

PHENOLIC WASTEWATER TREATMENT USING ACTIVATED CARBON IN A THREE PHASE FLUIDIZED-BED REACTOR

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ABSTRACT

Phenolic wastewater treatment by activated carbon in a laboratory scale three phase fluidized-bed reactor was investigated. The reactor with effective volume of 272 ml, 300 mm in height and 40 mm in diameter was made from transparent acrylic that allowed to observe the phenomena occurring inside. Aqueous solution containing 10 mg/l of phenol and air were used as representative agents that were continuously fed to the reactor at a constant flow rate of 1 and 2 l/min with co-current and up-flow, respectively. Comparison of the phenolic adsorption under five different adsorbents: (a) fresh GAC, (b) 1st reused GAC, (c) fresh Fe/GAC, (d) 1st reused Fe/GAC, and (e) 2nd reused Fe/GAC, have been carried out. The phenolic wastewater was re-circulated through the reactor and its concentration was measured with respect to time. The experimental adsorption results revealed that both fresh GAC and Fe/GAC gave the better results than reused GAC and reused Fe/GAC, respectively. The adsorption in all cases of GAC and Fe/GAC would follow pseudo-second order kinetic.

KEYWORDS

phenol, wastewater, activated carbon, three phase fluidized-bed reactor

I. Introduction

Phenol is one of important starting and/or intermediate materials in various industrial processes. Phenol is known or suspected to be carcinogens, it is well known for its high stability and toxicity. It has been declared to be a hazardous pollutant even at the very low concentration [1]. It can damage the skin and other tissues of the human and animals. When digested, phenol-containing liquids could also lead to liver damages, dark urine and irregular heart beats. Therefore, the treatment of phenolic wastewater is considerable importance in environmental protection. Researchers have been attempted to use many technologies for phenolic wastewater treatment, for example biological treatment [2], chemical precipitation or oxidation [3], and ion exchange [4]. However, there are few suitable processes for this high toxicity effluent with reasonable costs. Adsorption by granular activated carbons and its derivative is one of the conventional process representing an environmentally friendly alternative of phenolic treatment [5]. The three phase fluidized-bed reactor has received considerable attention and wide utilization in wastewater treatment due to several advantages. For example, first, this reactor has a more intensive contact between gas, liquid, and solid phase causing high mass transfer, high reaction rate, and small external mass transfer resistance between solid and liquid phase. Second, it could eliminate the operating problems such as bed clogging and high pressure drop, which occur in packed-bed operations. Third, it is a high efficient, simple, stable and economical operation compared to other reactor configurations [6]. In this research, the removal of phenol is investigated under the adsorption process with and without impregnation of Fe nanoparticles using a laboratory scale three phase fluidized-bed reactor. Adsorption results of fresh and reused activated carbons, GAC, including fresh and reused Fe catalysts supported on GAC, Fe/GAC, are also examined.

II. Experiments

2.1 Catalyst preparation

The test granulated coconut shell activated carbons were purchased from Carbokarn (Thailand) Co., Ltd. GAC was sieved to obtain in the size range of 0.4-2.0 mm particle diameter. Fe/GAC was prepared following the incipient wetness impregnation technique. The classified GAC was heated and held at 473 K for 4 hrs to eliminate their impurities, then impregnated with a solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to yield 5 %w/w of Fe. In order to obtain this %w/w, 0.5 ml of iron solution was impregnated on 1 g of GAC at 353 K. After impregnation, the samples were dried overnight at 353 K and subsequently calcined at 773 K under 0.8 l/min of nitrogen flow for 5 hrs.

2.2 Characterization

Following the Brunauer-Emmett-Teller, BET adsorption method, the specific surface area and porosities of the activated carbons and catalysts were measured via N_2 adsorption-desorption isotherms. Test materials were measured at 77 K using an automatic adsorption apparatus (BELSORP 28, BEL Japan Inc.). The morphological structures of the activated carbons and the Fe catalysts were characterized by Scanning electron micro scope, SEM (Hitachi S-3400N) at the National Nanotechnology Center.

2.3 Apparatus and procedure

The reactor with effective volume of 272 ml was made from transparent acrylic that allowed to observe the phenomena occurring inside. The outside diameter and height of the reactor were 40 and 300 mm, respectively. Aqueous solution of phenol and air were used as representative agents that were continuously fed to the reactor at a constant flow rate of 1 and 2 l/min with co-current and up-flow, respectively. Phenolic stock solution was prepared early by diluting 10 g of phenol crystal from Fisher Scientific with 1 liter of distilled water. Then, the aqueous solution containing 10 mg/l of phenol was prepared by mixing 5994 ml of distilled water with 6 ml of phenolic stock solution. The 6 liters of phenol was tested with a catalyst concentration of $0.83 \text{ g}_{\text{cat}}/\text{l}_{\text{phenol}}$. The aqueous temperature in the tank was constantly measured and controlled at 303 K using a thermocouple and a cooler. Comparison of the phenolic

adsorption under five different adsorbents: (a) fresh GAC, (b) 1st reused GAC, (c) fresh Fe/GAC, (d) 1st reused Fe/GAC, and (e) 2nd reused Fe/GAC, were carried out. In addition, the ozone generator was switched off in all experiments but would setting on in case of enhanced with ozone in next articles.

Figure 1
Schematic diagram of experimental apparatus:
1. hold-up tank
2. liquid pump
3. ball valve
4. liquid flow meter
5. air flow meter
6. ozone generator
7. air pump
8. three phase fluidized-bed reactor

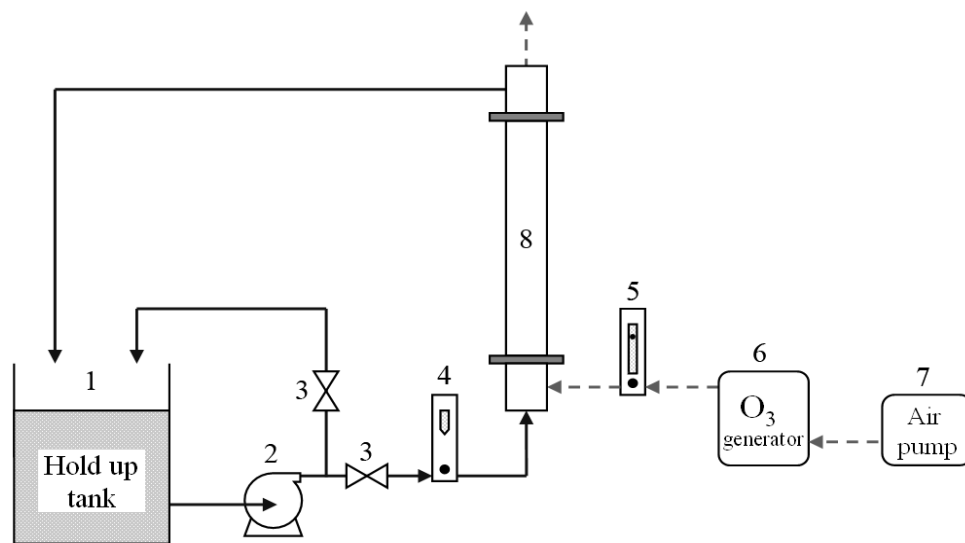


Figure 2
Fluidized-bed reactor



2.4 Chemical analysis

The progress of the reaction was followed by periodically taking liquid samples from the reactor and immediately analyzed after filtration through 0.45 μm nylon filter. Phenol was identified and quantified by High performance liquid chromatography (HPLC, Shimadzu, LC-20A Series) with a diode array detector at wavelengths of 210 and 254 nm. The 5 μm of C18 column (Inertsil ODS-3, 25 cm in length, 4.6 mm in diameter) was used as stationary phase. The mixture of 4 mM aqueous sulfuric solution and 20% v/v aqueous acetonitrile solution was used as mobile phase at 1.5 ml/min.

2.5 Analyzed data

The adsorption data were analyzed in term of the pseudo-first order and pseudo-second order kinetics as follows

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where q_e and q_t are adsorption ability at equilibrium and at time, t ($\text{mg}_{\text{phenol}}/\text{g}_{\text{adsorbent}}$) respectively; k_1 and k_2 are first and second order rate constants, respectively.

III. Results and Discussion

The specific surface area and porosity of the GAC and Fe/GAC are shown in Table 1. The surface area of GAC with Fe catalyst decreases after iron loading. GAC shows slightly larger total pore and micropore volume than Fe/GAC because it has smaller average micropore size than Fe/GAC. However, GAC has slightly higher BET area than Fe/GAC of 7 %. To clearly understand the coating, the morphology of GAC and Fe/GAC were determined by scanning electron micro scope (see Fig. 3 and 4), respectively. From the figures, they can be seen that Fe dispersedly coated on the surface of activated carbons. It should be noted that the porosity of the obtained Fe/GAC is significantly affected by the impregnation.

Sample	BET surface area (m^2g^{-1})	Pore size	Total pore volume (cm^3g^{-1})	Average pore diameter (nm)	Micropore volume (cm^3g^{-1})	Average Micropore diameter (nm)
GAC	1154 ± 22	micropore	0.49 ± 0.01	1.4 ± 0.04	0.49 ± 0.01	0.6 ± 0.01
Fe / Gac	1081 ± 22	micropore	0.46 ± 0.01	1.7 ± 0.04	0.46 ± 0.01	0.7 ± 0.0

Table 1
The porous characteristics of GAC and Fe/GAC

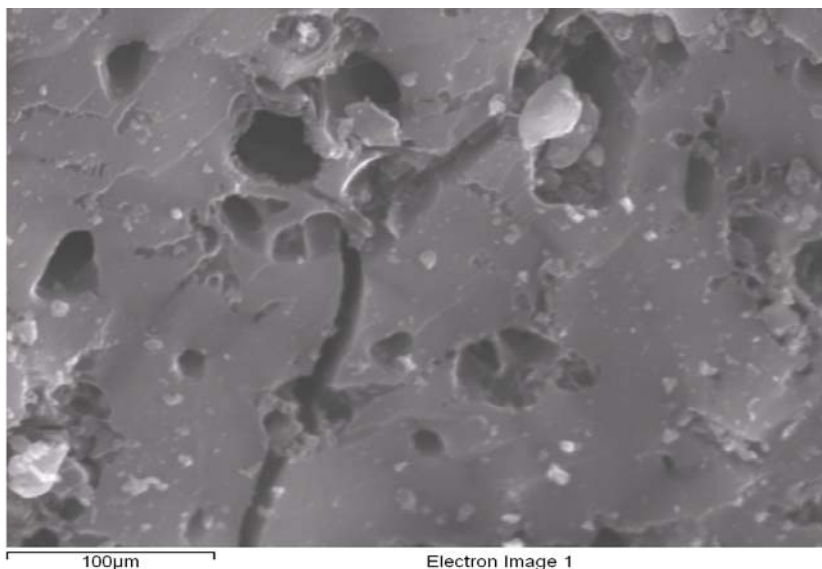
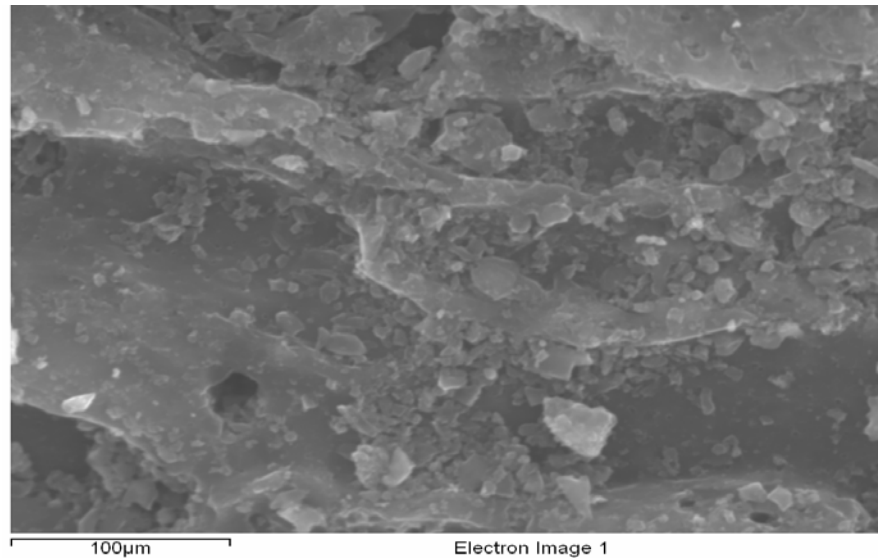


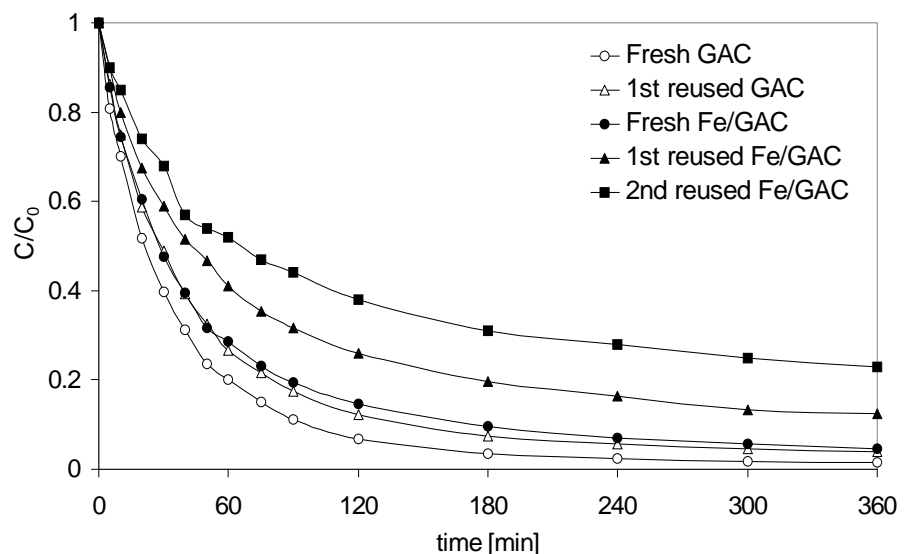
Figure 3
Scanning electron micro scope image of GAC

Figure 4
Scanning electron
micro scope image
of Fe/GAC



The adsorption of phenol from the initial concentration of 10 mg/l by treatment with a laboratory scale fluidized-bed reactor under five different adsorbents: (a) fresh GAC, (b) 1st reused GAC, (c) fresh Fe/GAC, (d) 1st reused Fe/GAC, and (e) 2nd reused Fe/GAC are shown in Fig. 5. The representative information is the average value of triplicated data in each experimental condition

Figure 5
Phenol
concentrations
as a function of
time of GAC and
Fe/GAC



From Fig. 5, when comparing the adsorption performance of phenol in any cases of Fe/GAC, fresh Fe/GAC shows the best result while 1st reused Fe/GAC significantly adsorbs phenol better than 2nd reused Fe/GAC. Similarly, fresh GAC adsorbs phenol better than 1st reused GAC. Fresh GAC has higher adsorption ability than reused GAC because of the decreasing and leaching of active adsorption surface area. Substantially, GAC adsorbs phenol faster than Fe/GAC in all cases. As a result of Fe molecules blocking some part of pore size of activated carbons, the pore volume and adsorption performance of Fe/GAC decrease accordingly.

The adsorption ability of phenol as a function of time of GAC and Fe/GAC is shown in Fig. 6. It revealed that fresh GAC gives the best result when comparing with the other cases. After the 360 minutes of experiment, the adsorption equilibriums were reached.

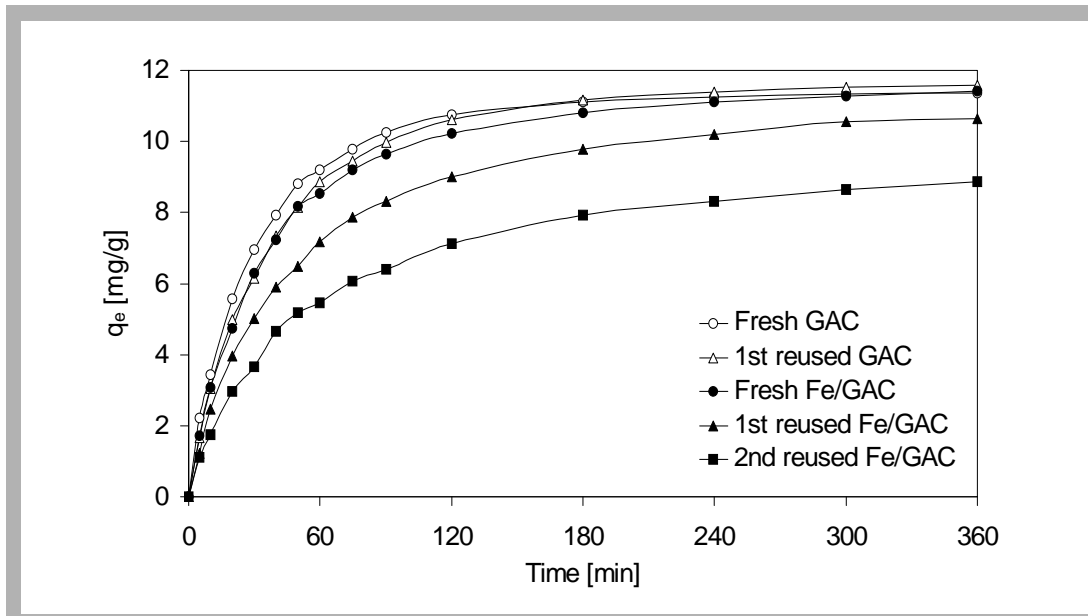


Figure 6
Adsorption ability
of phenol as a
function of time of
GAC and Fe/GAC

Various kinetic models including the pseudo-first order and pseudo-second order were tested for the experimental data to elucidate the adsorption mechanism. In case of the first-order rate equation of GAC and Fe/GAC, the values of k_1 and q_e were calculated from the slope and intercept of the plot of $\log(q_e - q_t)$ versus t (see Fig. 7). It was found that the correlation coefficients for the pseudo first-order model were lower than that of the pseudo second-order model. These parameters are summarized in Table 2. This implies that the adsorption process does not follow first-order kinetic.

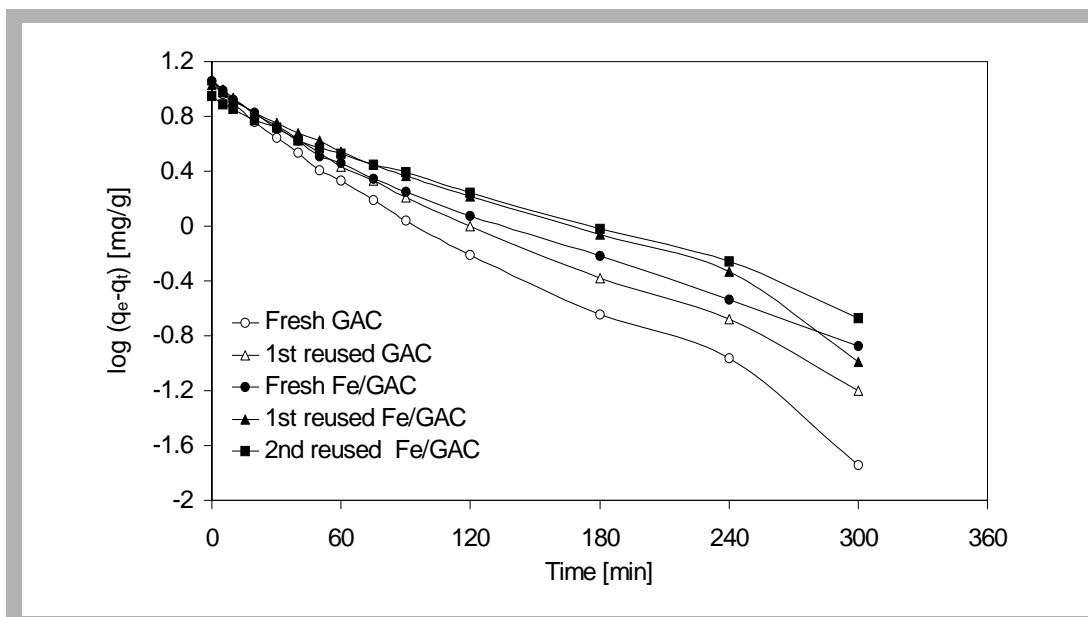


Figure 7
Pseudo-first order
of GAC and
Fe/GAC

In case of the second-order rate equation of GAC and Fe/GAC, the values of k_2 and q_e were calculated from the plot of t/q_t against t (see Fig. 8 and Table 2). The calculated q_e values agree well with experimental q_e values. The correlation coefficients for the pseudo-second order kinetic plots were very high. These results suggested that the appropriate adsorption kinetic of both GAC and Fe/GAC would follow pseudo-second order kinetic.

Figure 8
Pseudo-second order of GAC and Fe/GAC

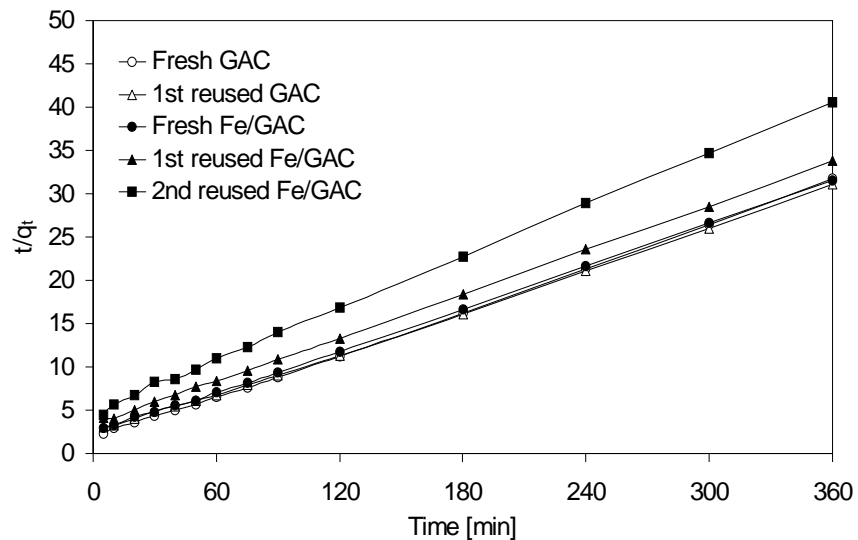


Table 2
Experimental and calculated adsorption ability, rate constant and R-square of GAC and Fe/GAC

Sample	$q_e(\text{exp})$	Pseudo-first order			Pseudo-second order		
		$q_e(\text{cal})$	k_1	R^2	$q_e(\text{cal})$	k_2	R^2
Fresh GAC	11.35	8.31	0.0200	0.9870	12.15	0.0040	0.9992
1 st reused GAC	11.60	8.86	0.0166	0.9885	12.67	0.0028	0.9991
Fresh Fe/GAC	11.41	8.11	0.0143	0.9789	12.39	0.0029	0.9996
1 st reused Fe/GAC	10.65	9.02	0.0140	0.9837	11.92	0.0021	0.9998
2 nd reused Fe/GAC	8.87	7.43	0.0117	0.9909	10.00	0.0021	0.9994

It should be noted that, fresh activated carbon has higher adsorption ability than doped activated carbon. However, in actual waste treatment, using fresh activated carbon in each batch of waste treatment is not practical. The phenol removal from ozone by ozonation is an alternative due to the lower cost. In the past batch after using fresh activated carbon, the efficiency of the adsorption kinetic decreases while the effect of ozonation increases. Ozonation exhibits a stronger effect when activated carbon enhanced with a noble metal, i.e. Fe in this research. The choice is between the fast removal in a short period (only GAC), or slightly fast removal during a long period, (Fe/GAC enhanced with O_3). The phenolic wastewater treatment in case of enhanced with O_3 would be presented in next articles.

IV. Conclusions

Adsorption of phenolic wastewater using activated carbons and Fe catalysts has been examined. The obtained conclusions are as follows:

- 1) The surface area of Fe/GAC decreases after iron loading. As a result of Fe molecules blocking some part of pore size of activated carbons, the pore volume and adsorption performance of Fe/GAC decrease accordingly.
- 2) Activated carbons adsorb phenol faster than Fe/GAC.
- 3) When comparing the adsorption performance of phenol between fresh and reused GAC or between fresh and reused Fe/GAC, it was found that both fresh GAC and Fe/GAC

gave the better results than reused GAC and reused Fe/GAC, respectively. This result is due to the decreasing and leaching of active adsorption surface area.

- 4) The adsorption in all cases of GAC and Fe/GAC would follow pseudo-second order kinetic.

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