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# Optimization and evaluation of reactive dye adsorption on bottle gourd peel

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ABSTRACT

The potential of bottle gourd peel, an agricultural waste, for adsorption of Reactive red 195-A (RRD) and Reactive blue 222 (RBD) from aqueous solution was evaluated. Batch adsorption experiments were conducted as function of contact time (0–250 min), initial dye concentration (50–200 mg/l), initial pH (2–10), sorbent dosage (0.2–1 g/l) and temperature (303, 313 and 323 K). The Langmuir and Freundlich and Temkin models were used to study the adsorption isotherms. The experimental data fitted well with the Temkin isotherm for adsorption of RRD to both the adsorbents and RBD to formaldehyde treated adsorbent. The maximum adsorption capacities at 303 K were found to be 245.5, 242.4 mg/g for RRD on to formaldehyde and acetic acid treated adsorbents respectively. Not with much significant difference, RBD was adsorbed on to formaldehyde treated and acetic acid treated adsorbent with adsorption capacities 244.9, 245.8 mg/g at 303 K, respectively. The kinetic data were analyzed using pseudo-first-order and pseudo-second-order models and results indicated that adsorption process follows pseudo-second order kinetics with correlation coefficient $R^2 > 0.90$. The thermodynamic analysis provided insights to the endothermic and spontaneous nature of the adsorption process. The results indicated that bottle gourd peel could be used as an alternative to the costly adsorbents used for dye removal.



## 1. Introduction

Synthetic dyes are chemical substances that can attach themselves to various surfaces. Most dyes are organic complex compounds and are highly resistant to degradation. They are extensively used in several industries such as food processing, paper, leather tanning, plastics, cosmetics, textile, and printing ink industries [1]. Furthermore, synthetic dyes also play a major role in groundwater tracing, sewage and water treatment. Their use in different industries lead to their discharge and accumulation in water bodies making them an environmental hazard [2]. It increases the toxicity and chemical oxygen demand (COD) of the effluent and reduces the aesthetic merits and light penetration. Synthetic dyes are also mutagenic and carcinogenic in nature making their removal a necessity [1]. According to the World Bank, 17–20% of the total industrial water pollution is contributed by the textile dyeing and treatment industry. Although, estimates on the volumes of dyes discharged in to the hydrosphere is unavailable it is fairly certain that this practice has deleteriously impacted the environment. Adsorption, coagulation, membrane separation and advanced oxidation are some of the most common methods employed for the removal of dyes from wastewater. Among these, adsorption is considered to be one of the most efficient techniques in modern wastewater treatment [3]. Adsorption is preferred over other methods of remediation due to its flexibility and simplicity of design, low initial cost, insensitivity to toxic pollutants and ease of operation [4]. Many textile based industries employ adsorption as the mode of hazardous organic/inorganic pollutants from effluents. Activated carbon is most sought after adsorbent for the removal of dye. However, a lot of studies have been conducted to replace activated carbon with other materials especially agricultural waste due to the high cost of commercial activated carbon [5]. Fruit and vegetable peels have been hugely favored as a replacement material for activated carbon. Orange, potato, banana and garlic peels are some of the agricultural residues tested and found suitable for adsorption of synthetic dyes from effluents [1,3,6].

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Bottle gourd (*Lagenaria siceraria*) belonging to *Cucumbertacea* family, is an important plant and its fruit is consumed as popular vegetable in Asia. The fruit is fleshy with shiny skin that is usually removed before consumption. Raw juice therapy of the fruit is recommended in India for general health, diuretic, cardiovascular disease control. Since peels are rich in polyphenol oxidase enzyme which is responsible for browning, are generally discarded. Therefore, evaluating the adsorption potential of bottle gourd peel worth noticed. This helps in the waste utilization of the bottle gourd processing plant.

In this study, we studied the efficacy of chemically modified bottle gourd peel powder as a potential adsorbent for the removal of dyes from wastewater. The effect of adsorbent dosage, initial dye concentration, initial pH on adsorption and also the kinetics and equilibrium isotherm studies were evaluated to determine the adsorption capacity of bottle gourd peel.

## 2. Materials and methods

### 2.1. Chemicals and materials

Bottle gourd peel was obtained from a local market in the Navi Mumbai, India. The peels were first washed to remove the adhering dirt and then were dried at 40 °C. The dried materials were crushed and sieved through 40 mm mesh. Reactive red 195-A and Reactive blue 222 dyes used in this study were purchased from Ciba Ltd. All the other reagent used were of analytical grade and purchased from Merck (Germany).

### 2.2. Chemical modification

The peel powder was subjected to chemical modification following two dissimilar strategies:

1. Acidification: About 10 g of the bottle gourd peel powder was mixed with 100 ml of concentrated acetic acid in an ultrasonic processor at 35 KHz. After 30 min, the sorbent was separated and dried in an oven.
2. Formaldehyde Treatment: About of 1 g of dry powder was mixed with 0.2% (v/v) aqueous formaldehyde solution for 24 h at 200 RPM. The biomass was then filtered and dried at 60 °C after washing with distilled water.

### 2.3. Characterization of adsorbent

Textural characterization of chemically modified bottle gourd peel was carried out by N2 adsorption using Autosorb I (Quantachrome Corporation, USA). The surface images the adsorbents of was captured before and after adsorption process by scanning electron microscopy (SEM model: Philips XL30). The experiments employed 100 ml dye solutions (RRD and RBD) with concentration of 100 mg/l at pH 2. About 0.5 g of bio-sorbents were added to these solutions and mixed for 24 h at 200 rpm. Then the peel powders were separated from solution by filtration using Whatman No. 1 filter paper and dried at 50 °C. The peels were then examined by SEM. The surface functional groups of adsorbent were analyzed by FTIR spectroscopy (SHIMADZU IR Prestige 21). The spectra were recorded from 4000 to 400 $cm^{-1}$ with number of scans 45. The point of zero charge (pzc) of the adsorbent was determined by electrolyte addition method [7]. The pH of 0.01 M NaCl solutions were adjusted between 2 and 12 by adding 0.1 N HCl or 0.1 N NaOH. Initial pH was stabilized through removal of gases from the solution by nitrogen sparging. To 50 ml of this solutions, 0.15 g Adsorbent (0.15 g) was added and agitated at 200 rpm at 25 °C for 24 h. After filtration, the pH of the filtrate was measured. The pH at which the difference between final and initial pH is zero is the point of zero charge.

### 2.4. Adsorption studies

The adsorption process for RRD and RBDs on to acidified and formaldehyde treated adsorbents were optimized for various factors such as contact time, initial pH, initial dye concentration, temperature, and adsorbent dosage. The studies were conducted by mixing various amounts of adsorbent (0.2–1 g) in jars containing 100 ml of a dye solution (50–500 mg/l) at various pH (2–10). Experiments to determine the pH optima were conducted by incubating the mixture containing 100 ml dye solution and 0.5 g of adsorbent at 25 °C for 24 h at 200 rpm to attain equilibrium. The initial pH of dye solutions were adjusted using 0.1 N NaOH and 0.1 N HCl. The residual dye concentration was determined in terms of change in absorbance (uQuant spectrophotometer, BioTek, USA). The samples were centrifuged and the absorbance were noted at 600 nm for RBD and at 540 nm for RRD. The results obtained after equilibrium was reached, were fitted to various adsorption isotherms.

Thermodynamics of the adsorption process was also developed under optimized conditions. All the samples were measured in triplicates and the mean values were used for the analyses. The equilibrium adsorption capacity and dye removal% were determined using the following equations:

$$qe = \frac{(Co - Ce)V}{W}$$

$$DyeRemoval(\%) = \left(\frac{Co - Ce}{Co}\right)100$$

where $q_e$ (mg/g) is the equilibrium adsorption capacity while $C_0$ and Ce are the initial and equilibrium dye concentrations (mg/l), respectively. V is the volume of the dye solution (L) and W is the dry weight of the adsorbent (g).

## 3. Results and discussion

### 3.1. Adsorbent properties

The BET surface area, total pore volume and average pore diameter of formaldehyde treated adsorbent were found as 0.2814 $m^2$/g, 0.000856 $cm^3$/g, 15.1 A°. For acetic acid treated adsorbent the BET surface area, total pore volume and average pore diameter were 0.2902$m^2$/g, 0.000813 $cm^3$/g, 15.6 A° respectively.

#### 3.1.1. SEM analysis

SEM image shows the uniform distribution of pores on the adsorbent which gives it a well-defined mesh-like appearance (Fig. 1). The pores appeared to be heterogeneous in nature. On analysis of the SEM images of the adsorbent post adsorption process it was evident that the pores were packed with dyes. The undulate and porous surface of adsorbent turned looser and more irregular with adsorption and this helps in the biosorption of dye molecules onto different parts of the adsorbent.

#### 3.1.2. FTIR analysis

The FTIR analysis of both the adsorbents before and after adsorption of RRD and RBD is shown in Fig. 2 and Table 1.

The spectra display several adsorption peaks, indicating the complex nature of the adsorbent material (Fig. 2). The FTIR analysis of formaldehyde treated adsorbent showed bands at 3547 $cm^{-1}$ before adsorption and at 3616 $cm^{-1}$ after adsorption of RRD,