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Adsorption of Brilliant Green dye from aqueous solution onto red clay

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HIGHLIGHTS

- Brilliant Green (BG) was adsorbed on naturally existing red clay (RC).
- RC possessed large surface area 100.3 m^2/g and pore volume 0.88 cm^3/g.
- The maximum monolayer adsorption of BG on RC was found to be 125 mg/g.
- BG adsorption on RC was found favorable.

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ABSTRACT

This study was aimed at the adsorption of Brilliant Green (BG) dye on naturally existing red clay (RC) through batch adsorption experiment. Adsorbent characterization showed Brunauer–Emmett–Teller surface area 100.28 m^2/g, pore volume 0.88 cm^3/g, and pore diameter 148.2 Å. Batch studies were carried out to investigate the effect of experimental factors such as pH (2–10), particle size (58–150 μm), adsorbent dose (0.3-1.5 g/L), contact time (5–1500 min), initial dye concentration (20–100 mg/L), and temperature (25–65 °C) on the adsorption of BG dye. Langmuir (R^2 = 0.993), Freundlich (R^2 = 0.997), Hansley (R^2 = 0.997) and Redlich–Peterson (R^2 = 0.999) isotherms were fitted to describe the equilibrium of BG adsorption process. Isothermal models showed that BG adsorption was a favorable process on RC. Adsorption kinetics were well fitted by Pseudo-second order kinetic model (R^2 = 0.999). Thermodynamic study revealed that BG adsorption on RC was spontaneous, favorable and physiosorptive. The maximum adsorption capacity of RC was found to be 125 mg/g. These results showed that BG dye can be effectively removed from aqueous solution employing RC as a cheap adsorbent.

1. Introduction

Several industries use dyes to accomplish different kinds of operation. The nature and amount of dyes vary from industry to industry, and from operation to operation. However, textile and leather industries are the biggest consumers of dyes, and hence, the biggest producers of dyeing wastewater in Pakistan [1,2]. According to Auta and Hameed [3], approximately 700,000 metric tons of 100,000 commercial dyes are produced globally, and 1–1.5% (⩽70,000 metric tons) of these dyes is discharged into wastewater [4]. Dyes are broadly categorized into cationic and anionic dyes, whereas the former is considered more toxic than the latter [5]. Thus, dyeing wastewater may damage the ecosystem of receiving water, and the environment in total, due to the carcinogenic, mutagenic, and allergenic characteristics of dyes. The treatment of such a toxic wastewater is necessary to avoid environmental contamination [6].

Several treatment technologies have been developed to decolorize dyeing wastewater. These treatment options include biological [2], physio-chemical [7], membrane filtration [8], ozonation [9] and advanced oxidation [10] and integrated treatment processes [11]. However, these processes face certain technical and economical limitations such as cost and production of sludge [12]. Adsorption process is an innovative and economical alternative due to its performance and ease of operation [13,14]. The target pollutant accumulates at the surface/interface of the adsorbent in aqueous medium. Several process conditions (pH, temperature, ionic strength, adsorbent dose, adsorbate properties) influence the adsorption process. The basic theory of adsorption can be found in the literature [14–16]. Adsorption process can be applied for the removal (~99%) of different types of pollutants such as

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heavy metals, organic compounds and pathogens [14,17]. Among organic pollutants, adsorption has been extensively investigated to treat dyeing wastewater. However, the performance of adsorption process depends on the properties of adsorbents, such as high adsorption capacity, and surface characteristics [14,15]. Activated carbon has been found one of the most prominent adsorbent due to its high surface area and adsorption capacity [3,15,17]. Besides its performance, commercial activated carbon is an expensive adsorbent. Therefore, several researchers are searching for sustainable adsorbents such as agriculture waste. However, these biosorbents require chemical and physical modifications to improve their performance and adsorption capacity [18,19].

Clay based adsorbents have also emerged as promising adsorbents for wastewater treatment [20,21]. Clays possess certain properties which make them an ultimate choice for adsorption process such as low cost, high availability, and environmentally friendly material. Resultantly, clays can substitute expensive activated carbon as well as low performing biosorbents [4,5,22]. These clays can be used either in their natural form or modified with some chemical agent, depending on the target pollutants [4]. Pakistan possesses different types of clays due to its topography. Red clay (RC) is one such material that is abundantly available in some parts of the country. So, RC can also be investigated as an adsorbent like other clay materials [4,20–22]. The adsorption of Brilliant Green (BG) dye on different types of clay materials has been extensively investigated. BG is used as a model cationic dye for adsorption studies to measure sorption efficiency (S%), and adsorption capacity of clay materials [4,5,22]. BG dye posses several health risks which include eye burns, skin irritation, coughing and shortness of breath, nausea, vomiting and diarrhea. It is therefore essential to remove this dye from water [22–24].

This study was aimed at using red clay as an adsorbent to remove BG dye from aqueous solution. The effect of different adsorption factors such as solution pH, adsorbent dose, particle size, agitation speed, initial dye concentration, contact time and temperature, was studied. Kinetic, isothermal and thermodynamic studies of the adsorption process were carried out to understand the equilibrium and mechanism of adsorption process.

2. Materials and methods

2.1. Preparation and characterization of adsorbent

Red clay was collected from the surrounding areas of Jhelum, Pakistan. The adsorbent was crushed, and was ground using lab scale ball mill. It was sieved to obtain different particles size to study the effect of particle size. The adsorbent was then dried at 100 °C in oven for 24 h. It was not subjected to any further chemical or physical treatment, and it was stored in sealed jars for further experimentation. The characterization of RC was carried out following the procedures described in literature [25]. The specific surface area and pore diameter were measured by N_2 adsorption isotherm at 77 K using the surface area and pore size analyzer (Quantachrome Nova 1200e, USA) employing the Brunauer–Emmett–Teller (BET) method. The Barrett–Joyner–Halenda (BJH) method was used to calculate the pore distribution for RC. The RC samples were degassed before subjecting to surface analyses. Scanning electron micrographs were recorded by SEM (JSM 5910, JEOL Japan) to obtain visual information about the morphology of RC samples. Fourier transform infrared (FTIR) spectroscopy was carried out using FTIR spectrometer (Jasco, USA) to characterize the type of functional groups present on RC [20]. The point of zero charge (pH_{ZPC}) of the RC was determined using the pH drift method as reported in the literature [24]. A stepwise addition of 0.1 M HCl and/or 0.1 M NaOH solutions were used for pH adjustment.

2.2. Dye solution

Brilliant Green dye (Merck, Germany) was purchased from the market, and was used in this experiment without any further purification. The stock solution (1000 ppm) of BG dye ($C_{27}H_{34}N_2O_4S$, FW: 482.62 and bulk density 500 - 600 kg/m^3) was prepared by dissolving accurately weighed quantity of dye in 1 L of double distilled and deionized water. The experimental solutions of desired concentration were prepared accordingly by diluting the stock solution with distilled water. The concentration of BG dye was measured at λ_{max} = 625 nm [22] using UV–Visible spectrophotometer (PG instrument T60, UK).

2.3. Adsorption studies

Adsorption studies were carried out in batch mode to investigate the effect of experimental factors (pH, adsorbent dose, initial dye conc., contact time and temperature) on the adsorption of BG on RC. The effect of experimental factors such as pH (2–10), adsorbent particle size (58–150 μm), RC dose (0.3–1.5 g/L), contact time (5–1500 min), BG dye concentration (20–100 mg/L), and temperature (25–65 °C), was investigated employing one factor one time approach.

BG experimental solutions (V = 100 mL) were taken in glass flasks (250 mL), and mixed with known amount of RC at predefined experimental conditions. The detail of experimental conditions has been presented for each experiment in the relevant sections of Result and discussion. A common set of experimental conditions, adsorbent dose (m) of 0.4 g/L, dye concentration (C_o) 50 mg/L, contact time (t) 4 h, stirring speed of 100 rpm, pH 7.0 and temperature 25 °C, was used for all the experiments except where stated differently. The solution was then gently agitated in an isothermal shaker to achieve the equilibrium between RC–BG suspensions. After the experiment, the suspensions were centrifuged, filtered to remove RC particles, and residual concentration of BG in the filtrate was determined by spectrophotometer. Sorption efficiency (S%), and adsorption capacity (q) were calculated as followed:

$$S(\%) = (C_o - C_e) \times \frac{100}{C_o} \quad (1)$$

$$q = (C_o - C_e)V/W \quad (2)$$

where C_o (mg/L) is the initial concentration of dye, C_e (mg/L) is the concentration of dye at equilibrium, V (L) is the volume of dye solution, and W (g) is the mass of adsorbent. All the experiments were run in triplicate, and the results were reported as mean ± SD. Adsorption kinetics were investigated in order to find out rate limiting step. This task was carried out by finding rate of BG adsorption as a function of time. The quantity of the dye adsorbed at time t, q_t (mg/g) was calculated using the following equation:

$$q_t = (C_o - C_t)V/W \quad (3)$$

where C_t (mg/L) is the concentration of dye at any time t [22].

3. Results and discussion

3.1. RC characterization

The surface characterization of RC show that its BET surface area is measured to be 100.28 m^2/g, BJH pore surface area 238.5 m^2/g, pore volume 0.88 cm^3/g, and pore diameter 148.2 Å. Further chemical and physical characteristics of RC are given in Tables 1 and 2. SEM micrographs display visual information about the surface morphology of the adsorbent material as shown in