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Decolorization of Acid Blue 9 Dye Wastewater Using Waste Furnace Slag

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Effluent streams from textile manufacturing facilities usually contain highly colored dye chemicals even though they are considered to be non-toxic chemicals. Colored effluents will interfere with the transmission of sunlight and upset the biological metabolism processes, even for a concentration of 1~2 mg/L (Chaudhuri and Sur 2000; Kuo 1992). In order to reduce the color of the effluent stream to meet the acceptable discharge standard, many treatment methods have been proposed. The methods include adsorption, chemical coagulation, chemical oxidation and biological treatments. Due to the stability of dyes, conventional biological treatment methods for industrial or municipal wastewater are ineffective in decolorizing dye wastewater (Shu and Huang 1995; Perkowksi et al. 1996). This has led to the study of other treatment methods for decolorizing textile dye waste streams which including adsorption, chemical coagulation and chemical oxidation methods (Davis et al. 1994). Adsorption is one of the physical wastewater treatment methods. Among adsorbents, activated carbon adsorption is an effective adsorbent for organic or dye chemicals and is widely used in water treatment or advanced wastewater treatment. However, its high initial cost and the need for a costly regeneration system make it less economically viable as an adsorbent (Viraraghavan and Alfaro 1998). Cost effectiveness, availability and adsorptive properties, are the main criteria for choosing an adsorbent to remove organic compounds (Li et al. 2000). Taking these criteria into consideration, many researchers have investigated the adsorptive properties of unconventional adsorbents such as olive shells (Darwish et al. 1996), montmorillonite (Jun et al. 1996), fly ash (Banerjee et al. 1995), and others. In this research, a waste material from steeling-making process, basic oxygen furnace slag (BOF slag), is used as an adsorbent.

This research affords the opportunity to study the adsorption process of dye wastewater (Acid blue 9) using the byproduct of steel-making plants.

MATERIALS AND METHODS

The adsorbent used in this research was BOF slag, which was the final byproduct of steel-making plants of China Steel Corporation (CSC). In steeling-making process, molten iron is converted into steel with oxygen and other flux materials in

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basic oxygen furnace (BOF). The byproduct slag in the BOF after being solidified is called BOF slag. The yearly product of BOF slag by the China Steel Corporation is about million tons that cause a disposal problem. Currently, BOF slag is being used in construction of roads, agriculture application or concrete aggregate. The temperature in furnace is over 1400℃ that makes BOF slag possess porous texture. Many small holes are found on the surface of slag. The properties of the BOF slag make it have the capacity of adsorption of materials from aqueous solution.

BOF slag is a sandy material dark gray in color and with angular, porous chunk structures. The BOF slag has wide particle size distribution, which can be from few μm to few cm. The major components of BOF slag are calcium oxide (CaO), Silicon dioxide (SiO_2), Ferrous oxide (FeO) and other oxides. The detailed chemical constituents and physical characteristics of the BOF slag are summarized in Table 1 and 2. The BOF slag obtained from the CSC was sieved by a mechanical vibration siever to obtain a reasonably uniform particle size (35~50 mesh, 50~100 mesh, 100~140 mesh, 140~200 mesh and less than 200mesh). This was washed with distilled water and dried at 103℃ for 1 hour to remove water. The heated product was cooled and stored in a desiccator.

Acid blue 9 (Erioglaucine, CI 42090, FW 792.86) was obtained from Aldrich, Milwaukee, WI. Acid blue 9 has the highest absorbency at 625 nm. A uv/vis spectrum photometer (Hitachi uv/vis spectrum photometer 5342) was used to measure the absorbency of acid blue 9 at 625 nm. The concentration of acid blue 9 used in the experiment was 20 mg/L.

The factors effect the adsorption will be studied like pH value of solution and particle sizes. A pseudo-first-order kinetic model was used to investigate the adsorption mechanism. The experimental data of isotherm adsorption will be examined by the Freundlich adsorption isotherm equation. A fixed-bed BOF slag column was also conducted in the continuous adsorption experiment to obtain the breakthrough curve of adsorption of acid blue 9 by BOF slag.

The batch experiments were conducted using a jar-test machine (Model JT 6, J.K. Mechanical Cop., Taiwan, R.O.C.). The samples were agitated at 150 rpm at room temperature (23±2℃). The equilibrium time required for the maximum adsorption of acid blue 9 onto the adsorbent was determined by analyzing acid blue 9 concentration after 0, 1, 2, 3, 4, 6, 8 and 16 h contact time.

Experiments were conducted to determine the pH range at which the maximum adsorption of acid blue 9 takes places on the adsorbent. The pH of the acid blue 9 wastewater was then varied by the adding of 1N H_2SO_4 or 1N NaOH solution. Phosphate buffer was added to the samples to maintain the pH level. The pH was varied from 2.0 to 10.5. In the batch isotherm experiments, different amounts of adsorbent were added into the beaker, which contained 500 mL of acid blue 9 wastewater. The pH of the wastewater was adjusted to an optimum pH value obtained from the previous study. After mixing for the established equilibrium time, the final pH of the reaction mixture was recorded and the wastewater was filtered, centrifuged and analyzed for acid blue 9 concentration.

A Pyrex glass tubing with 20mm i.d., 30cm length was used as a continuous adsorption column. A 200-μm pore size corundum disk was placed inside the column to prevent clogging effluent and also to support the adsorbent material. 20g of adsorbent were packed into the column. A 2-cm layer of glass fiber was put above the adsorbent to prevent a shortcut of flow.

The influent solution was fed to the column from the overhead tank. The amount of the effluent solution passing through the column was continuously recorded. Samples were collected periodically until the effluent concentrations of acid blue 9 were the 95% same as the influent concentrations.

Table 1. The major components of BOF slag.

Material	CaO	MgO	SiO_2	Al_2O_3	FeO	P_2O_5	MnO	Fe_2O_3
Weight %	45 ~ 52	4 ~ 6	13 ~ 16	0.9~1.7	5~20	1.6~2.1	4~7	1~8

Table 2. The physical properties of BOF slag.

Compacted unit weight T/M^3	Water absorption %	Compress-ive strength T/cm^2	MOHS Hardness	Na_2SO_4 soundness loss %	Losangeles abrasion loss %	pH value
2.77	1.29	1.2	7	1.33	17.6	9.6

RESULTS AND DISCUSSION

Figure 1 shows the time profiles of acid blue 9 concentration for adsorption of acid blue 9 on different particles of BOF slag. A surface intraparticle diffusion model, pueudo-first-order adsorption equation was used to analysis the adsorption phenomena. The pueudo-first-order adsorption equation is in the form:

$$dq_t / dt = k_1(q_e - q_t) \tag{1}$$

where k_1 is the rate constant of pueudo-first-order adsorption, q_e denotes the amount of material adsorbed by absorbent at equilibrium and q_t is the amount of adsorption at time t. After definite integration by the initial condition $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, equation (1) becomes

$$log(q_e - q_t) = log\, q_e - \frac{k_1}{2.303}t \tag{2}$$

The rate constant, k_1, can be obtained from the slope of the plot $log(q_e\text{-}q_t)$ vs. t. based on the experimental data. The plot is shown in Figure 2 and the k_1 values for different particle sizes are listed in Table 3. The high correlation coefficients of the kinetic data in the model prove that the model can represent the adsorption phenomena.

Table 3. The calculated k_1 for different particle sizes of BOF slag.

Particle size(mesh)	30~50	50~100	100~140	140~200	<200
k_1	0.785	0.942	0.875	0.650	0.893

Batch kinetic studies showed that an equilibrium time of 3 hours was needed for the adsorption of acid blue 9 on BOF slag (Fig. 1). As shown in Fig. 1, the equilibrium time needed for different sizes of BOF slag is nearly same. The BOF slag has a high adsorption capacity in the first 1-hour adsorption time, especially for particle sizes smaller than 140 mesh. From the experimental data and the intraparticle diffusion model demonstrate that the major adsorption mechanism is the surface intraparticle adsorption. After the adsorption process, the acid blue 9 wastewater showed a significant reduction in acid blue 9 concentration (by 98, 96.5, 94, 91.5, 75% decolorization efficiency for BOF slag < 200 mesh, 140~200 mesh, 100~140 mesh, 50~100 and 35~50 mesh respectively).

The adsorption of acid blue 9 as a function of pH was over a pH range of 2~10 (Figure 3). The optimum pH for the adsorption of acid blue9 onto BOF slag is between 2~4. Because of the basic characteristics of BOF slag, using a pH control system to maintain the pH value to optimum value is necessary.

The adsorption isotherms of BOF slag were analyzed and evaluated using the Freundlich isotherm equation. The non-linear and linearized forms of the equation are as follows :

$$\frac{x}{M} = kC_e^{1/n} \tag{3}$$

$$log\left(\frac{x}{M}\right) = log(k) + \frac{1}{n}log(C_e) \tag{4}$$

Where x is the weight of the acid blue 9 adsorbed; M is the weight of the BOF slag used; C_e is the equilibrium concentration of acid blue 9 remaining in the solution, k and n are the empirical constants, known as capacity factor and intensity factor respectively.

The calculated values for k and n, along with the statistical analysis of the data are presented in Table 4. The high values of correlation coefficient show that the adsorption of acid blue 9 on different particle sizes of BOF slag is described well by the Freundlich isotherm. The effect of particle size on the adsorption was also examined. The surface area controls the adsorption capacity of solid particles; a smaller particle size has the higher surface area than a larger one that makes a smallest particle size (< 200 mesh) has the highest adsorption capacity (Fig. 4).

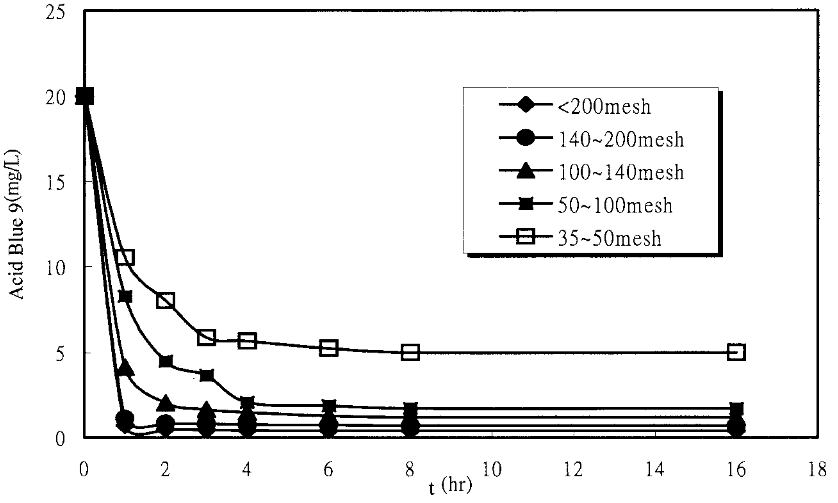

Figure 1. The time profiles of acid blue 9 concentration for adsorption of acid blue 9 on different particles of BOF slag (20 mg/L acid blue 9, 50 g/L BOF slag, pH=9.8)

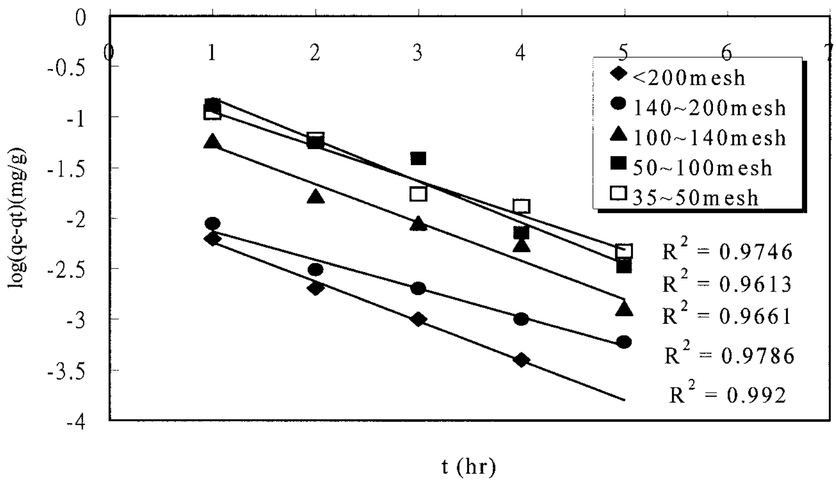

Figure 2. The kinetics of pueudo-first-order adsorption equation for differsnt particle sizes of BOF slag. (20 mg/L acid blue 9, 50 g/L BOF slag, pH=9.8)

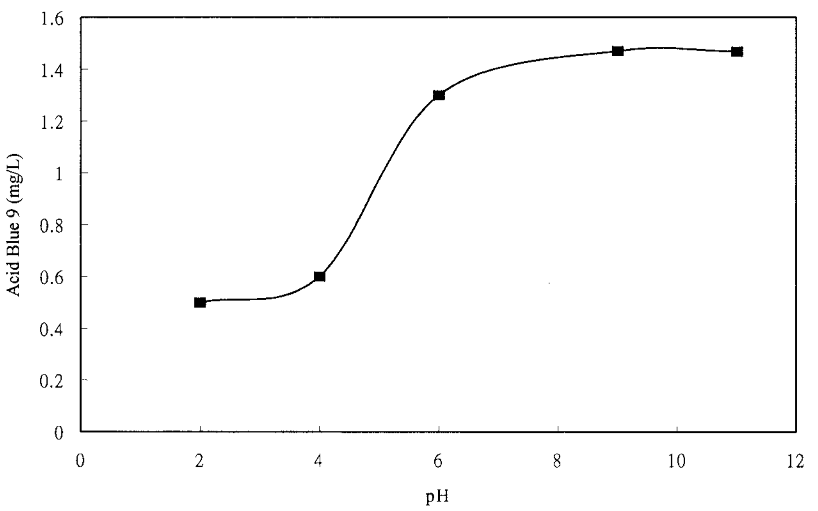

Figure 3. The pH effects on the adsorption of acid blue 9 by BOF slag (50g/L, 100~140 mesh BOF slag, 20mg/L acid blue 9)

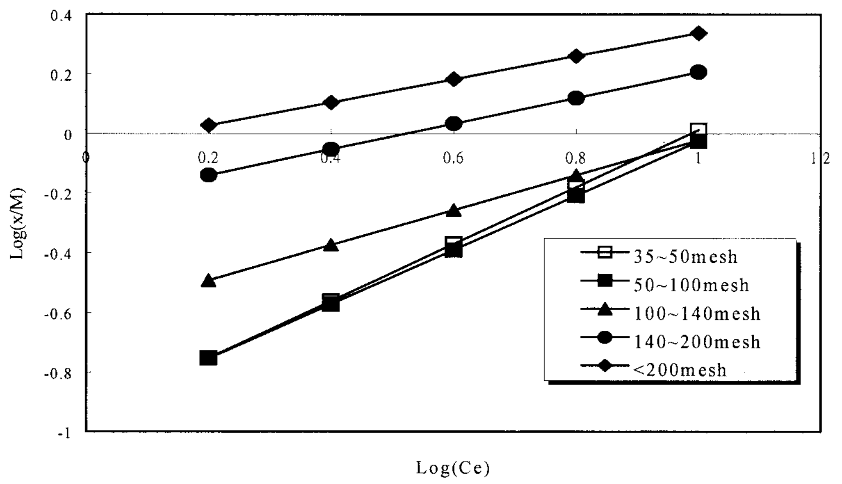

Figure 4. The particle size effects on the isotherm adsorption of acid blue 9 by BOF slag50g/L BOF slag, 20 mg/L acid blue 9)

Desorption of acid blue 9 from saturated BOF slag on leaching with water was also conducted. A maximum concentration of acid blue 9 with 1.0 mg/L was leached from the saturated BOF slag. Increasing the amount of BOF slag did not result in increasing desorption of acid blue 9.

Table 4. The calculated k and n values in the Freundlich isotherm equation and the variance of the equation

	n	k	R^2
30~50 mesh	0.72	0.086	0.9664
50~100 mesh	0.76	0.18	0.9898
100~140 mesh	1.28	0.99	0.9468
140~200 mesh	2.88	2.20	0.9985
< 200 mesh	1.92	2.10	0.9896

A continuous column adsorption study was also performed to establish data on the isotherm adsorption that would be observed in the column application. The continuous column adsorption experiment was conducted using 20 g of BOF slag with 50~100 mesh and 15 mg/L influent concentration of acid blue 9. The influent flow rate was 1.27mL/min. The experimental data showed that the throughout volume for the exhaustion point with 0.95 of the initial concentration of acid blue 9 is 900mL (Fig. 5). The adsorption capacity of the BOF slag in the continuous adsorption, in terms of micrograms of acid blue 9 adsorbed per gram of BOF slag, was obtained by dividing the total weight of acid blue 9 adsorbed by the total weight of BOF slag used. The calculated value is 0.73 mg/g. For comparison purpose, the capacity was also determined from the isotherm adsorption study at an equilibrium concentration of 14.25 mg/L. The value is 0.9 mg/g which is nearly same as the value in the continuous column adsorption.

A kinetic approach which derived by Thomas was also used for scale-up purpose dependent on the breakthrough curve of adsorption of acid blue 9 by BOF slag. The Thomas equation is as follows (Reynolds and Richard 1996):

$$\frac{C}{C_0} \cong \frac{1}{1+e^{\frac{k_1}{Q}(q_0 M - C_0 V)}} \tag{3}$$

where C=effluent solute concentration; C_0=influent solute concentration; k_1=rate constant; q_0=maximum solid-phase concentration of the sorbed solute; M=mass of the adsorbent; V=throughput volume; Q=flow rate.

Equation 3 can be rearranged as

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_1 q_0 M}{Q} - \frac{k_1 C_0 V}{Q} \tag{4}$$

From equation (4), it can be seen that this is a straight-line equation of the form $y = ax + b$ with $y = \ln(C_0 / C - 1)$, $x = V$, $a = -k_1 C_0 / Q$, $b = k_1 q_0 M / Q$.

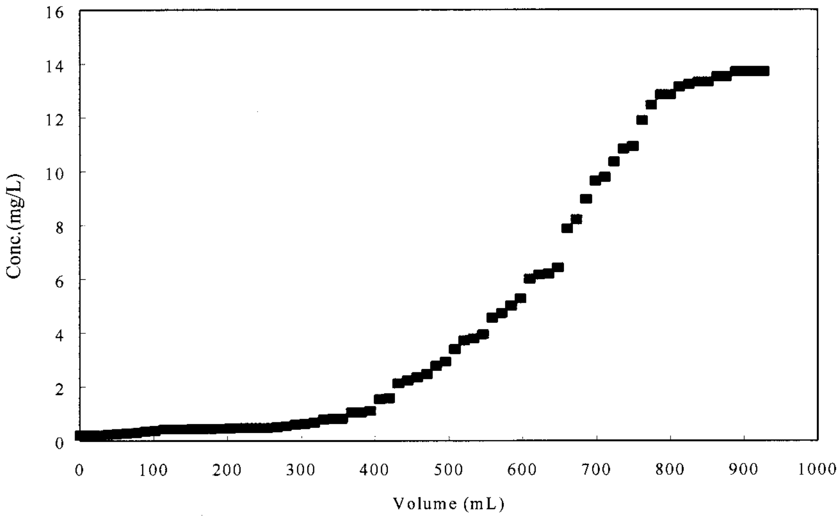

Figure 5. Continuous adsorption of acid blue 9 by BOF fixed-bed column (20g, 100~140 mesh BOF slag, 15mg/L influent acid blue 9)

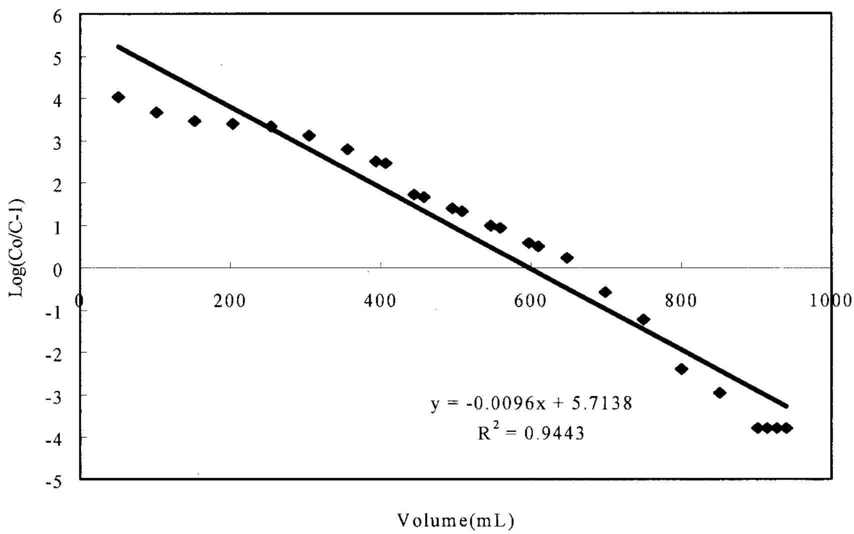

Figure 6. The plot for Thomas kinetic equation

After reducing the data from breakthrough curve, the plot for the Thomas kinetic equation is shown in Figure 6. The calculated rate constants, k_1 and q_o, are 13.54 l/kg-sec and 0.45×10^{-4} kg/kg. It is believed that the calculated data can be used in the designing of a fixed-bed column.

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