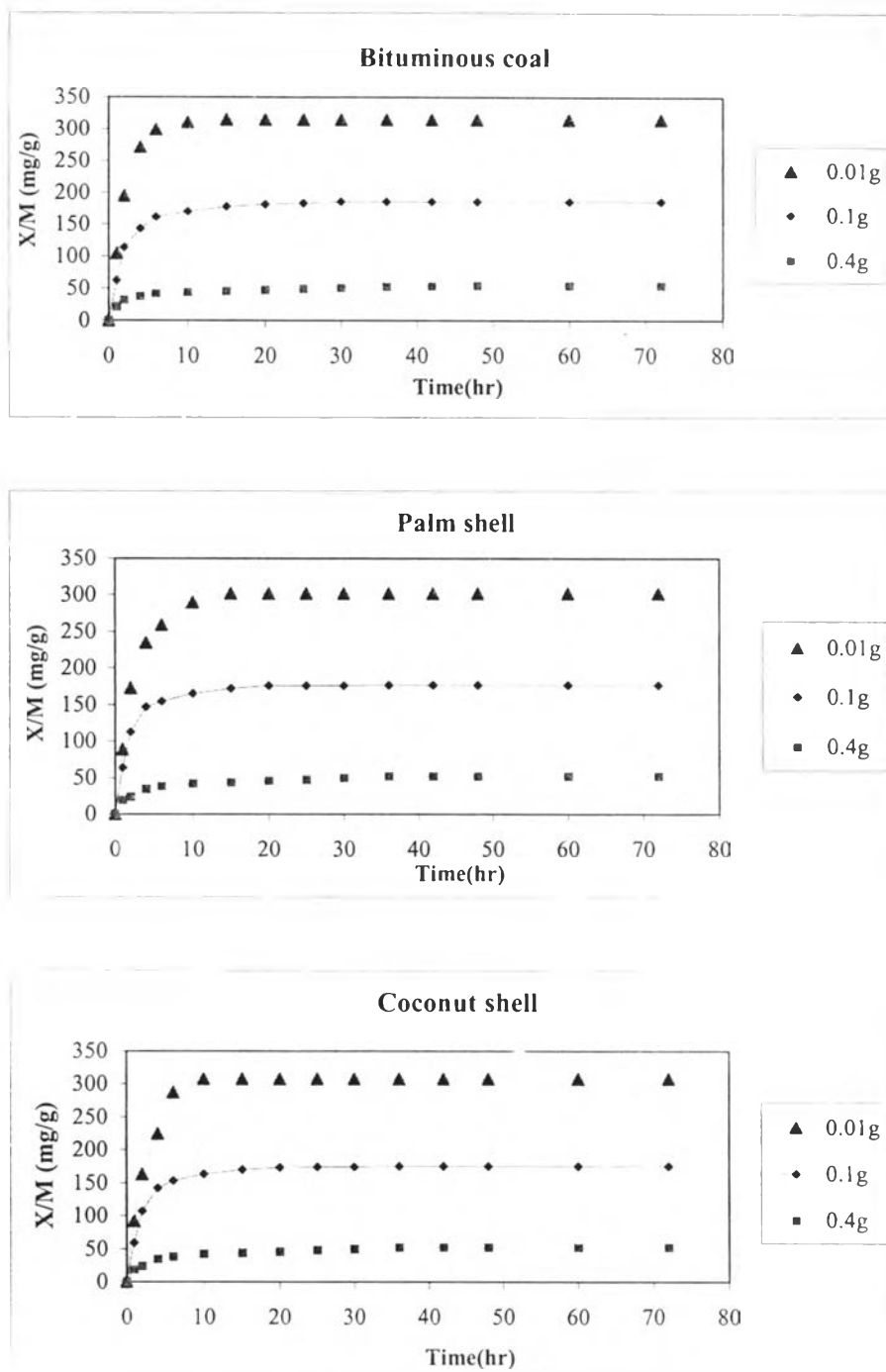


Figure 4.1 Equilibrium time profiles for the adsorption of 4-nitrophenol by bituminous coal, palm shell and coconut shell at room temperature.

Table 4.1 Adsorption model parameters for 4-nitrophenol on bituminous coal, palm shell and coconut shell .

Model	equation	parameter	Bituminous coal	Coconut shell	Palm shell
Langmuir	$X/M = abC_e/(1+bC_e)$	a	256.41	263.16	250.00
		b	0.17	0.10	0.11
		ab	42.74	26.25	26.59
Freundlich	$X/M = KC_e^{1/n}$	K	45.69	36.05	35.42
		1/n	0.42	0.46	0.46

Comparing these two adsorption isotherm models, Freundlich model gives more satisfactory fit to the 3 types of GAC. Langmuir model cannot fit the data well, especially for the higher concentration because the adsorption sites of the GAC are not uniform and multiple-layer adsorption may occur [11]. The Freundlich constants (K and 1/n) of selected adsorbents are related to adsorption capacity and adsorption intensity, respectively, of adsorbent [49].

The Freundlich K value of 45.69 obtained from bituminous coal experiment is the highest, followed by the coconut shell and palm shell, which have K values of 36.05 and 35.42, respectively. There is no significant difference in Freundlich 1/n values among the 3 types of activated carbon as shown in Table 4.1. The results implied that bituminous coal based activated carbon is the best adsorbent for 4-NP adsorption in this study.

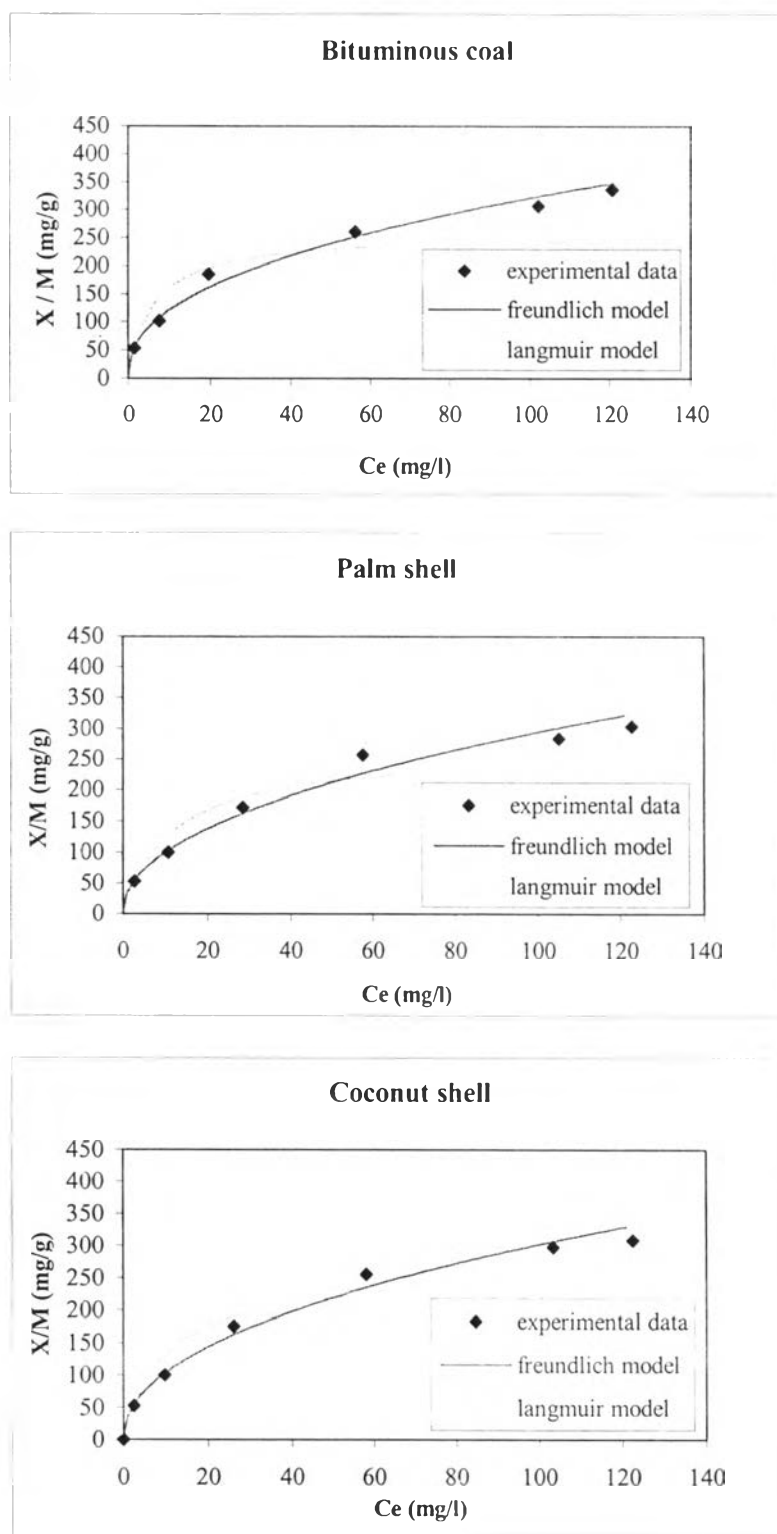


Figure 4.2 Adsorption isotherms of 4-nitrophenol for the 3 types of GAC.

4.1.2 Desorption

The results of the desorption of 4-nitrophenol from the 3 types of GAC at 45°C and pH 7 were shown in Figure 4.3. The 4-nitrophenol was desorbed from bituminous coal, palm shell and coconut shell at 2 hr as with the three values of 10.02 mg/g, 6.82 mg/g and 4.21 mg/g respectively. Considering the desorption rate of these 3 types of GAC, bituminous coal showed the highest desorption rate. Therefore, Bituminous coal was selected as the adsorbent subsequent experiments.

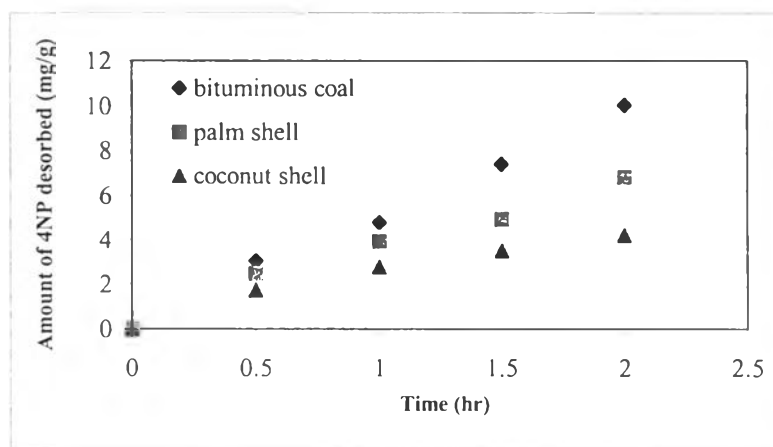


Figure 4.3 Desorption of 4-nitrophenol from the 3 types of GAC at 45°C and pH 7

The desorption tests with different pH were shown in Figures 4.4 and 4.5 at temperature 30°C and 45°C respectively. The desorption rate at every pH was increased with the increase of temperature. These results were good agreement with Salvador et al. [50], who studied the regenerating activated carbon by thermal desorption with liquid water under subcritical condition. Moreover, at the same temperature, the desorption rate increased with increasing pH as well.

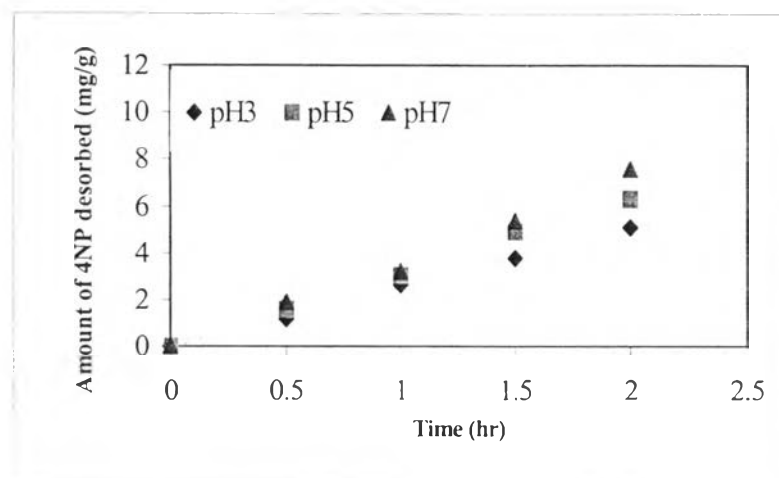


Figure 4.4 Desorption of 4-nitrophenol from bituminous coal at pH 3, 5, 7 and 30°C

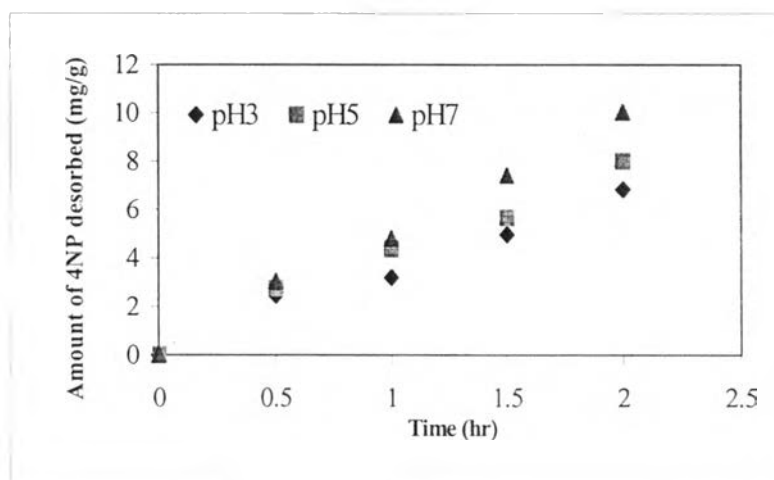


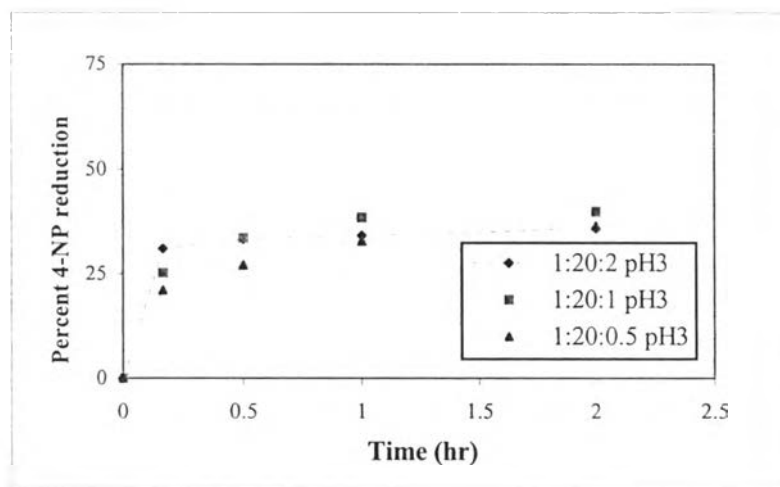
Figure 4.5 Desorption of 4-nitrophenol from bituminous coal at pH 3, 5, 7 and 45°C

4.2 The application of Fenton's reagent to oxidize 4-NP-adsorbed GAC

Bituminous coal based activated carbon was selected as the adsorbent for the study on the regeneration by Fenton's reagent. In this work, the application of Fenton's reagent to oxidize 4-NP adsorbed onto GAC was done under adiabatic condition. Experimental investigation was carried out to prove the Fenton's oxidation of 4-NP- adsorbed GAC which might be affected by pH, Fe^{2+} and H_2O_2 level. Figure 4.6 shows the reduction of 4-NP adsorbed onto GAC by Fenton's oxidation under different molar ratios of 4-NP: H_2O_2 : Fe^{2+} such as 1:20:0.5, 1:20:1 and 1:20:2. Even

different Fe^{2+} concentration, the degree of degradation of 4-NP adsorbed onto GAC by Fenton's oxidation is quite the same, which were around 35-39 % time of 2 hr. Normally, with higher catalyst concentration, higher rate of OH^\bullet radical production and more degradation of organic substances should be obtained. However, from the results, it implied that catalyst concentration at ratio 1:20:0.5 was excessive for degradation of 4-NP because it could react with entire amount of H_2O_2 within 2 hr.

(a)



(b)

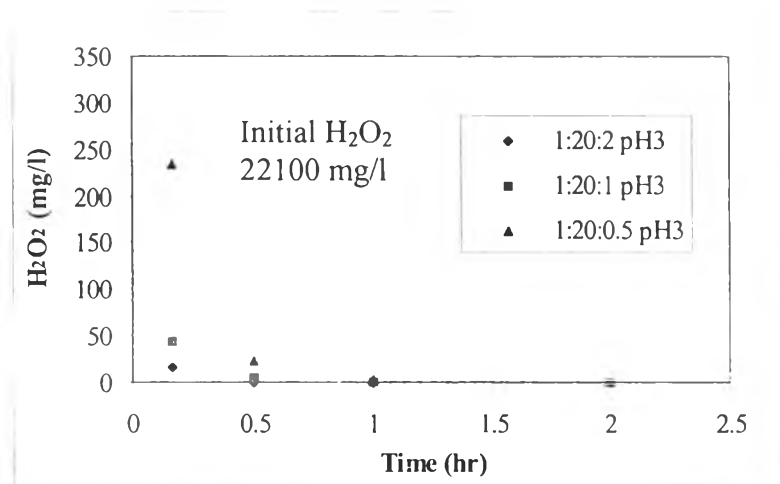
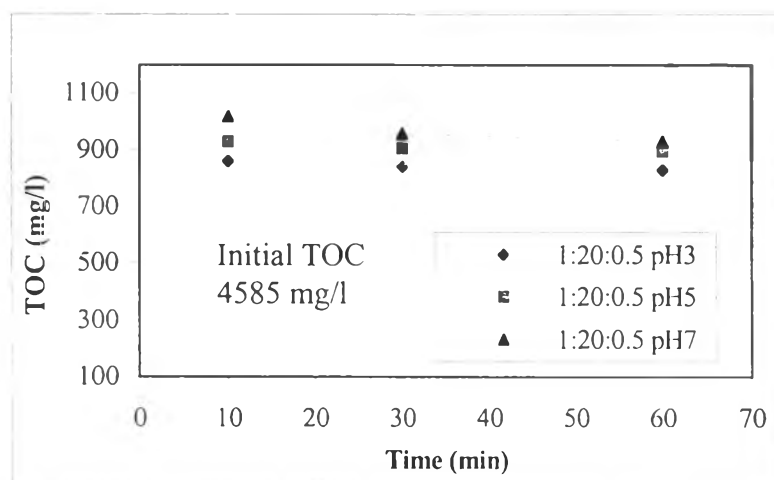


Figure 4.6 The Fenton's oxidation of 4-NP adsorbed GAC with various molar ratios of 4-NP: H_2O_2 : Fe^{2+} at initial pH 3. (a) Percent 4-NP reduction (b) the remaining of H_2O_2

With molar ratio ($\text{H}_2\text{O}_2 : \text{Fe}^{2+}$) of 20:0.5 and initial pH 3, degradation of 4-NP in solution by Fenton's reaction was greater than that adsorbed in GAC, as shown in Figure 4.7. The reduction of 4-NP in solution was 99% by Fenton's reagent within 10 minutes. However TOC concentration was still remained as much as 825.5 mg/l even the reaction time was prolonged to two hours. The undegraded organic substances may be intermediate compound such as hydroquinone, benzoquinone, 4-nitrocatechol, 1,2,4-trihydrobenzene and 3,4,5-trihydroxy nitrobenzene [51].

(a)



(b)

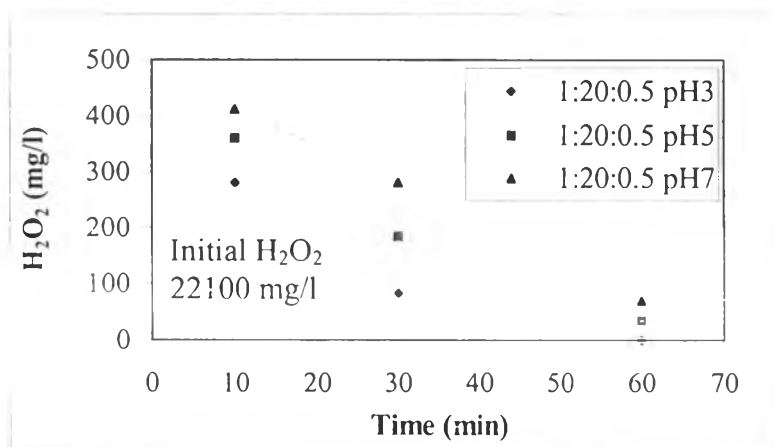
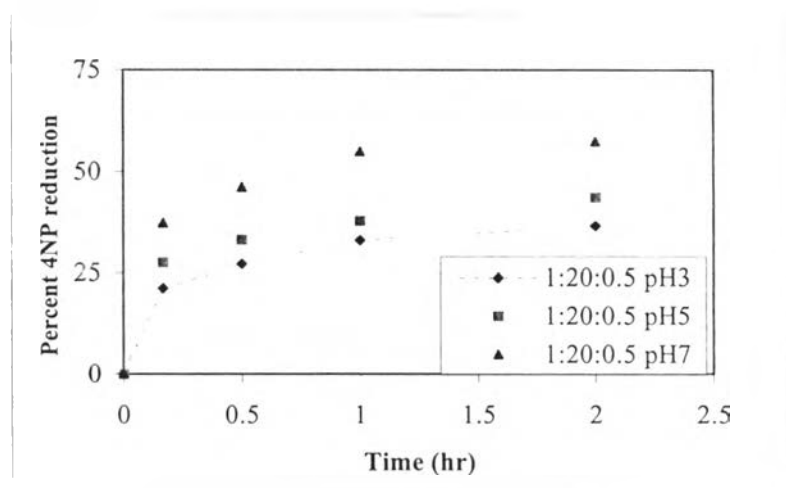


Figure 4.7 The Fenton's oxidation of 4-NP in solution with molar ratio of 4-NP: H_2O_2 : Fe^{2+} 1:20:0.5 at varying initial pH 3, 5 and 7. (a) the remaining of TOC reduction (b) the remaining of H_2O_2

The degradation of 4-NP in GAC by Fenton's reagent was less than that in solution because of the limitation of OH^\bullet radical through diffusion into surface of GAC. The generated OH^\bullet radical in solution can be exhausted by reacting with the original reactants; Fe^{2+} and H_2O_2 as shown in equation (4.3) and (4.4) with the reaction rate faster than diffusion rate. The experiments were conducted further in order to investigate pH condition for increasing the degradation of 4-NP adsorbed into GAC.

(a)



(b)

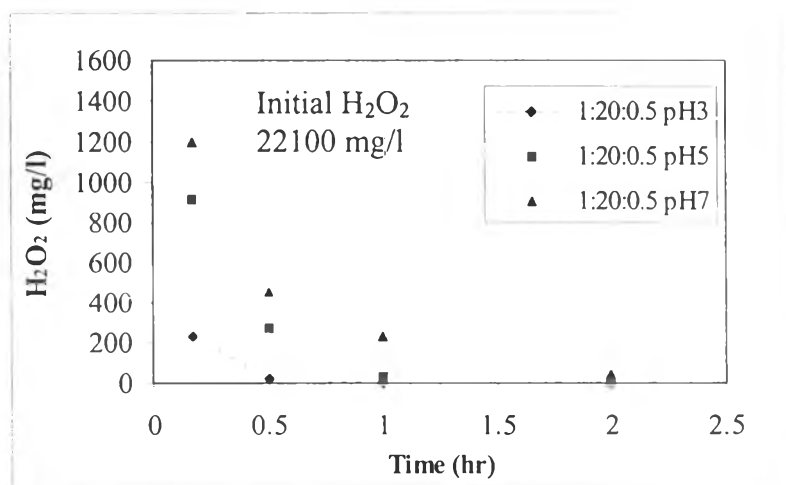


Figure 4.8 The Fenton's oxidation of 4-NP adsorbed GAC by under reaction condition 4-NP: H_2O_2 : Fe^{2+} molar ratio of 1:20:0.5 at varying initial pH 3, 5 and 7. (a) Percent 4-NP reduction (b) the remaining of H_2O_2

The results of the reaction with the same molar ratio of Fenton's reagent but varying initial pH 3, 5 and 7 are shown in Figure 4.8. Fenton's reagent can react with 4-NP in GAC at pH 7 better than at pH 3, the degradation efficiencies of which 59% and 39%, respectively. Generally, Fenton's reagent can occur in solution very well at pH around 3 [42]. According to the experiment of Fenton's reaction in solution, the remaining of TOC in solution at pH 3 and 2 hr was less than those at pH 5 and 7, which are 825.5, 892.5 and 927.9 mg/l respectively. When Fenton's reagent in GAC was studied, the result was opposite. This can be explained by that OH^\bullet radical at pH 3 was generated rapidly from equation (4.1) and spent in solution as equation (4.3) and (4.4) better than diffuse through the GAC. The reduction of OH^\bullet radical resulted in decreasing of H_2O_2 , even it can be changed to H_2O_2 as in equation (4.5).

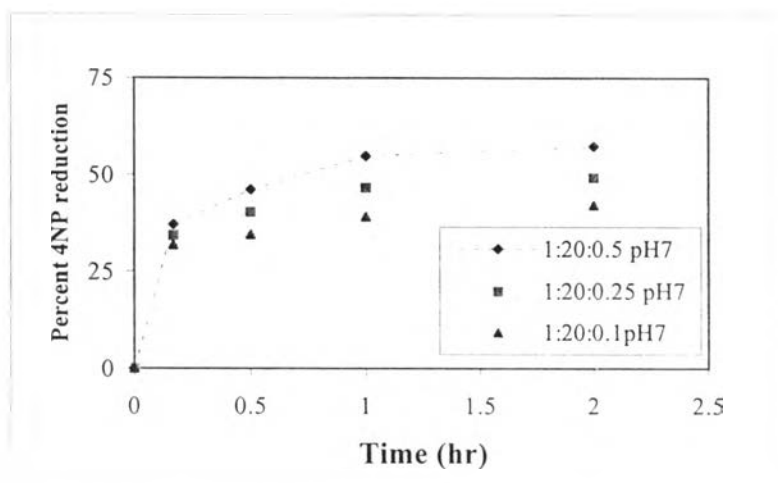
The increasing of pH in Fenton's reaction may be the reason of OH^\bullet consuming in solution slowly. Under the more neutral pH conditions, ferric ions exist mostly as hydroxy complexes (e.g. FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_2^-$, etc.) and more importantly, insoluble oxide phases ($\text{FeOOH}_{(s)}$, $\text{Fe}_2\text{O}_{3(s)}$, $\text{Fe}(\text{OH})_{3(s)}$, etc.) [37]. When Ferrous ion was oxidized into Ferric ion, Fenton-like (Fe^{3+} and H_2O_2 in equation 4.2) will occur at the same time. So reaction rate of equation (4.1) was slow down. OH^\bullet radical was likely to be generated slowly, so OH^\bullet radical was used for equation (4.3) and (4.4) with the less rate as well. Therefore, OH^\bullet radical can diffuse and react with 4-NP in GAC more. Moreover, the catalyst in the form of ferric precipitated on GAC surface can increase the opportunity of OH^\bullet radical generated closer and react with 4-NP in GAC. Therefore, the investigation of GAC regeneration would be done at initial pH 7. The selection of ratio for GAC regeneration would be the next experiment.



4.3 Regeneration of GAC by Fenton's reagent at pH 7

The degradation of 4-NP in GAC at initial pH 7 was chosen to apply for GAC in-situ regeneration. This investigation is determining optimal ratio of H_2O_2 to Fe^{2+} for regenerating 4-NP in GAC by Fenton's reagent.

(a)



(b)

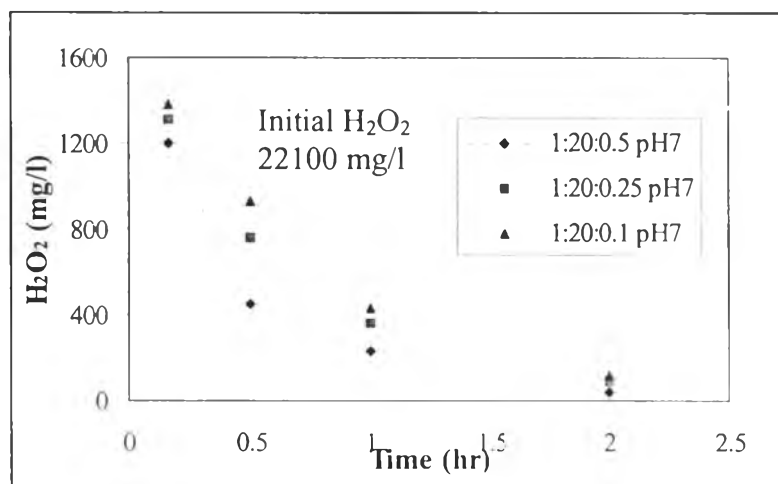
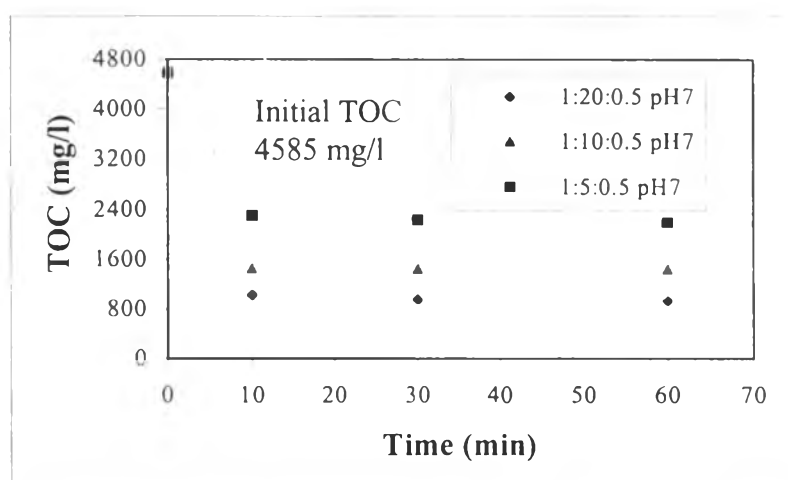


Figure 4.9 The Fenton's oxidation of 4-NP adsorbed GAC with varying molar ratio 4-NP: H_2O_2 : Fe^{2+} from 1:20:0.1 to 1:20:0.5 at initial pH7. (a) Percent 4-NP reduction (b) the remaining of H_2O_2

Under pH 7, the degradation of 4-NP adsorbed onto GAC decreased when the amount of catalyst (ferrous) decreased as shown in Figure 4.9. Within reaction time of 2 hours, H_2O_2 still remained in the solution and was the least when the molar ratio of reagent is 1:20:0.5. Therefore, the ferrous molar of 0.5 for one molar of 4-NP at pH 7 would be the condition for further studies on the effect of initial concentration of H_2O_2 because of providing the highest degradation and least H_2O_2 remaining at 2 hr.

(a)



(b)

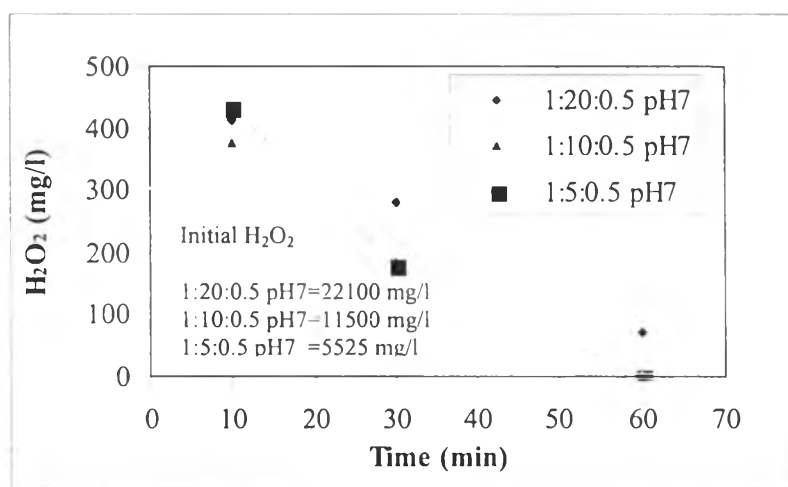
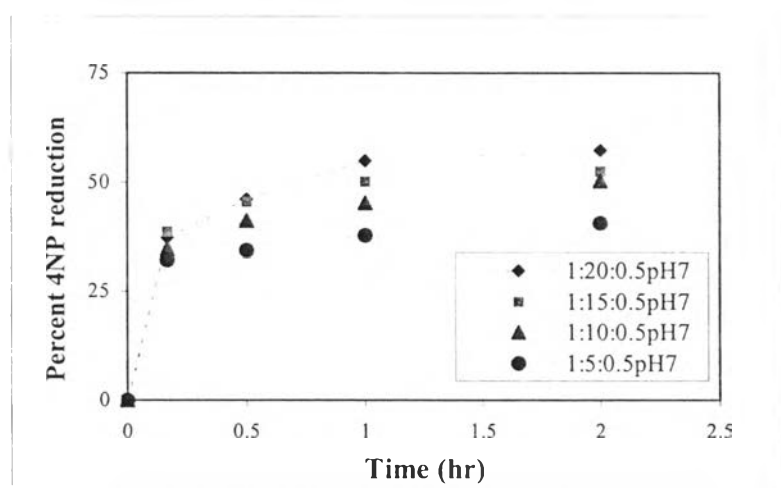


Figure 4.10 The Fenton's oxidation of 4-NP in solution by varying molar ratio of 4-NP: H_2O_2 : Fe^{2+} from 1:5:0.5 to 1:20:0.5 at initial pH 7 (a) the remaining of TOC (b) the remaining of H_2O_2

The various moles of H_2O_2 (5, 10, 15, 20) versus one mole of Fe^{2+} were applied and the highest degradation was obtained at a ratio of 1:20:0.5, as shown in Figure 4.11. As a result of Fenton's oxidation in 4-NP solution by various H_2O_2 concentrations (Figure 4.10), the degradation showed in the same manner. Even though, percent degradation at ratio of 1:5:0.5 was the lowest, but it provided 40% regeneration at 2 hr. In addition, with this ratio, percent degradation at 1 hr was 37%, which is not significantly different from that obtained at 2 hours. The increment of percent degradation does not proportional to the H_2O_2 added due to the faster loss of H_2O_2 by other reactions.

(a)



(b)

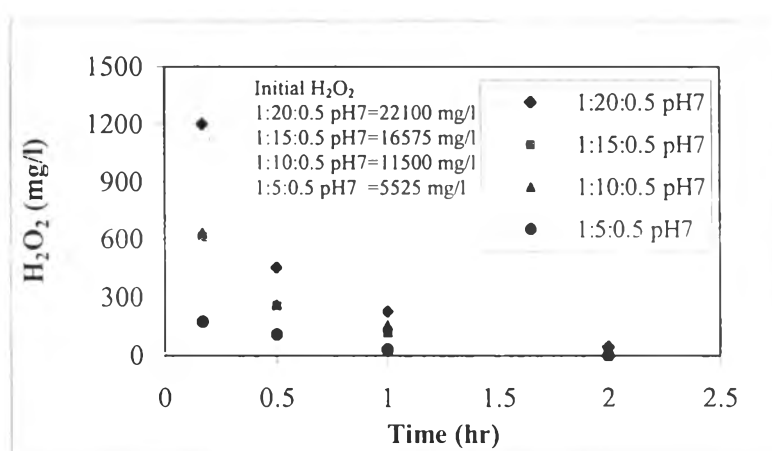


Figure 4.11 The Fenton's oxidation of 4-NP adsorbed GAC by varying molar ratio of 4-NP: H_2O_2 : Fe^{2+} from 1:5:0.5 to 1:20:0.5 at initial pH 7. (a) Percent 4-NP reduction (b) the remaining of H_2O_2

Therefore, three batches of 4-NP regeneration in GAC would be studied by adding 5 moles H_2O_2 and 0.5 moles Fe^{2+} for one mole of 4-NP at each batch. Figure 4.14 shows that 4-NP in GAC was reduced up to 75% for the third batch and the reduction of H_2O_2 during the experiment in each time was nearly used up.

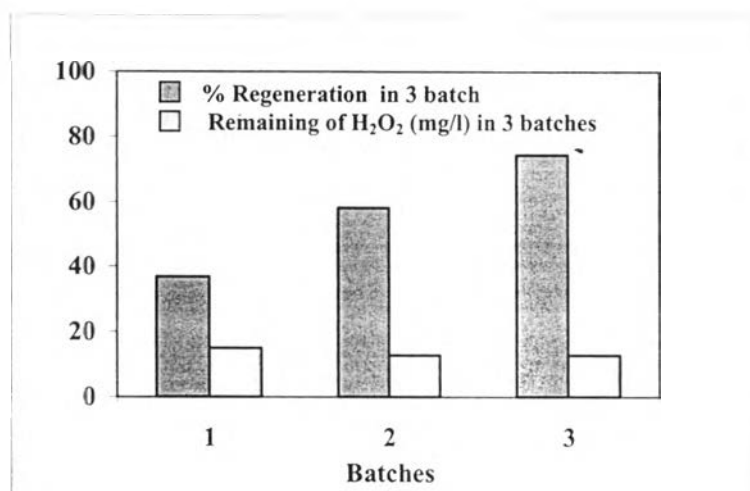


Figure 4.12 The regeneration of 4-NP in GAC in 3 batches at molar ratio of 1:5:0.5

4.4 Reuse of activated carbon after regeneration

The adsorption efficiency of GAC which was regenerated by Fenton's reagent with molar ratio of 5:0.5 at pH 7, three batches adding of H_2O_2 and Fe^{2+} was checked to determine the adsorption isotherm. The two adsorption isotherm models and parameters are shown in Figure 4.13 and Table 4.2 respectively.

Table 4.2 Adsorption model parameters for 4-nitrophenol on regenerated GAC

Model	equation	parameter	Regenerated GAC	correlation coefficients
Langmuir	$X/M = abC_e/(1+bC_e)$	a	192.30	0.95
		b	0.11	
		ab	20.19	
Freundlich	$X/M = KC_e^{1/n}$	K	28.32	0.98
		1/n	0.44	

The Freundlich isotherm of regenerated GAC was fitted better than Langmuir isotherm. Comparing adsorption capacity at 5 mg/l equilibrium concentration of regenerated GAC (53.58 mg/g) with virgin GAC (90.25 mg/g), the reduction is 36.19%.

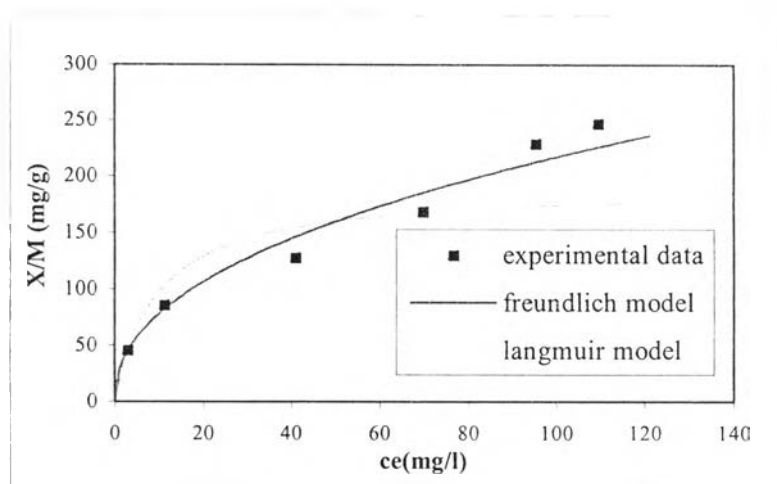


Figure 4.13 Adsorption isotherms of 4-nitrophenol on regenerated GAC.

4.5 Role of Fenton's reaction to GAC

In order to verify the role of catalyst (Fe^{2+} and Fe^{3+}) which may be adsorbed in GAC during regenerating process, the second regeneration by Fenton's without ferrous was proceeded.

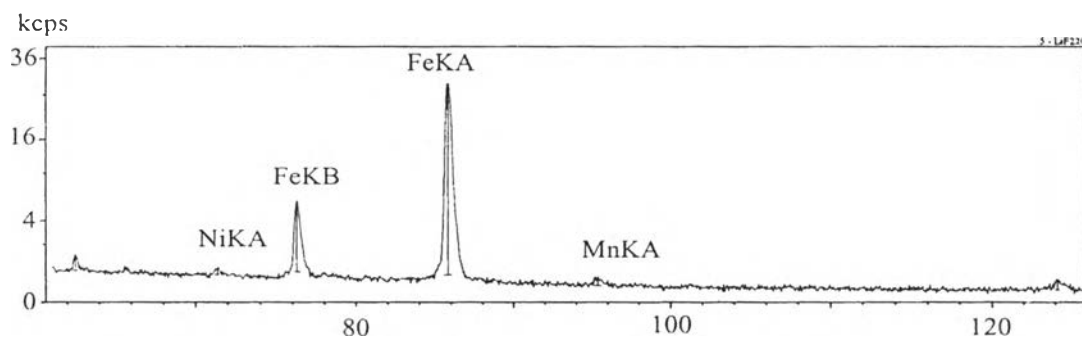
Table 4.3 showed the reduction of 4-NP in virgin GAC and in regenerated GAC by Fenton's reagent without ferrous at pH 7. Both give the low % reduction but slightly higher obtained from regenerated GAC. The reduction of H_2O_2 in regenerated GAC indicated that Fenton's reaction occurred. The experiment of oxidation of 4-NP in solution by Fenton's reagent without ferrous was also conducted. The result shows that 4-NP did not decrease within 1 hr. Therefore, catalyst may come from GAC itself as well as adsorbed ferrous or ferric during previous regeneration. Because the total iron before and after regeneration were determined by Atomic Absorption Spectrophotometer (AAS) with the values of 4676 and 4525 mg/l, respectively.

Table 4.3 The reduction of 4-NP in GAC and 4-NP in regenerated GAC by H_2O_2 at pH 7

Time (hr)	Regenerated GAC		Virgin GAC	
	H_2O_2 (mg/l) remaining	% reduction of 4-NP	H_2O_2 (mg/l) remaining	% reduction of 4-NP
0	6732	0	6732	0
1	5725	5.37	6450	2.51

Figure 4.14 showed that iron in GAC could be detected by X-ray fluorescence (XRF). So, the remaining of iron in GAC after regeneration was considered as an advantage in order to assist the degradation of organic substances as catalyst for the reaction

(a)



(b)

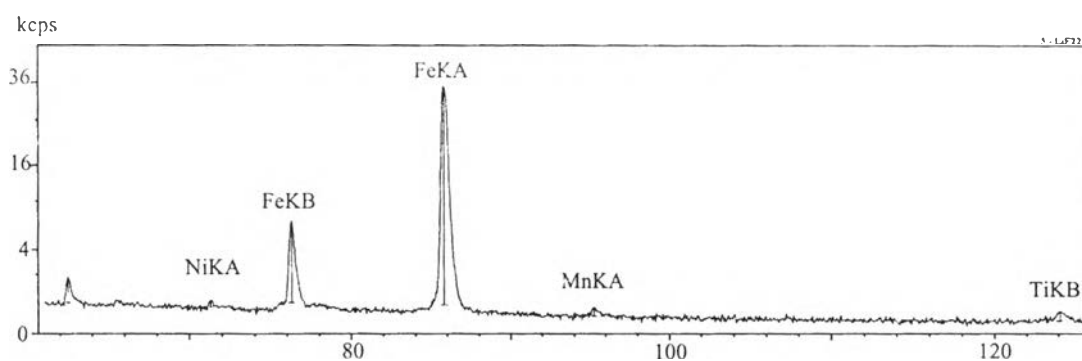


Figure 4.14 XRF Spectrum of GAC from bituminous coal (a) virgin GAC (b) regenerated GAC.