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Cationic dye removal from aqueous solution by waste biomass produced from calcination treatment of rice bran

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ABSTRACT

Biomass-derived adsorbents, prepared from rice bran (RB) and treated by calcination at 600, 800, and 1000 °C (RB600, RB800, and RB1000), were characterized in terms of their properties. The adsorption of methylene blue (MB) and crystal violet (CV) on the biomass adsorbents was evaluated. The amount of MB and CV adsorbed was related to the physical properties of the adsorbent. For both dyes, the adsorption capacity increases with time, and the equilibrium time is about 8 and 48 h for uncalcined RB and RB1000, respectively. The adsorption kinetics of dyes is better described by a pseudo-second-order kinetic model. Moreover, the amount of MB or CV adsorbed onto uncalcined RB decreased with increasing temperature, whereas adsorption onto RB1000 increased with increasing temperature. The enthalpies implied by the temperature dependence were $\Delta H = -4.89$ to -54.77 kJ/mol and 11.13–50.21 kJ/mol, for uncalcined RB and RB1000, respectively, which suggested that the adsorption of the dyes onto uncalcined RB or RB1000 should be regarded as physical adsorption, or between physical adsorption and chemical adsorption but dominated by physical adsorption. The equilibrium data of dyes fitted well to the Freundlich adsorption isotherm models. The amount of dyes adsorbed onto uncalcined RB or RB1000 increased at approximately pH 6.0 or 10.0, respectively, which suggests that MB and CV were adsorbed on the surface of the adsorbent through interactions between the electrons of the negatively charged adsorbent surface and the cationic dyes in solution.

Introduction

Currently, synthetic dyes are extensively used in the pharmaceutical industry and other industries such as paper and textile. Most of these dyes are difficult to decolorize due to their complex structures and synthetic origins [1,2]. The effluents that contain the dyes are highly colored and cause serious water pollution. Today, there are more than 10,000 dyes with different chemical structures available commercially. Dyes are broadly classified as anionic, cationic, and non-ionic, depending on the ionic charge on the dye molecules. Cationic dyes are more toxic than anionic dyes [3]. This is because cationic dyes can easily interact with negatively charged cell-membrane surfaces, enter into cells, and concentrate in the cytoplasm, which can lead to health problems. Therefore, dye pollution, mostly in industrial wastewater, has become an increasingly major environmental problem [4]. Methylene blue (MB) and crystal violet (CV) are two dyes that have been shown to have harmful effects on living organisms after short periods of exposure [5]. MB, a cationic dye, often serves as a model compound for removal of dyes and organic contaminants from aqueous solution. MB can have some harmful effects on human beings [6,7]. CV is harmful by inhalation, ingestion, and through skin contact, and has also been found to cause cancer and severe eye irritation in human beings [8].

The adsorption process is widely used in wastewater treatment, with the advantages of simplicity in operation, low cost, and insensitivity to toxic substances or high sensitivity to toxic substances relative to other separation methods, such as chemical precipitation, membrane processes, oxidative degradation, photocatalytic degradation, sonochemical degradation, electrochemical degradation, and integrated chemical–biological degradation [9]. These methods possess drawbacks due to of their inapplicability to large scale units along with both energy and chemical intensiveness. Moreover, activated carbon is an effective but expensive adsorbent due to its high costs of manufacturing. It is also cannot be used treat a large quantity of effluents because of economic consideration.

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Recently, attention has been focused on the development of low-cost adsorbents for the treatment of wastewater. Many low-cost adsorbents (some crude lignocellulosic materials) have been used for the removal of dyes from aqueous solution, which included bagasse pitch, banana pitch, coir pitch, apple pomace, wheat straw, corncob, barley husk, kudzu, pine sawdust, peanut hull, and kohlrabi peel [10–18], but there is still a need for adsorbents which are cheap, easily available, and efficient.

Rice bran (RB), the outer shell of the rice grain, is abundantly available as a byproduct of the rice-milling industries and creates potential environmental problems. The annual generation of RB is estimated to be around 120 million tons, accounting for about one-fifth of the annual gross rice production throughout the world. Any possible use of the RB generated will yield economic, as well as environmental dividends [19,20]. These materials are pyrolyzed or carbonized under an inert atmosphere to remove volatile organic constituents, leaving behind a highly porous carbonaceous residue. Biomass (coffee bran, rice bran, wood biomass and so on) pyrolysis induces the changes of specific surface area and surface functional groups. In general, the calcination treatment leads to an increasing the specific surface area, pore volume, and mean pore diameter of biomass. These reports indicate that the obtained biomass by calcination treatment would be useful as an adsorbent for water purification [21–24]. Therefore, the calcination treatment is one of the most useful treatment for producing the adsorbent which has a high adsorption capability.

Previous reports have demonstrated the feasibility of adsorption by using pyrolyzed or carbonized RB. The low-cost availability of this waste biomass makes it more attractive as a valuable raw material [25,26]. It is easily conceivable that adsorptive treatment using RB or carbonized RB will be recognized as a promising technique due to its ease of operation, simplicity of design, high efficiency, and comparable low cost of application in decoloration process.

Therefore, the object of this investigation was to explore the potential of RB and calcined RB as a low-cost adsorbent for the removal of MB and CV from aqueous solutions. We investigated the kinetics, thermodynamics and isotherms for the adsorption of MB and CV onto RB and calcined RB.

Materials and methods

Materials

MB and CV were purchased from Wako Pure Chemical Industries, Ltd. (Structure of MB and CV is shown in Fig. 1) Adsorbent RB was purchased from The Osaka Daiichi Rice Deal Co., Ltd. The RB was placed in a muffle furnace and the desired temperature (600, 800, 1000 °C) was maintained for 2 h to obtain RB600, RB800, and RB1000, respectively. The RB sample that did not undergo any calcination treatment will be referred to as uncalcined RB hereinafter.

Electron microscopy was carried out with a scanning electron microscope (JSM-5200; JEOL, Japan), and the specific surface area, pore volume, and mean pore diameter of each adsorbent was measured by using a specific-surface analyzer (NOVA4200*e*; Yuasa Ionics, Japan). The amount of silica on the adsorbent surface was measured with an electron-probe microanalyzer (JXA-8530F, FEOL, Japan) with an accelerating voltage of 15.0 kV and beam diameter of 5 μm.

The percentage yield was calculated from the weight of the adsorbent before and after calcination. The pH was measured by the following method: adsorbent (1.0 g) was added to distilled water (50 mL, pH 7.0). The suspension was shaken at 100 rpm for 24 h at 25 °C. The sample was filtered through a 0.45 μm membrane filter and the pH of the filtrate was measured with a digital pH meter (Seven Easy pH, Mettler, Toledo, Japan). The number of surface functional groups of the adsorbent was determined by the following method [27]: adsorbent (0.1 g) was mixed with a solution of NaOH and HCl (0.05 mol/L, 20 mL). The suspension was shaken at 100 rpm for 24 h at 25 °C. The excess base or acid in the filtrate (5 mL, obtained by filtration of the suspension through a 0.45 μm membrane filter) was titrated against HCl or NaOH (0.01 mol/L). Surface acidity or basicity was calculated on the assumption that NaOH neutralizes all of the acid groups and HCl neutralizes all of the basic groups. Special-grade NaOH and HCl were used (Wako Pure Chemical Industries, Ltd.).

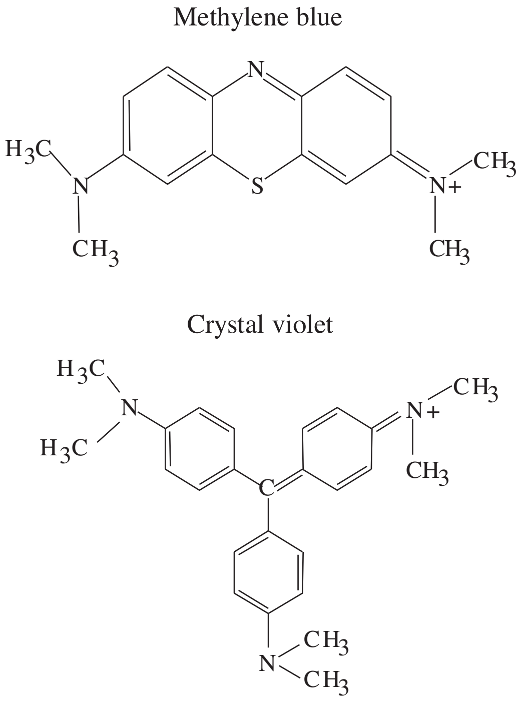

Fig. 1. Structures of methylene blue and crystal violet.

The number of acidic or basic groups on the surface is calculated by Eq. (1):

$$\text{The number of acidic or basic groups on the surface} = \frac{(0.05 \times V_1 - 0.01 \times V_2)}{W} \qquad (1)$$

in which V_1 is the volume of NaOH or HCl (mL), V_2 is the volume of HCl or NaOH (mL), and W (g) is the mass of the adsorbent.

The number of hydroxyl groups was measured by fluoride-ion adsorption [28]. In this procedure, the adsorbent (0.05 g) was added to an aqueous solution of NaF (0.01 mol/L, 50 mL) at pH 4.6. Then the pH was adjusted with aqueous solutions of acetic acid (0.2 mol/L) and acetate buffer (0.2 mol/L). The solution was shaken at 100 rpm for 24 h at 25 °C, and then filtered through a 0.45 μm membrane filter. The concentration of fluoride ions in the filtrate was measured and the number of fluoride ions on the adsorbent was calculated.

The pH_{pzc} (pzc = point of zero charge) of the samples was measured using a method reported previously. An aqueous solution of sodium chloride (0.01 mol/L, 50 mL) was placed in a closed vial. The pH was adjusted to either pH 2 or 12 by addition of an aqueous solution of hydrochloric acid (0.1 mol/L) or sodium hydroxide (0.1 mol/L), respectively. The solutions were agitated at 25 °C for 48 h. The final pH values of the solutions were measured. The pH_{pzc} is the point where the curve pH_{final} versus $pH_{initial}$ crosses the line $pH_{final} = pH_{initial}$.