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Decolorization of acid black 24 by the FeGAC/H₂O₂ process

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Abstract

FeGAC/H₂O₂ process was developed and employed in this research for the treatment of acid back 24. The removal efficiencies of five treatment processes (GAC, FeGAC, H₂O₂, GAC/H₂O₂, and FeGAC/H₂O₂) were studied in this research. The adsorption capacity of granular activated carbon (GAC) was greatly improved by the coating of iron oxide on GAC surface (FeGAC). The presence of H₂O₂ significantly improved the removal abilities of FeGAC and GAC. For instance, at solution pH 2, the removal efficiency of FeGAC/H₂O₂, GAC/H₂O₂, H₂O₂, FeGAC, and GAC were 76, 74, 59, 11, and 7%, respectively. The possible removal mechanisms of FeGAC/H₂O₂ process were proposed in this research. When treating the actual dye contaminated wastewater, the removal efficiencies of FeGAC/H₂O₂ and GAC/H₂O₂ were approximately six times greater than that of H₂O₂ process.

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1. Introduction

Dyeing and finishing processes in textile industries produce large volumes of wastewater. The removal of dyes from industrial effluent is a major concern in the textile industry, with the increase in stringent legislation. For example, to comply with Taiwan's environmental regulations, wastewater that is produced from dye manufacturers and dyeing industries has to adhere to COD < 100 mg/L and ADMI (American Dye Manufacturers Institute) colour value <550. Colour in dyeing wastewater is the most noticeable contaminant even at very low concentrations [1]. Due to the difficulty of removing colour from wastewater, the present standard was modified from 1998s ADMI colour value <400. Even with the present standard (ADMI colour value <550), many manufacturers still had difficulty in complying with this regulation.

Current treatment methods, such as biological processes, were commonly employed in the industry to remove organic

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contents from wastewater, however, the removal of color to the desired level remained difficult. Chemical coagulation process removes dye reasonably well, but produces a large amount of sludge [2]. Similarly, activated carbons can remove dye from wastewater effectively; however, the cost of activated carbons and subsequent treatment of spent carbons is expensive [1,3-6]. Therefore, a number of researchers tried to employ various processes, such as Fenton reaction [7,8], TiO₂/UV [9,10], UV/H₂O₂ [11], and $H_2O_2/UV/Fe^{2+}$ [12] processes to treat dye-contaminated wastewater with fairy well removal efficiencies. However, the production of large amounts of sludge occurred in these processes, and this resulted in high disposal cost in Taiwan. Therefore, more efficient and economical technologies with which to treat dye-contaminated wastewater are required.

The purpose of this research is to develop an alternative treatment process (FeGAC/H₂O₂) to overcome the limitations cited above and to solve the obstacles that Taiwan's dyeing industries are currently encountering. The FeGAC/H₂O₂ processes developed in this research was tried to combine both advantages of iron oxide coated

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granular activated carbon (FeGAC) and H_2O_2 . FeGAC has high adsorption capacity of dyes due to GAC surface and the coating of iron oxides. In addition, the oxidation ability of H_2O_2 was enhanced by the catalytic properties of FeGAC.

2. Experimental

Hydrogen peroxide (35%) and acid black 24 (C.I. No. 26370, C₃₆H₂₃N₅Na₂O₆S₂) were purchased from Fluka Chemical Co. and Aldrich Chemical Co., respectively. Acid black 24 was not purified prior to use. Dye concentration was measured at 572 nm through spectrophotometric method (Hitachi U-2000). Granular activated carbon (GAC) employed herein was from Calgon Carbon Corporation (F400), which was provided courtesy of the manufacturer. F400 had a total N2 BET surface area of 800–900 m²/g, an apparent bulk density of 0.54 g/cm³, a particle density of 0.78 g/cm^3 , and a pore volume fraction of 0.82. Prior to use in this study the GAC was sieved between 425 and 600 mm, baked in an oven at 200 °C for 2 days, and washed several times with deionized water via tumbling in a roller for a day. This GAC slurry was filtered, dried completely in an oven at 110 °C, cooled in a desiccator, and stored at room temperature in a covered glass container until further use. All the other chemicals used in this study were reagent grade and double distilled water was employed for preparing all the solutions and reagents.

The iron oxide coated granular activated carbon (FeGAC) was prepared as follows. A known amount of $Fe(NO_3)_3$ solid was dissolved in deionized water, then mixed with GAC. The applied iron dosage in this research was about 40 mg Fe(III)/g GAC. This suspension was mixed for 12 h before dried in an oven at 90 °C for 3 days. The resulting mixture was cooled to room temperature, and washed several times with double distilled water to remove detachable iron oxide. The resulting FeGAC composite adsorbent was dried in the oven at 105 °C for another 3 days and stored at room temperature in a covered glass container until needed.

The amount of Fe oxide coating on the FeGAC surface was measured by extracting the composite FeGAC in a boiling, concentrated (10%) HNO₃ solution for 12 h. The total iron in the extraction solution was measured by flame atomic absorption spectrophotometry (AAS).

2.1. Adsorption isotherm studies

Adsorption capacities of FeGAC and GAC were determined from adsorption isotherm tests. A known amount of adsorbent was added into a series of 250 mL bottles that contained known concentrations of dyes adjusted to desired pH values (pH 2, 4, and 6). These bottles were rotated for 5 days in a shaker and pH was repeatedly adjusted to the desired pH value throughout the experimental period by adding either 1 M HNO₃ or 1 M NaOH solution. Adsorption capacity (q_e ,

Table 1 Experimental condition for the various treatment processes for the removal of acid black 24

Process	Test conditions					
	GAC(g/L)	FeGAC(g/L)	H ₂ O ₂ (mL/L)	pН		
(1) GAC	2	_	_	2, 4, 6		
(2) FeGAC	_	2	_	2, 4, 6		
$(3) H_2O_2$	_	_	0.1	2, 4, 6		
(4) GAC/H ₂ O ₂	2	_	0.1	2, 4, 6		
(5) FeGAC/H ₂ O ₂	-	2	0.1	2, 4, 6		

Dye initial concentration = 120 mg/L, contact time 3 h.

mg of dye adsorbed/g of absorbent) was determined using the following relationships:

Adsorption capacity,
$$q_{\rm e} = (C_{\rm i} - C_{\rm f}) \times \frac{V}{m}$$
 (1)

where C_i and C_f are the initial and final concentrations of dye, respectively, *V* the reaction volume, and *m* the mass of adsorbent added (GAC or FeGAC).

2.2. Treatment efficiency

The removal efficiencies of five treatment processes (GAC, FeGAC, H₂O₂, GAC/H₂O₂, and FeGAC/H₂O₂) were studied in this research in a batch reactor. A known amount of adsorbent (GAC or FeGAC) and/or H₂O₂ was added into a sealed 1 L reactor filled with known concentrations of dye wastewater with the pH adjusted to the desired value. Samples were collected and analyzed at predetermined time frames. The various experimental conditions are given in Table 1. Blanks containing no GAC or FeGAC were used for each series of experiments as controls.

3. Results and discussion

3.1. Adsorption capacity

To better understand the adsorption properties of the FeGAC, the adsorption isotherms studies were performed in this work. The adsorption capacities of GAC and FeGAC were investigated at three different solution pHs in this research. The amount of Fe oxide coating on the FeGAC surface was approximately 37 mg Fe/g of GAC. The experimental results of GAC and FeGAC are shown in Fig. 1a and b, respectively. Comparing with adsorption onto uncoated GAC, the Fe oxide coating on GAC significantly increased adsorption capacities of acid black 24. The experimental results indicated that the adsorption capacities of GAC and FeGAC were greatly influenced by solution pH as well. In general, the adsorption capacities of GAC and FeGAC were both increased with decreasing solution pH as shown in Fig. 1a and b, respectively. This was probably due to the negative charge of acid black 24. Because at lower pH solution, the surface of GAC had more positive adsorption sites that



Fig. 1. The adsorption capacities of acid black 24 onto (a) GAC and (b) FeGAC at various initial pH.

could attract negative adsorbate. For example, the adsorption capacities of GAC at pH 6, 4, and 2 were about 40, 52, and 62 mg/g, respectively, as indicated in Fig. 1. The adsorption capacities of FeGAC were approximately 60, 80, 120 mg/g at solution pH 6, 4, and 2, respectively. Similar observation was reported by Al-Dges et al. [1]. The author studied the adsorption of methylene blue dye (cationic dye) on to GAC. The author indicated that the adsorption capacity of cationic dye was increased with increasing pH due to the negative charge carboxylate anionic surface functional groups on carbon surface. On the other hand, the negative charge of anionic dye would be attracted to the adsorbent surface at low pH.

The capacity of an adsorbent can usually be described using an adsorption isotherm, which is an expression of distribution of an adsorbate between the adsorbed phase and the solute phase under equilibrium conditions and constant temperature. Two commonly used adsorption isotherms are the Freundlich and Langmuir isotherms were employed in this research [13,14].

The Freundlich isotherm assumes that adsorption is a physical process and has the form:

$$q = KC^n \tag{2}$$

where *K* is the Freundlich isotherm constant $((dm^3/mg)^n)$; *C* the concentrations of dye in solution (mg/dm^3) ; *n* the Freundlich isotherm exponent (dimensionless); *q* the surface concentration (mg adsorbate/g adsorbent).

The Langmuir isotherm was derived assuming a monolayer adsorption with a constant adsorption energy and adsorbate that will not migrate on adsorbent surfaces.

$$q = \frac{Q_0 bC}{1 + bC} \tag{3}$$

where q is the surface concentration (mg adsorbate/g adsorbent); Q_0 the Langmuir isotherm constant related to a max-

imum surface coverage corresponding to complete monolayer coverage (mg adsorbate/g adsorbent); b the Langmuir isotherm constant related to the enthalpy of adsorption; C the concentrations of dye in solution (mg/dm³).

Isotherm constants, K, n, Q_0 , and b, were estimated by fitting a set of experimental data to isotherm models (Eqs. (2) and (3)) by using nonlinear regression methods [15].

Parameters for both isotherms are shown in Table 2. The Langmuir isotherms with higher R^2 (between 0.96 and 0.99) seemed to better describe both GAC and FeGAC adsorption behaviours than Freundlich isotherms did (R^2 between 0.90 and 0.98). These results could be further demonstrated in Fig. 2. The Langmuir isotherms for both GAC and FeGAC were better fit the experimental data at pH ranged tested (2, 4, and 6). In general, Freundlich isotherms were under predicted the adsorption capacities at low solution dye concentration ranges and over predicted the adsorption capacities at the higher dye concentrations. This result indicated that the dye adsorbed onto GAC and FeGAC were likely monolayer. The

The Freundlich and Langmuir parameters of adsorption isotherms for acid black 24 at various pH

Parameter	Adsorbent						
	GAC			FeGAC			
	pH 6	pH 4	pH 2	pH 6	pH 4	pH 2	
Freundlich							
Κ	15.91	21.36	30.16	31.09	30.15	40.19	
п	4.61	4.90	5.79	6.48	4.51	4.08	
R^{2a}	0.91	0.97	0.98	0.98	0.95	0.90	
Langmuir							
Q_0	45.11	59.82	71.39	61.74	95.50	151.29	
b	0.18	0.15	0.14	0.36	0.09	0.07	
R^2	0.98	0.97	0.96	0.97	0.99	0.96	

^a R^2 : Correlation coefficient.



Fig. 2. Adsorption isotherms of acid black 24 onto GAC and FeGAC at various pH: (a) GAC pH 6; (b) GAC pH 4; (c) GAC pH 2; (d) FeGAC pH 6; (e) FeGAC pH 4; (f) FeGAC pH 2.

 Q_0 obtained in Langmuir isotherms indicated the maximum adsorption capacities of the GAC at pH 6, 4, 2 were about 45, 60, and 71 mg/g, respectively, and the maximum adsorption capacities of FeGAC at pH 6, 4, 2 were about 62, 95, 151 mg/g, respectively.

3.2. Removal efficiency

Five treatment processes (namely, GAC, FeGAC, H_2O_2 , GAC/ H_2O_2 , and FeGAC/ H_2O_2) were investigated in this research. Fig. 3a, b and c depict results of treating acid black 24 with these five treatment processes at initial pH 2, 4, and 6, respectively.

3.2.1. Solution pH 6

At solution pH 6, the removal efficiency sequence was $FeGAC/H_2O_2 > FeGAC > GAC = GAC/H_2O_2 > H_2O_2$. At the end of 180 min of reaction time, the removal efficiencies were approximately 60, 30, 15, 15, and 5% (Fig. 3c). Experimental results indicate that H₂O₂ alone could only remove 5% of acid black 24. However, both GAC and GAC/H₂O₂ could remove roughly 15% of dye, which was much less than either FeGAC/H₂O₂ (60%) or FeGAC (30%) removed. This indicated that within a neutral pH, the GAC was not an appropriate catalyst for H₂O₂. The removal efficiency of FeGAC/H₂O₂ was two times higher than the removal efficiency of FeGAC. Thus, FeGAC could catalyze the oxidation of H₂O₂ and produce higher removal rates. Furthermore, the removal efficiency of FeGAC/H₂O₂ was approximately four times faster than that of the GAC/H₂O₂ process. The superior removal by FeGAC/H₂O₂ processes was probably due to the catalytic reaction between coated irons and H₂O₂.

3.2.2. Solution pH 4

When the solution pH decreased from 6 to 4, the removal efficiency sequence was modified slightly, as follows: FeGAC/H₂O₂ > H₂O₂ > GAC/H₂O₂ > FeGAC > GAC with discoloration removal efficiencies of 56, 43, 37, 18, and 13%, respectively, (Fig. 3b). FeGAC/H₂O₂ remained the best method among these five processes. In terms of removal efficiency H₂O₂, GAC/H₂O₂ and FeGAC are second, third and fourth, respectively. H₂O₂ was more reactive at lower pH.

3.2.3. Solution pH 2

At pH 2, the removal efficiency sequence was altered again. That is, the removal efficiencies for FeGAC/H₂O₂, GAC/H₂O₂, H₂O₂, FeGAC and GAC were 78, 74, 59, 11, and 7, respectively (Fig. 3a). The catalytic property of GAC was more significant in the lower pH ranges, which, due to the acidic solution of the actual wastewater's pH, benefited the GAC/H₂O₂ process.

3.2.4. Effects of solution pH

Solution pH was one of the major factors that affected the final treatment results. Fig. 4 summarized the removal effi-



Fig. 3. Removal of acid black 24 for various treatment processes at various initial pH: (a) pH 2; (b) pH 4; (c) pH 6.

ciencies for these processes under various solution pH. When solution pH decreased from 6 to 2 following 3 h of reaction time, the removal efficiencies of GAC/H₂O₂ increased from 14 to 74%. Similarly, when pH decreased from 6 to 2, the removal efficiency of FeGAC/H₂O₂ increased from 62 to 78%. Among the five processes investigated herein, FeGAC/H₂O₂ had the best removal efficiency. Solution pH



Fig. 4. Effect of initial pH on removal of acid black 24 by various processes (Co = 120 mg/L; 0.1 ml/L H_2O_2).

had a greater influence on GAC/H_2O_2 and H_2O_2 processes than the other processes, such as FeGAC/H₂O₂, FeGAC and GAC did. Fig. 4 reveals that the catalytic abilities of GAC and FeGAC were more effective under acidic conditions. However, the FeGAC/H₂O₂ still remained effective under neutral pH conditions.

3.3. Initial reaction rate

Initial reaction rate for these treatment processes were also examined (Table 3). The initial reaction rates at pH 2 for FeGAC/H₂O₂, GAC/H₂O₂, H₂O₂, FeGAC, and GAC were approximately 8.71, 8.30, 7.05, 0.06, and 0.39 mg/min, respectively. This experimental result was in agreement with the overall removal rate displayed in Fig. 4. At the pH range tested herein, the reaction rate for GAC was less than 0.6 mg/min. While the initial reaction rate for FeGAC increased with an increase in pH, the initial reaction rate of H₂O₂, GAC/H₂O₂, and FeGAC/H₂O₂ decreased with a pH increase. Among these processes, FeGAC/H₂O₂ had the highest initial removal rate at the tested pH ranges. Even at

Table 3

Initial reaction rate (mg/min) by various treatment processes under different initial pH values

Processes	Initial reaction rate (mg/min)				
	pH 2	pH 4	pH 6		
GAC	0.39	0.09	0.56		
FeGAC	0.06	0.01	1.92		
H_2O_2	7.05	3.52	0.54		
GAC/H ₂ O ₂	8.30	3.22	0.66		
FeGAC/H ₂ O ₂	8.71	5.15	6.10		

high pH, FeGAC/H₂O₂ could effectively remove dye from wastewater. For example, at pH 6, the initial reaction rate of FeGAC/H₂O₂ was 3, 10, and 13 times higher than FeGAC, GAC/H₂O₂, and H₂O₂ processes, respectively. Conversely, GAC/H₂O₂ can only effectively remove dye at low pH ranges, which is similar to H₂O₂ processes.

3.4. Adsorption kinetics

A suitable model is needed to further assessing the contribution of mechanisms of the mass transfer and chemical reaction in these reaction processes. Many mathematically complex models, such as the homogeneous surface diffusion model, the pore diffusion model and the heterogeneous diffusion model, have been developed to describe the transport of species inside the adsorbents in a batch reactor. However, due to the mathematically complexity nature of theses models, these models were inconvenient for practical use [16]. Therefore, more simplify models were applied in this research for future practical applications [17]. Five commonly used kinetic analysis models were discussed in this research.

Generalized first order equation was proposed by Kannan and Sundaram [6]:

$$\frac{1}{q_t} = \left(\frac{K_{\rm a}}{q_{\rm e}}\right) \left(\frac{1}{t}\right) + \frac{1}{q_{\rm e}} \tag{4}$$

where q_t is the amount of dye adsorbed (mg/L) at various time *t*, q_e the maximum adsorption capacity and K_a the first order rate constant for the adsorption process (L/min). Maximum adsorption capacity (q_e) was obtained through previous isotherms tests.

Pseudo-first-order equation [17–19]:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = K_1(q_\mathrm{e} - q_t) \tag{5}$$

Through integration, the above equation becomes

$$\log(q_{\rm e} - q_t) = \log q_{\rm e} - K_1 \times \frac{t}{2.303} \tag{6}$$

where K_1 is the pseudo-first-order rate constant. Pseudo-second-order equation [17]:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = K_2 (q_\mathrm{e} - q_t)^2 \tag{7}$$

The solution of the above equation is as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_{\rm e}^2} + \frac{t}{q_{\rm e}} \tag{8}$$

where K_2 is the pseudo-second-order rate constant.

Intra-particle diffusion model [20,21]:

$$q_t = K_{\rm p} \times t^{1/2} + C_{\rm p} \tag{9}$$

where q_t is the amount of dye adsorbed at time *t*, K_p the intra-particle diffusion rate constant (mg min^{1/2}/g) and C_p the intercept.

Two-box models [22,23]:

$$C(t) = A + B_1 \exp(-D_1 t) + B_2 \exp(-D_2 t)$$
(10)

where C(t) is the adsorbate concentration at time t, A the equilibrium adsorbate concentration in solution, B_1 and B_2 are parameters, and D_1 and D_2 are parameters related to the physical properties of adsorbent, such as internal diffusion and external mass transfer of the metal ions. The difference between the initial and equilibrium adsorbate concentration is equal to the sum of B_1 and B_2 [23]. The adsorption kinetics, two-box model, is approximated by a double-exponential function. The above equation was to describe the adsorption processes that rapid adsorption occurs initially, followed by a much slower phase, which takes from a few hours to several weeks depending on the type of the adsorbent [22]. These two-step processes were in agreement with our experimental observations. Therefore, the model was applied in this research as well.

Results of these models are shown in Table 4. To evaluate these models, the sum of error squares (SSE) was calculated as follows:

$$SSE = \left(\frac{q_{cal} - q_{exp}}{N}\right)^{0.5}$$
(11)

where q_{cal} and q_{exp} are model predicted and experimental values, respectively, and *N* the number of data points. In general, a better model has a smaller SSE value.

According to the results of SSE as listed in Table 5, intraparticle diffusion model seems to be the best fitted model with smallest SSE (less than 0.971) among these five models for describing GAC, FeGAC, GAC/H₂O₂, and FeGAC/H₂O₂ systems. The intra-particle diffusion model indicated that the adsorbate species are most probably transported from the bulk of the solution into the solid phase through intra-particle dif-

Table 5 Summary of sum of error squares (SSE) for various models Table 4

Statistical results of the application of the kinetic equations and models for various processes

Parameters	pН	I Processes					
		GAC	FeGAC	GAC/H ₂ O ₂	FeGAC/H ₂ O ₂		
Generalized	first o	rder equation	l				
Ka	2	503.7	5753.3	12.0	39.7		
	4	1542.7	17045.1	37.7	39.2		
	6	199.0	72.2	174.3	15.3		
Pseudo first	order	reactions					
K_1	2	0.0004	0.0002	0.0073	0.0029		
	4	0.0001	0.0008	0.0015	0.0034		
	6	0.0013	0.0025	0.0035	0.0067		
Pseudo seco	nd orc	ler reactions					
K_2	2	8.03E-06	1.14E-06	2.46E-04	3.52E-05		
	4	3.13E-06	2.74E-06	1.13E-04	6.60E-05		
	6	4.41E-05	6.94E-05	5.03E-05	2.53E-04		
Intra particle	e diffu	sion Model					
K _p	2	0.19	0.34	0.27	0.36		
$C_{\rm p}$		1.45	0.00	41.08	42.28		
K _p	4	0.07	0.82	0.48	0.72		
$C_{\rm p}$		0.24	0.00	16.25	25.04		
Kp	6	0.57	0.76	0.61	0.47		
Cp		0.71	8.22	1.05	29.74		
Two-box mo	odel						
B_1	2	0.040	0.000	0.059	0.06		
D_1		0.011	0.000	0.023	0.02		
D_2		0.206	0.008	0.530	2.27		
B_1	4	0.000	0.180	0.068	0.13		
D_1		1.000	0.016	0.015	0.02		
D_2		0.019	1.000	0.198	0.28		
B_1	6	0.126	0.139	0.122	0.088		
D_1		0.009	0.020	0.015	0.015		
D_2		1.000	0.224	1.914	0.360		

Processes	Models							
	Generalized first order	Pseudo-first order	Pseudo-second order	Intra particle diffusion	Two-box model			
GAC								
pH 2	6.892	1.196	1.359	0.184	0.000			
pH 4	2.843	0.469	1.639	0.754	0.925			
рН б	6.752	1.516	1.766	0.371	0.770			
FeGAC								
pH 2	0.551	0.423	0.561	0.971	0.988			
pH 4	6.103	1.487	5.021	0.822	0.834			
pH 6	14.252	5.746	0.865	0.515	0.269			
GAC/H ₂ O ₂								
pH 2	15.803	21.102	4.677	0.300	0.293			
pH 4	15.806	13.625	15.327	0.782	0.196			
рН б	6.802	4.880	7.853	0.495	0.549			
FeGAC/H ₂ O ₂								
pH 2	44.858	40.324	39.559	0.158	42.935			
pH 4	25.815	26.868	28.044	0.734	24.461			
pH 6	13.704	29.399	26.505	0.436	19.164			



Fig. 5. Proposed reaction pathways of acid black 24 oxidized by H₂O₂.

fusion/transport process and this process is probably the rate limiting step in these systems. Dye was first adsorbed onto the FeGAC surface, then oxidized by H_2O_2 through catalytic reaction between FeGAC and H_2O_2 . Two-box model can describe GAC, FeGAC and GAC/ H_2O_2 fairly well. However, it was unable to fit the FeGAC/ H_2O_2 as indicated with SSE between 19 and 42. The pseudo-first-order equation can fit GAC and FeGAC systems with reasonable accuracy, but was unable to explain the GAC/ H_2O_2 and FeGAC/ H_2O_2 systems. Therefore, the intra-particle diffusion process might be used in the future for this type of systems.

3.5. Removal mechanisms

The possible reaction pathways of the FeGAC/H₂O₂ and GAC/H₂O₂ processes are proposed as shown in Fig. 5. The acid black 24 is oxidized by H_2O_2 to form the resulting compound as illustrated in Fig. 5d. The structure of acid black 24 is not a flat structure due to the rotation nature of the compound. The compound will rotate between nitrogen atoms

and arenas (single bonds). As a result, it is not easy to be adsorbed by GAC or FeGAC. However, the resulting compound of Fig. 5d has π -electron stacking effect and it has a flat structure due to double bonds between nitrogen atoms and arenas. Therefore, it is more readily adsorbed in the pores of GAC and FeGAC. Since FeGAC has better catalytic ability for H₂O₂ and higher adsorption capacity for acid black 24 than that of GAC. As a result, the FeGAC/H₂O₂ process has higher removal ability than that of GAC/H₂O₂ process.

3.6. Treatment efficiency for actual wastewater

Actual dye wastewater from one major dye manufacturer in northern Taiwan was tested in this study. Fig. 6 presents that the removal efficiency for FeGAC/H₂O₂, GAC/H₂O₂, and H₂O₂ were 62, 60, and 12%, respectively. The adsorption capacity of both GAC and FeGAC were negligible under the dosage employed herein. The experimental results demonstrate that the catalytic ability of GAC and FeGAC



Fig. 6. Decolorization of actual dye wastewater (initial pH 1.9; 10 ml/L $\rm H_2O_2;$ 4 g/L GAC or FeGAC).

were significant. Due to the addition of GAC and FeGAC, the removal efficiency of H_2O_2 increased nearly six times.

4. Conclusions

FeGAC/H₂O₂ process was developed and demonstrated herein to treat dye-containing wastewater. In general, under acidic conditions the removal efficiency sequence among the five processes tested were FeGAC/H₂O₂ > GAC/H₂O₂ > H₂O₂ > FeGAC > GAC. A lower solution pH results in a higher adsorption capacity efficiency of the GAC and FeGAC processes. The adsorption capacity of FeGAC was improved significantly by the presence of H₂O₂ and the intra-particle diffusion process could be used to describe the adsorption processes. In FeGAC/H₂O₂ process, the higher adsorption capacity of FeGAC might due to the H₂O₂ oxidation of acid black 24 from non flat structure to flat structure. As a result, acid black 24 was readily adsorbed by FeGAC after oxidation process.

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