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Decolourization of hazardous brilliant green from aqueous solution using binary oxidized cactus fruit peel

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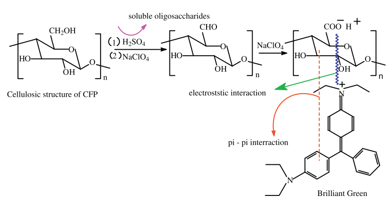
HIGHLIGHTS

- Removal of brilliant green using chemically activated cactus fruit peel.
- Maximum adsorption of BG was observed at pH 3.
- Pseudo-second order and Langmuir model showed the best describe the BG adsorption.
- The magnitude of ΔH° revealed that physical forces were involved in adsorption.

GRAPHICAL ABSTRACT



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ABSTRACT

Binary oxidized cactus fruit peel (CFP) was used as adsorbent for the removal of brilliant green (BG). The prepared adsorbent was characterized by Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and Energy dispersive X-ray (EDAX). Batch adsorption studies were performed as a function of contact time, initial solution pH, initial BG concentration and temperature. Initial solution pH alters the adsorbent surface charge and BG structure and optimum adsorption was found at pH 3. Kinetic analysis revealed that adsorption experimental data was best fitted by pseudo-second order model. The equilibrium adsorption data was found to follow the Langmuir isotherm model and maximum monolayer capacity was found to be 166.66 mg g^{-1} at 20 °C. Thermodynamics of BG adsorption revealed the process was spontaneous and exothermic in nature. The magnitude of enthalpy change (ΔH°) was found to be 25.43 kJ/mol, revealed that physical forces were involved in adsorption of BG onto CFP.

1. Introduction

Dyes are colour organic compounds release in effluent water of many industries, such as textiles, leather, paper, printing, and cosmetics. Discharging dyes into the hydrosphere have long time adverse effect in environment as dyes give water undesirable colour, reduce sunlight penetration and are objectionable for drinking and other uses [1]. Brilliant Green (BG) is widely used as biological stain, dermatological agent, veterinary medicine, and an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus, textile dying and paper printing etc. However, BG have adverse effect to the humans and environment such causes irritation to the gastrointestinal tract and respiratory tract, symptoms include nausea, vomiting and diarrhea while on degradation BG produces, carbon oxides, nitrogen oxides, and sulfur oxides [2–4]. Therefore, wastewater containing BG must be purified before release in the environment.

Various treatments have been applied for the removal of synthetic dyes from wastewaters such as coagulation, flocculation, ion exchange, membrane filtration, photo-catalysis and photo-oxidation. But major drawbacks of these technologies are long operation time, high sludge production, high cost, not eco-friendly etc. [5,6]. Adsorption is enraging as a growing alternative technique for the decolourization of dyes contains effluents. Major advantage of adsorption is use of low cost material epically agricultural based

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biomass. Fruit peels and fruit shells based adsorbents such as pine-fruit-shell [7], jackfruit peel [8], rambutan peel [9], banana peel [10], coconut shell [11,12] etc. have been investigated for the scavenging of dyes and proved to be potential adsorbent.

In last decades, Cactus fruit (*Opuntia ficus-indica)* have attracted attention in food, nutritional and pharmacological science. Cactus fruits are consumed as fresh vegetables, added to casseroles, cooked, canned, or used in salads, syrups, alcoholic drinks, fruit juices and in cheese production [13]. Cactus fruit is highly nutrias and have several medicinal applications such as anticancer, antiviral effect, anti-oxidant properties, anti-diabetic (type II) effect etc. Cactus is widely cultivated in arid and semi-arid parts of Europe, America, Asia and Africa. Its fruit weight ranges from 100 to 150 g (depending on origin, cultivar and edaphic condition) and edible part is pulp covered by the thick peel layer [14]. This fruit peel of cactus is considered as solid waste and has no economic value and use of CFP as an alternative low cost adsorbent will help to reduce the cost of solid waste disposal and environmental contamination.

In the present work, cactus fruit peel was twice oxidized and its potential for the removal of brilliant green (BG) dye was investigated. The kinetics, isotherms and thermodynamics of BG adsorption were investigated to find the rate and nature of adsorption process.

2. Materials and method

2.1. Materials

Brilliant Green (BG) dye [C.I. = 42,040, chemical formula = $C_{27}H_{34}N_2O_4S$, FW = 482.62] was supplied by Koch Light laboratories Ltd. England. The structure of BG is illustrated in Fig. 1. The dye and acid solutions were prepared by dissolving an accurately weighed/volume of BG/acid in de-ionized water.

2.2. Preparation of adsorbent

Cactus fruit peel was collected locally and washed with de-ionized water to remove the dirt and pulp and then dried in an oven at 60 °C. Dried biomass was grind and sieved to get the particle ranges from 75 to 150 μm. Thereafter, 15 g powdered peel was mixed with 100 mL of 1.0 M H_2SO_4 and stirred for 2 h at 80 °C and then filtered and washed with de-ionized water. In presence of H_2SO_4, soluble components of CFP dissolved in acidic solution and CFP surface get oxidized. Filtered material was further oxidized by adding 100 mL of 1.0 M $NaClO_4$ for 18 h at 80 °C. Thereafter, treated powdered peel was filtered and thoroughly washed with de-ionized water, dried at 60 °C and stored for further adsorption studies.

The skin of the fruits peel generally contains cellulose, hemicelluloses, mucilage, gum, proteins, chlorophyll pigments, and pectin etc. [15] and these components are expected to be oxidized during oxidation. But it is very difficult to show the oxidation mechanism for all the components. Cellulose is the one of the most abundant component of fruit feel. Therefore, only oxidation mechanism for cellulosic moiety has been shows in Fig. 1.

2.3. Characterization of CFP

The surface morphology of CFP before and after BG adsorption was evaluated using a Quanta FEG 450, electron microscope (Amsterdam, Netherland). EDAX study was performed to confirm the adsorption of BG onto CFP using energy dispersive analyzer unit (EDAX, Apollo X), attached with scanning electron microscope. FTIR spectra of CFP before and after dye adsorption were recorded using a Perkin Elmer Spectrum 100 FTIR Spectrometer over a range of 650–4000 cm^{-1}. For the determination of point of zero charge (pH_{zpc}), a series of flask containing 10 ml of 0.1 M KCl was prepared and its initial pH was adjusted between 2 and 11.23 using HCl and NaOH. Then, 0.025 g of CFP was added to each solution. These flasks were kept for 24 h at 30 °C and the final pH of the solutions was measured with a pH meter. A graph was plotted between final pH vs. initial pH and pH_{zpc} was determined at $\Delta pH = 0$. [16].

2.4. Batch adsorption study

2.4.1. Equilibrium and kinetic studies

Batch equilibrium adsorption studies were performed by placing 0.025 g of the CFP in 10 mL of dye solution of different initial concentrations ranges from 50 to 500 mg L^{-1} at 20, 30 and 40 °C. Kinetic studies were performed at different concentrations (25, 50, 200 and 500 mg L^{-1}) in a series of conical flask containing 0.025 g of the CFP and 10 mL of BG and samples were collected at different time interval. Then the concentration of BG in the supernatant solution was analyzed using a HACH LANGES DR-6000 UV–Visible Spectrophotomer at maximum wavelength (624 nm). The equilibrium adsorption capacity of CFP for BG was calculated from the relationship:

$$q_e = \frac{(C_o - C_e) \times V}{m} \quad (1)$$

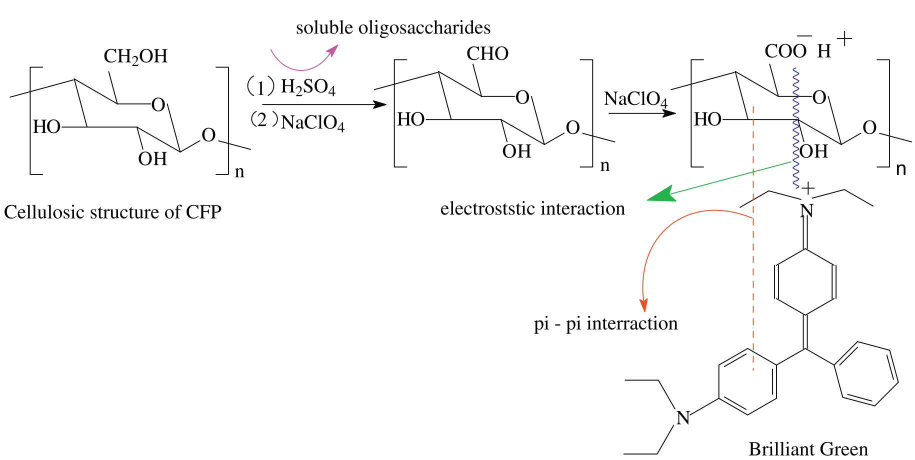

Fig. 1. Proposed oxidation mechanism of CPF and its interaction with BG.