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# Application of unripe grape juice waste as an efficient low cost biosorbent for dye removal

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## ABSTRACT

*This search deals with application of a new non-conventional biomaterial waste, unripe grape juice (Verjuice) waste for basic dye removal from aqueous solutions. It was found that the introduced bioadsorbent is very suitable for uptake of cationic dyes from aqueous solutions without needing to any pretreatment or chemical modifications. Adsorption experiments were conducted using column fixed bed system and the performance of the columns was investigated using breakthrough analysis. The effects of different system variables such as adsorbent dose, initial dye concentration, pH of solution and flow rate were studied. In order to find out the possibility of reuse, desorption study was also carried out in this investigation.*

**Keywords:** unripe grape waste, Cationic dye; Removal; Column system; Breakthrough curve.

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## INTRODUCTION

Nowadays, one of the major environmental problems contacting humanity is the increasing worldwide contamination of freshwater systems with thousands of industrial chemical materials. Among of all pollutant contained in industrial sewage, dyes are the most undesirable ones, as human eyes can easily recognize them. Since, many industries (particularly the textile industry) use dyes to color their products and also consume substantial volumes of water. In addition to, dyes can significantly affect photosynthetic activity in aquatic systems. Furthermore, some dyes degrade into compounds that have toxic, mutagenic or carcinogenic influences on living organisms [1].

The removal of color from aquatic systems caused by presence of dyes is extremely important from the environmental viewpoint because most of these dyes are toxic, mutagenic and carcinogenic. Adsorption techniques are widely used to remove certain classes of pollutants from waters, especially those that are not easily biodegradable such as dyes. Adsorption in column (or

in fixed-bed adsorber) is the most common and efficient way for purification of wastewater but this application is limited by the high cost of adsorbents. A successful adsorption process not only depends on dye adsorption performance of the adsorbents, but also on the constant and continued supply of the materials for the process [2]. So it is preferable to use low cost adsorbents, such as an industrial waste, natural ores, and agricultural byproducts. In recent years, many researches have studied on removal of MB from aqueous solutions and used different agricultural solid wastes such as Papaya seeds [3], Grass waste [4], Untreated guava leaves [5], Modified rice straw [6], Rubber seed shell [7], Hazelnut shell [8], Modified sawdust [9], Cereal chaff [10], Wheat shells [11], Neem leaf powder [12] and sawdust [13].

Methylene blue (MB) or tetramethylthionine chloride is one of the basic dyes with the structure of heterocyclic aromatic chemical compound that was chosen as test probe for the evaluation performance of the adsorbent introduced in this study. The cationic dyes were commonly used initially for dyeing of silk, leather, plastics, paper, cotton mordanted with tannin, and also in manufacturing of paints and printing inks [14]. Though MB is not hazardous compared to other dyes, acute exposure to MB will cause increased heart rate, vomiting, and shock [15, 16]. Hence, the necessity for the dye containing water to undergo treatment before disposal to the environment.

The purpose of this work was to investigate the removal of methylene blue by a biomaterial waste (Verjuice) that is available as plentiful and free of charge, as a new sorbent for dye removal from aqueous solutions. This waste is available as plentiful at the end of each summer in north of Iran in huge amounts and discarded as waste after taking the juice from unripe grape. Application of this biomaterial waste for dye removal has been examined in this study and is reported for the first time.

## MATERIALS AND METHODS

The verjuice from unripe grape was obtained from a local sour grapes (unripe grape) juice shop in Guilan province (North of Iran). The waste was first washed with sufficient water, dried and powdered before use. Methylene blue (MB) dye was selected as typical cationic dye for adsorptive properties of the biomaterial waste employed in the present study. Analysis of methylene blue dye was performed as described before [13]. During adsorption experiments, the column capacity was calculated as the following:

$$Q_e = (C_i - C_e) \times V_e \times 100/m \quad (1)$$

Where  $C_i$  and  $C_e$  are the initial and effluent concentration of dye in the liquid phase ( $\text{mg L}^{-1}$ ),  $V_e$  is the volume of the influent solution (L) and  $Q_e$  is the mass of dye adsorbed by unit mass of bioadsorbent (mg/g). The regeneration efficiency (RE) was also calculated using following equation:

$$\% \text{ RE} = (V_{b1} / V_{b2}) \times 100 \quad (2)$$

Where  $V_{b1}$  and  $V_{b2}$  are the volumes of the breakpoints observed for the regenerated and fresh columns respectively.

## RESULTS AND DISCUSSION

### Effect of pH

The pH of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. For this investigation, 0.50 g of the sorbent (Verjuice) packed in a glass column (fixed bed depth of 5 cm<sup>3</sup>), and then methylene blue solution with concentration of 50 mg L<sup>-1</sup> in different pH values 4, 6, 8 and 10 passed through the column with constant flow rate (3 mL min<sup>-1</sup>). Sample solutions were withdrawn at predetermined time intervals for the colour removal analysis. The breakthrough curves were obtained by plotting C<sub>i</sub>/C<sub>0</sub> vs. the volume of the outlet solution (Fig 1).

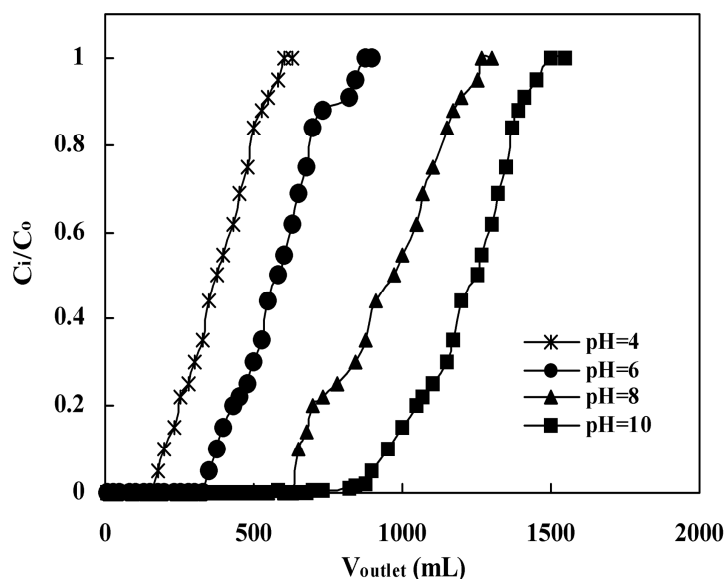


Figure 1 Breakthrough curves obtained for the sorption of MB by at different pHs

As the results clearly show maximum adsorption happens at pH 10. It is interesting to note that 0.50 g of this adsorbent can remove more than 99% of MB from about 950 mL of 50 mg L<sup>-1</sup> solution at pH 10. It was also noted that lower adsorption percentage of adsorbent at highly acidic conditions (pH ≤ 6) is probably due to the presence of high concentration of H<sup>+</sup> ions on the surface of adsorbent competing with methylene blue (a cationic dye) for adsorption sites in the adsorbent. With an increase in the solution pH, the electrostatic repulsion between the positively charged methylene blue and the surface of adsorbent is lowered and consequently the removal efficiency is increased.

### Effect of initial concentration of dye

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dyes ranging from 40 to 100 mg L<sup>-1</sup>. To perform this experiment, fixed amounts (0.5 g) of adsorbent were packed in column and washing with dilution NaOH solution to reach the optimum pH value. Then column treated with different concentration of MB solution. The result obtained is shown in Fig 2. Results from this study show that the adsorption process is highly dependent on the initial concentration of the dye in solution and removal capacity of MB decreases as its initial concentration increases.

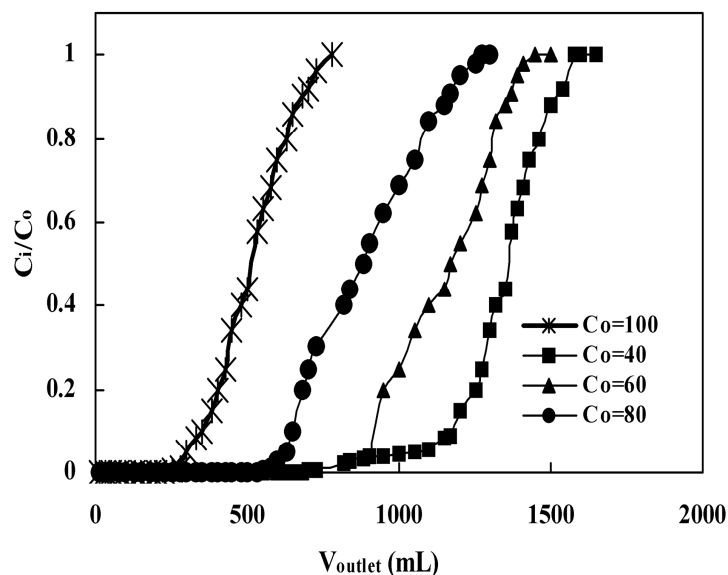


Figure 2. Breakthrough curves for the sorption of MB at different concentration

#### Effect of sorbent dose

For performing of this experiment, different values of sorbent (0.25, 0.50 and 1.0 g) packed in a glass column, and after adjusting of optimum pH, methylene blue solution with concentration of  $50 \text{ mg L}^{-1}$ , passed through the column with constant flow rate ( $3 \text{ mL min}^{-1}$ ). The outlet solution was analyzed in order to obtain the breakthrough curve. The results are shown in Fig 3. The results indicate that sorption capacity increased as the sorbent dose was increased. Higher uptake observed at the higher bed height can be due to an increase in the surface area of the biosorbent, which provides more binding sites for the sorption of MB dye molecules.

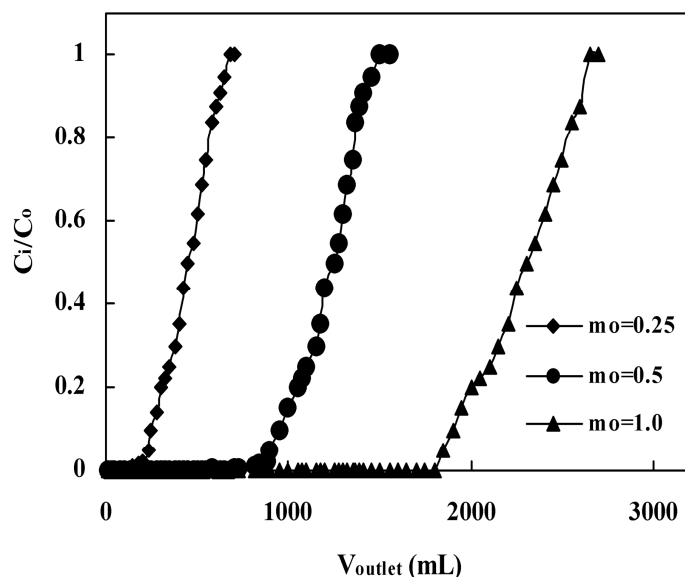


Figure 3. Breakthrough curves for the sorption of MB at different dose of biosorbent

### Effect of flow rate

In a packed column of uniform cross-sectional area, the volumetric flow rate was directly proportional to the overall linear flow through the bed. To study the influence of flow rate, the dye solutions were allowed to flow through the sorbent bed at different flow rates such as 2, 3 and 5 mL min<sup>-1</sup>. The eluents from the column were collected and analyzed for the respective residual dye concentration. The breakthrough plot of MB obtained at different flow rates is shown in Fig 4. It is evident from the figures that as the flow rate increased, due to decreased contact time between the dyes and sorbent at higher flow rates, the service times were shortened and therefore the volume treated. For this reason, flow rate 3 mL min<sup>-1</sup> was chosen for all experiments.

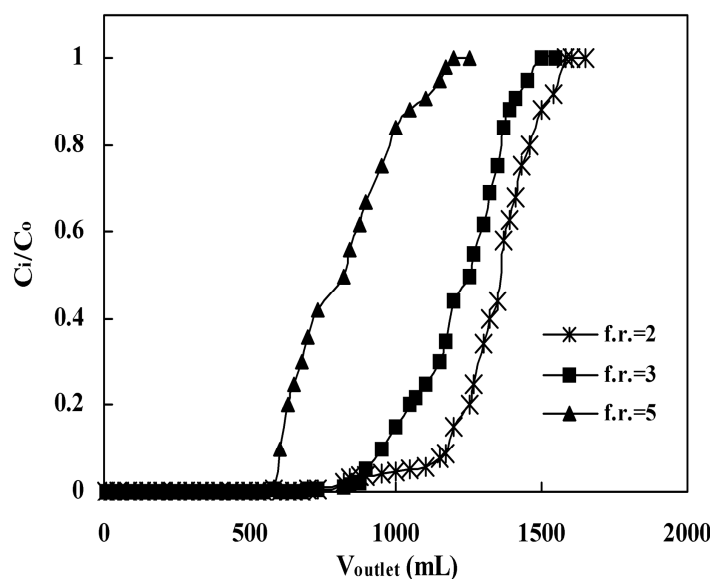


Figure 4. Breakthrough curves for the sorption of MB at different flow rates

Another main advantage of the introduced adsorbent is that the breakthrough curves observed under different conditions were steep which indicate that the breakthrough occurs near the point of exhaustion. Therefore a single operation can be applied for waste treatment. When the breakthrough curves become flat, it means that breakpoint concentration is reached before the column is fully exhausted, so a multiple column installation should be used.

### Column Regeneration and Recycling of sorbent bed

In order to find out the possibility of desorption for frequent applications, the regeneration of the used column was also investigated. Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. If the adsorbed dyes can be desorbed through using neutral pH water, then the attachment of the dye of the adsorbent is by weak bonds. For performing this experiment after the sorption process, the column was eluted with HCl and C<sub>2</sub>H<sub>5</sub>OH solutions, respectively, at the rate of 2 mL min<sup>-1</sup>. Eluents were collected and analyzed for dye content. It was found that the exhausted column can be regenerated easily using dilute HCl solution (0.10M) or ethanol as washing solutions with high efficiency (75-80 %). When the

regenerated column was reused for dye sorption the maximum loss in sorption capacity was about 15 % for at least three sorption/desorption cycles.

### CONCLUSION

The experimental results have shown that Verjuice adsorbent is suitable for the sorption of MB. It is environmentally friendly material, free of charge and high regeneration efficiency. Adsorption was an effective process for decolonization of textile wastewaters. The adsorption studies revealed that the optimum pH for adsorption of MB was found to be 10 and adsorbent dosage was 1 g for the adsorbent. This new and cheap biosorbent was able for the removal of methylene blue dye from aqueous solution over a wide range of concentration. The introduced adsorption system seems both very economical and efficient for the removal of cationic dyes such as MB from aqueous solutions. Desorption of the exhausted adsorbent in column can be performed using common chemicals with high performance. The adsorbent introduced in this study seems to be very promising for application in wastewater treatment in textile or other industries dealing with dyes and dyeing. Column studies confirm that the biomaterial which is discarded as waste can be used as an efficient adsorbent for dye removal technology.

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