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Removal of Dyes from Aqueous Solution by Sorption with Coal Fly Ash

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ABSTRACT

The use of coal fly ash (FA), a massive byproduct of coal-fired power plants, for removal of dyes, methylene blue (MB) and rhodamine B (RB), from aqueous solution has been studied. Eight different types of FAs obtained from power plants utilizing Australian, Chinese, Colombian (3 types), Indonesian, Philippine and Thailand coals were employed as adsorbent materials of the dyes. Batch experiments were performed by contacting 1.0 g of FA and 50 mL of MB or RB aqueous solution of desired concentration with continuous stirring at various pH and temperature of 25 ºC. The effects of reaction time, pH of solution, and initial concentration of dye on the adsorption of MB and RB were studied. The adsorption equilibrium was established within a few minutes in both MB and RB adsorption with a Colombian FA. Some of other FAs require 30 -60 min to attain the adsorption equilibrium for both dyes and more than 20 hrs required with Thailand FA. The adsorption of MB increased slightly and linearly with increasing the solution pH. In the RB adsorption, the maximum adsorption was observed between pH 2.8 and 4.5. The adsorption capacity depends significantly on the chemical and/or physical characteristics of individual FA. The adsorption capacity of MB was found more than 2.0×10^{-5} mol/g and 1.6×10^{-6} mol/g for a Colombian FA and Thailand FA, respectively. The adsorption capacity of RB was smaller than that of MB for all the FAs studied. This study demonstrates that FA is an effective adsorbent for the removal of dyes from aqueous solution and the possibility of using FAs for a simple and inexpensive method of removal of color from wastewaters.

INTRODUCTION

Discharge of colored wastewaters from various industries such as textile and dyeing, pulp and paper, and food process industries is currently a major problem for environmental management especially in developing countries. One of the most effective techniques for removal of color from such wastewaters is sorption by activated carbon[1-3]. However, owing to expensive price of it, the use of activated carbon for removal of color from wastewaters is limited. In recent years, many studies have been carried out to find out inexpensive alternatives, i.e. peat, clay, steel plant slag[4], and bagasse fly ash[5], etc. Some kinds of FAs have also been studied as adsorbents for removal of dyes from aqueous solution[4,6]. One of the main subjects today is to find some efficient utilization of FAs instead of disposing them. Concerning to this, we have reported the utilization of FA for removal of phosphate from aqueous solution by crystallization as hydroxyapatite[7]. We are studying the utilization of FA for environmental protection. In this study, the adsorption of basic dyes, methylene blue (MB) and rhodamine B (RB), on various FAs in order to find out the possibility of using FA for a simple and inexpensive method of color removal from wastewaters.

EXPERIMENTAL

Materials

Eight different kinds of fly ashes (FAs) were used in this study. FAs of Australian, Chinese and Philippine coal were obtained from Calaca coal-fired power plants in the Philippines. Three kinds of Colombian FAs were supplied from power plants in Colombia, i.e., Thermopaipa, Thermozipa and Themotasajero. Thailand FA was obtained from Mae Moh power plant in Thailand and Indonesian FA was from the power plant in Indonesia. All the FAs were dried at 107 ºC in an oven for 24 h and stored in a decicator before use. Methylene blue (MB) and Rhodamine B (RB) supplied from Wako Pure Chemicals, Japan were used as obtained. All other chemicals used in this study were reagent grade. Water purified by a Barnstead RO-pure and NANO-pure system was used for preparing all the solutions.

Chemical Composition of fly ashes

Chemical composition of fly ash samples was determined by ICP-AES after microwave digestion with HNO_3 and HF mixed acid. The reliability of the analyses was confirmed by two standard reference materials of fly ash, 1633a distributed by NIST, USA and JCFA-1 supplied by Japan Geological Survey.

Adsorption studies

Stock solutions of dyes (1.00×10^{-3} mol/L) were prepared by dissolving accurately weighed amount of individual dye in water and subsequently diluted with water to the required concentration. Adsorption experiments were carried out with 125 mL Erlenmeyer flasks in a thermo-regulated water bath at 25 ºC. A 50 mL of dye solution of known initial concentration was contact with a required dose of FA at a constant stirring of c.a. 200 rpm by a magnetic stirrer. After a specified stirring time period, the reaction mixture was vacuum filtered and the pH of the filtrate was measured. Then the dye concentration in the filtrate was determined by measuring absorbance at the wavelength of maximum absorption (663 nm for MB and 554nm for RB) using a Hitachi model U-3200 spectrophotometer. The pH of solutions was adjusted by adding either HCl or NaOH solution. The percentage removal of the dye and amount of adsorbed (mol/g) were calculated by the following relationships:

$$\text{Percentage removal} = 100\,(C_i - C_f) / C_i \qquad (1)$$

$$\text{Amount of adsorbed} = 50\,(C_i - C_f) / 1000\,m \qquad (2)$$

where C_i and C_f are the initial and final concentrations (mol/L) of the dye, respectively and m is the mass of FA (g) dosed.

RESULTS AND DICUSSION

Chemical Composition of fly ashes

The major element composition of the respective FAs as oxides is shown in Table 1. The composition is considerably different depending on the place of original coal production. The pH of the leachate solutions after 1 day stirring of 50 mL of water with 1 g of individual FAs were 3.8, 5.1, 6.5, 6.5, 10.5, 11.1, 11.6 and 12.0 for FA of Colombia (Zipa), Indonesia, Australia, Colombia(Paipa), Colombia(Tasajero), Thailand, China and Philippine coal, respectively.

Table 1. Major element composition of FAs as oxide (wt. %)

FA Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO
Australia	50.78	31.28	4.87	2.58	0.73	0.17	0.49	2.47	0.034
China	43.52	20.53	10.47	2.52	8.26	1.19	1.25	0.91	0.149
Colombia(Paipa)	54.03	21.69	4.25	0.62	0.71	0.31	1.24	1.09	0.015
Colombia(Zipa)	41.41	16.82	16.71	0.59	0.46	0.32	1.25	0.83	0.088
Colombia(Tasajero)	57.87	24.89	8.03	0.53	1.06	0.24	101	1.26	0.021
Indonesia	34.21	15.19	5.91	5.61	13.52	6.88	1.14	0.71	
Philippine	46.16	31.91	8.67	1.52	6.85	1.47	0.85	1.62	0.109
Thailand	51.17	25.15	8.57	1.89	5.82	0.36	2.73	0.69	0.067

Removal of Dyes with Fly Ashes

Effect of reaction time

The relation between removal of dyes and reaction time were studied to see the rate of dye removal. Figure 1 depicts the effect of reaction time, i.e., stirring time, on the removal of MB with various FAs. Because of extremely slow equilibrium attainment with Thailand FA, the data with Thailand FA are not included in Figure 2. As seen in Figure 2, MB adsorption equilibrium was established within a few min with Colombia (Paipa) FA. Some of other FAs require 30min to 60 min to attain the adsorption equilibrium whereas FAs of Indonesia and Philippine coals need 3 hr or more to attain the equilibrium. It takes more than 20 hr for the equilibrium attainment with Thailand FA. Similar results were obtained for the adsorption of RB. However the longer time is required to attain the adsorption equilibrium of RB compared to that of MB for individual FAs.

Effect of pH

The effect of pH of the dye solution on the removal of dyes with various FAs were determined at fixed concentration, 2.0 x 10^{-4} mol/L, of dyes over a pH range of 1.0 – 11.0. The effect of pH on the adsorption of MB was not significant for all the FAs studied. The amount of adsorption of MB on the individual FA was slightly increased with increasing the solution pH. On the other hand, the effect of pH on the adsorption of RB was different from that of MB. The effect of pH on the adsorption of RB is shown in Figure 2. Although the shape of the adsorption curve is different among individual FAs, the maximum adsorption of RB was observed between pH 2.8 and 4.5 for most of FAs. Both in the acidic and basic pH regions of the maximum adsorption pH, the amount of RB adsorption decreased.

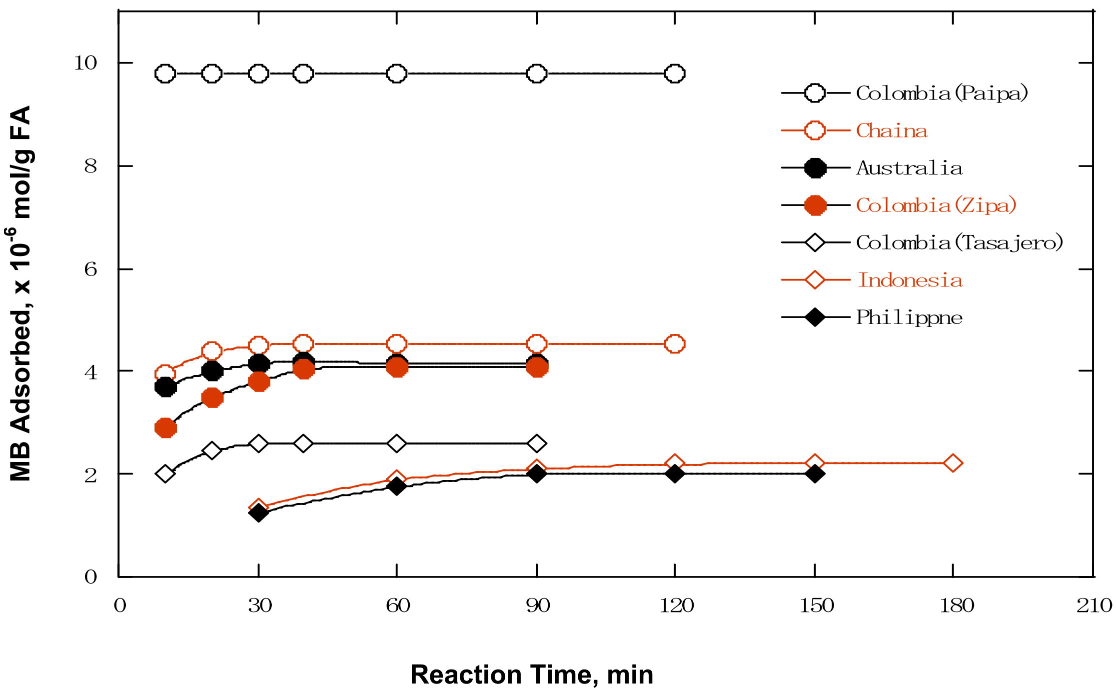

Figure 1 Removal of Methylene Blue from Aqueous Solution by Fly Ashes as a Function of Reaction Time

1 g of FA is dosed into 50 mL of 2 x 10^{-4} mol/L MB solution

Effect of Initial Dye Concentration

The effect of initial concentration of MB or RB on the removal of the dye with various FAs was studied to obtain the adsorption capacity. Figure 3 is the plot of the amount of MB removed per gram of individual FAs against initial MB concentration. As seen in Figure 3, the smooth curve approaches the plateau region with increasing the initial MB concentration for individual FAs. This plateau value represents the adsorption capacity for individual FAs. Although most of the curves in Figure 3 were still increasing, we did not perform the experiments at the initial MB concentration higher than 1.0 x 10^{-3} mol/L due to experimental difficulty. The results in Figure 3 indicate that the adsorption capacity of MB varies from more than 2.0 x10^{-5} mol/g (Colombia (Paipa)) to 1.6 x 10^{-6} mol/g (Thailand). The reason is not clear at this moment for this large difference of

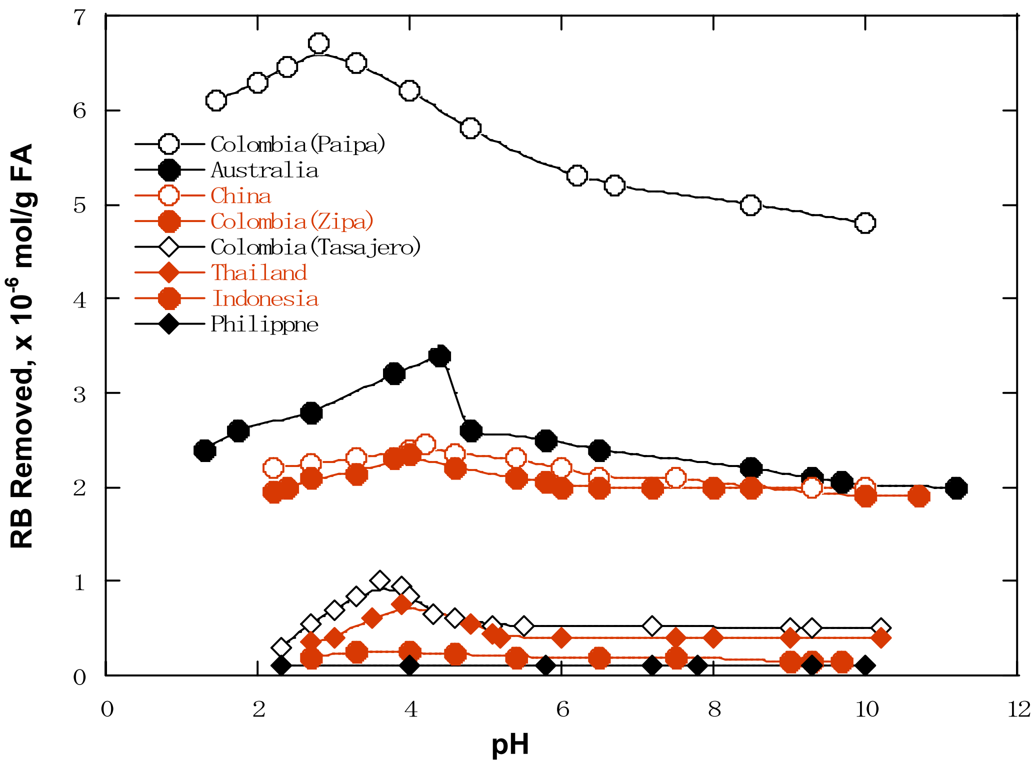

Figure 2 Effect of pH on Rhodamine B Removal by Fly Ashes

1 g of FA is dosed into 50 mL of 2x10^{-4} mol/L RB solution
pH of the solution was adjusted by adding HCl or NaOH

adsorption capacity occurs among the FAs. Similar results were obtained for the experiment of effect of initial RB concentration on the removal of RB with various FAs. However the adsorption capacity of RB was smaller compared to that of MB for individual FAs. For example, the capacity was 8.0 x 10^{-6} mol/g and 2.5 x 10^{-7} mol/g for Colombia (Paipa) and Thailand FA, respectively.

CONCLUSION

Removal of dyes, MB and RB, from aqueous solutions by sorption with various types of FAs has been experimentally determined. The adsorption behavior strongly depended on the characteristics of individual FAs. The adsorption capacity of MB varied from more than 2.0 x 10^{-5} mol/g (Colombia (Paipa) FA) to 1.6 x 10^{-6} mol/g (Thailand FA) among the FAs tested. The adsorption capacity of both MB and RB were high enough over a wide pH range between 1.0 and 11.0. These findings indicate that FA could be employed as an effective and inexpensive adsorbent for the removal of dyes and color from water and wastewater, in particular for the removal of MB and RB.

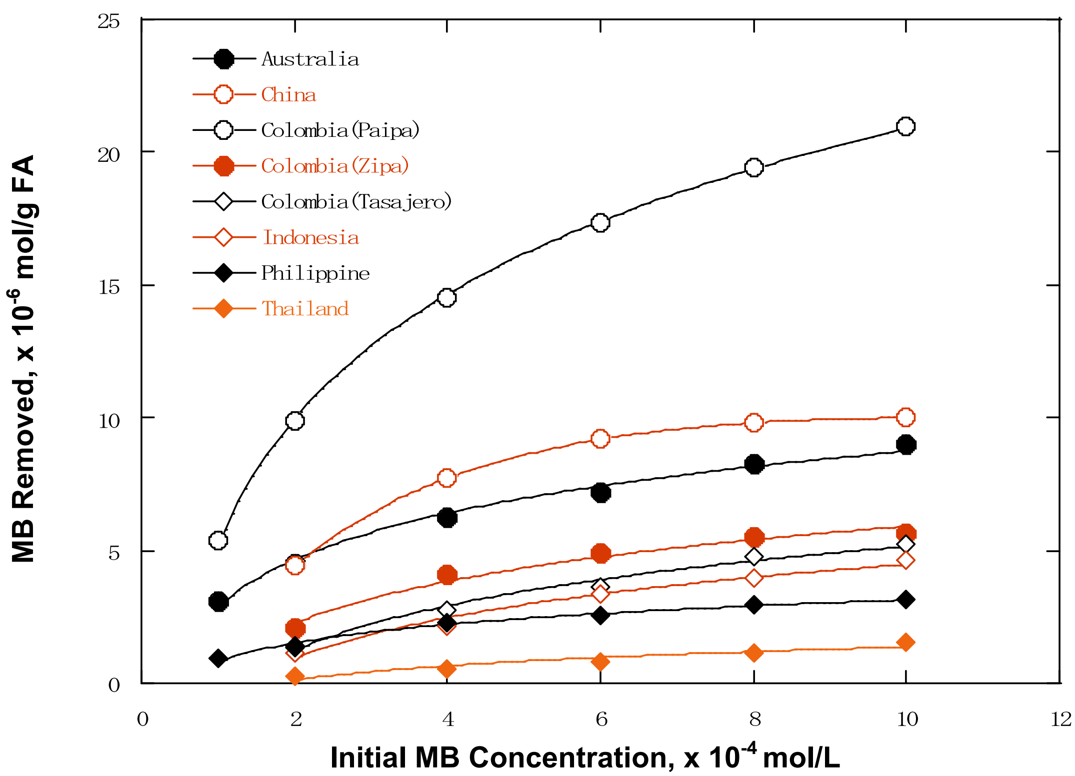

Figure 3 Relation between MB Removal and Initial MB Concentration

1 g of FA is dosed into 50 mL of MB solution

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