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Adsorption of Acid Black 1 Wastewater by Basic Oxygen Furnace Slag

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Effluent streams, especially those from textile manufacturing facilities using dyeing process, can be highly colored even though they are considered to be non-toxic. Due to the stability of dyes, conventional biological treatment methods for industrial and municipal wastewater are ineffective for decolorizing such effluent streams, resulting many times, in an intensely colored discharge from water treatment facilities. This has led to the study of other 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. However, its high initial cost and the need for a costly regeneration system make it less economically viable as an adsorbent. Cost effectiveness, availability and adsorptive properties, are the main criteria for choosing an adsorbent to remove organic compounds. 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 (Viraraghavan and Alfaro, 1998). In this research, a waste material, basic oxygen furnace slag, is used as an adsorbent.

Steel-making plants that use blast furnace generate large quantities of solid residues as final waste byproduct, basic oxygen furnace slag (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 blast furnace is over 14000°C 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.

This research affords the opportunity to study the adsorption process of dye wastewater using the byproduct of steel-making plants. The objectives of this research were to demonstrate BOF slag as an alternative adsorbent; to investigate the equilibrium sorption characteristics of dye chemical, acid black1, using BOF slag.

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MATERIALS AND METHODS

The sorbent used in this research was BOF slag, which is the final byproduct of steel-making plants of China Steel Corporation (CSC). It 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 and 140-200 mesh). This was dried at 103°C h to remove water. The heated product was cooled and stored in a desiccator.

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 %	Compressive 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

Acid black 1 (Naphtol blue black, $C_{22}H_{14}N_6O_9S_2Na_2$, FW616.49, 85%) was obtained from Fisher Scientific, Springfield, NJ. Acid black 1 has the highest absorbency at 628 nm. A uv/vis spectrum photometer (Hitachi uv/vis spectrum photometer 5342) was used to measure the absorbency of acid black 1 at 628 nm. The concentration of acid black 1 used in the experiment is 20 mg/L.

The 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±20°C). The equilibrium time required for the maximum adsorption of acid black 1 onto the adsorbent was determined by analyzing acid black 1 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 black 1 take places on the adsorbent. The pH of the acid black 1 wastewater was then varied by the adding of 1N H_2SO_4 or 1N NaOH solution. Phosphate buffer was added to the samples to maintam 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

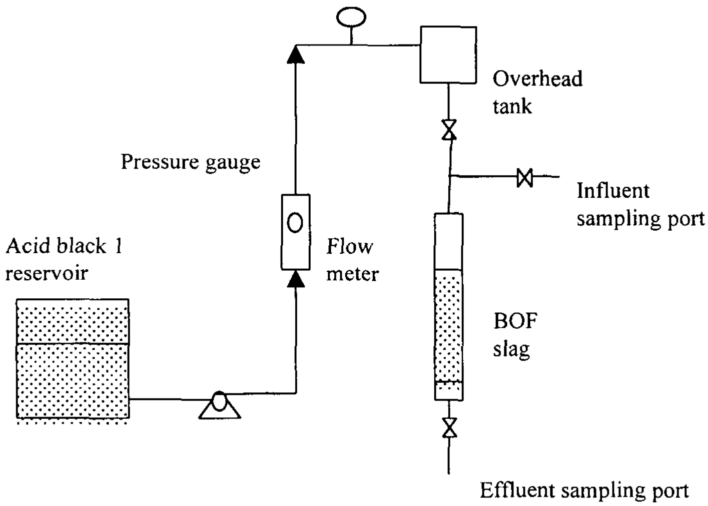

Figure 1. The schematic diagram of the continuous column test

the beaker, which contained 500 ml of acid black 1 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 black 1.

A schematic diagram of the continuous column test is shown in Figure 1. The column is a pyrex glass tubing with 20mm i.d., 30cm length. 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 were the same as the influent concentrations.

RESULTS AND DISCUSSION

Batch kinetic studies showed that an equilibrium time of 3 h was needed for the adsorption of acid black 1 on BOF slag (Fig. 2). As shown in Fig. 2, the equilibrium time needed for different sizes of BOF slag is nearly same. After treatment with BOF slag, the acid black 1 wastewater showed a significant increase in pH (pH = 10.1 ± 0.2), a significant reduction in acid black 1 concentration (by 84, 78, 71, 70% for BOF slag < 200 mesh, 140~200 mesh, 100~140 mesh and 50~100 mesh respectively). The adsorption of acid black1 as a function of pH was over a pH range of 2-10 (Fig. 3). The optimum pH for the adsorption of acid black1 onto BOF slag is 2-4. Because of the basic characteristics of BOF slag, using a pH control system to adjust the pH value to optimum value is necessary.

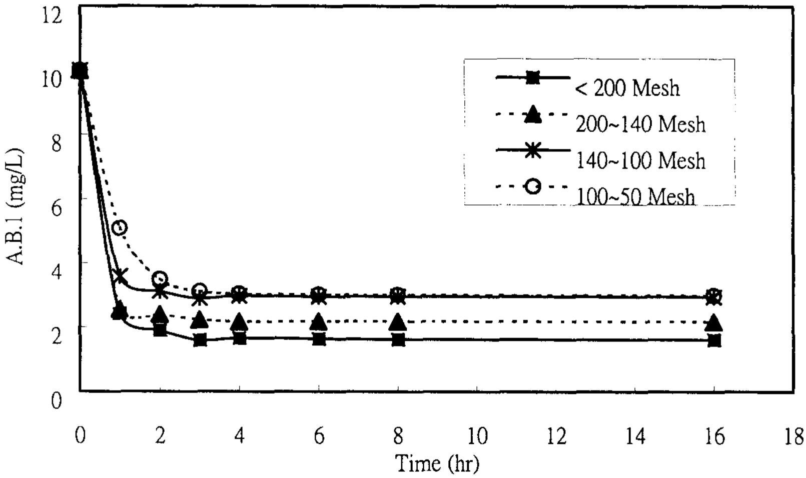

Figure 2. The equilibrium time needed for the adsorption of acid black 1 on BOF slag (10 mg/L, 2 g/L BOF slag, pH = 9.8±0.2)

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

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

$$\log\left(\frac{x}{M}\right) = \log(k) + \frac{1}{n}\log(C_e) \tag{2}$$

Where x/M is the weight of the acid black1 adsorbed; M is the weight of the BOF slag used; C_e is the equilibrium concentration of acid black 1 remaining in the solution, k and n are the empirical constants, known as capacity factor and intensity factor respectively. The data were fit into the Freundlich adsorption isotherm equation. Calculated values for k and n, along with the statistical analysis of the data are presented in Table 3. The high values of correlation coefficient show that the adsorption of acid black 1 on different particle sizes of BOF slag is described well by the Freundlich isotherm (Table 3 and Fig. 4). The effect of particle size on the adsorption was also examined. The surface area controls the adsorption capacity of solid particles (Schure, et al., 1985); 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).

Desorption of acid black 1 from saturated BOF slag on leaching with water was also conducted. A maximum concentration of acid black 1 with 1.5 mg/L was leached from the saturated BOF slag. Increasing the amount of BOF slag did not result in increasing desorption of acid black 1.

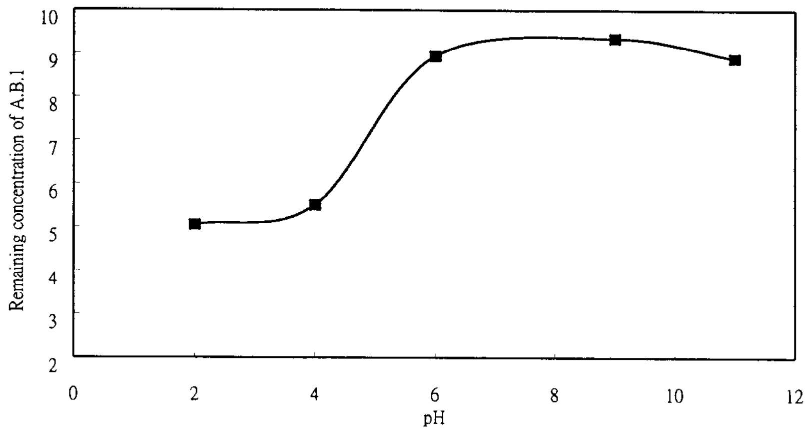

Figure 3. The pH effects on the adsorption of acid black 1 by BOF slag (100~140 mesh BOF slag 2 g/L, 20 mg/L acid black 1)

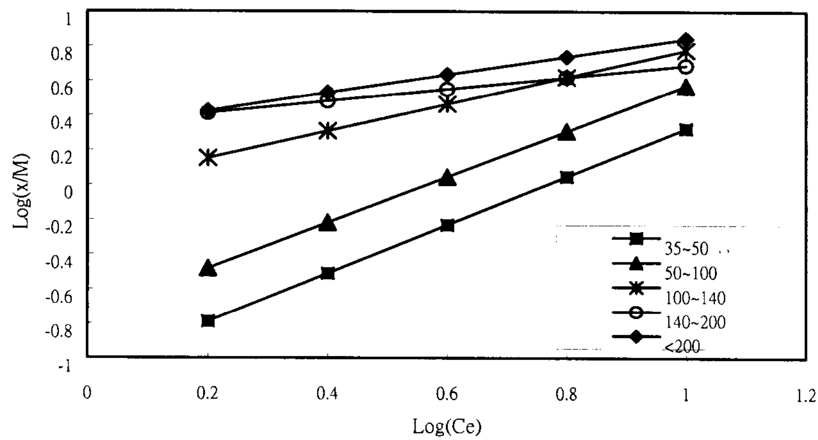

Figure 4. The particle size effect on the isotherm adsorption of acid black 1 by BOF slag (4 g/L BOF slag, 20 mg/L Acid Black 1, pH=3.5±0.2)

Table 3. The calculated values of k and n in the Freundlich isotherm equation and the variance

	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

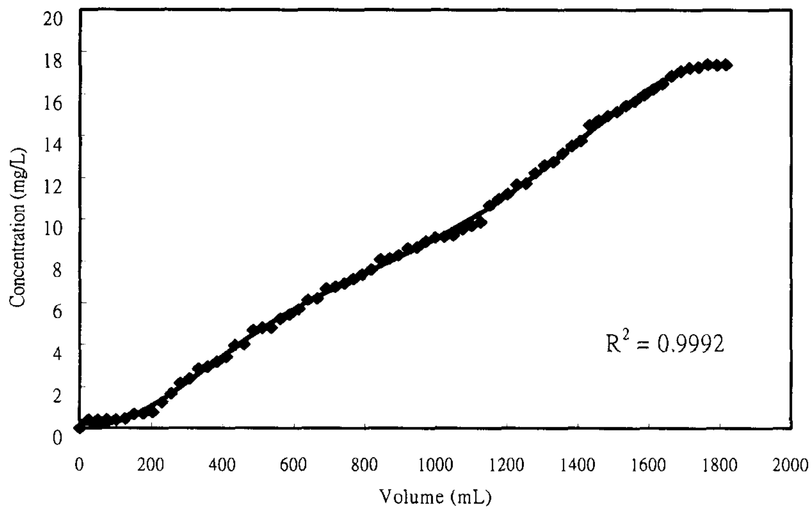

Figure 5. Fix-bed breakthrough profile for acid black 1 by BOF slag (20 g BOF slag, 20 mg/L acid black 1)

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 20 mg/L influent concentration of acid black 1. Figure 5 indicates that a nearly linear breakthrough was observed in the continuous adsorption. The adsorption capacity of the BOF slag in the continuous adsorption, in terms of micrograms of acid black 1 adsorbed per gram of BOF slag, was obtained by dividing the total weight of acid black 1 adsorbed by the total weight of BOF slag used. The calculated value is 1.74 mg/g. For comparison purpose, the capacity was also determined from the isotherm adsorption study at an equilibrium concentration of 20 mg/L. The value is 1.73 mg/g which is nearly same as the value in the continuous column adsorption.

REFERENCES

Banerjee K, Cheremisinoff PN, Cheng SL (1995) Sorption of organic contaminants by fly ash in a single solute system, Environ Sci Technol, 29:2243-2251.

Darwish NA, Halhouli KA, Aldhoon NM (1996) Adsorption of phenol from aqueous systems onto spent oil shale, Sep Sci Technol, 391:705-710.

Davis RJ, Gainer JL, O'Neal G, Wu IW (1994) Photocatalytic decolorization of wastewater dyes. Wat Environ Res, 66(1):50-53.

Jun S, Chung KH, Moon CH (1996) Adsorption of Cadmium species on montmorillonite investigated by 113Cd NMR spectroscopy. Environ Technol, 17:655-661.

Viraraghavan T, Alfaro FdeM (1998) Adsorption of phenol from wastewater by peat, fly ash and bentonite, J of Haz Mat, 57:59-70.

Schure MR, Soltys PA, Natusch DF, Mauney T (1985) Surface area and porosity of coal fly ash, Environ Sci Technol, 19:82-86.