



Biodecolourisation of Bismarck Brown dye using Orange peel

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Dyes discharged from dyeing units and textile industries pollute the environment, particularly aquatic systems and cause considerable damage to organisms. Removal of colour is a prerequisite for discharge of treated textile effluents into the environment. Though several physical and chemical methods are available for decolourisation, biosorption is considered as cost effective and ecofriendly technique. Hence, in the present study, we explored possibilities of using orange peel for decolourisation of Bismarck brown dye, one of most common dyes used in the textile industry. Orange peel in different quantities (0.2, 0.4, 0.6 and 0.8 g/100 mL) was tested with 0, 100, 200, 300 and 400 ppm concentrations of Bismarck Brown dye for ten days. The decolourisation activity proportionally increased with the increase in the treatment period. The dye concentration of 100 ppm was tested with 0.4 g orange peel in different pH ranges of 2, 4, 6, 8 and 10 and the absorption was high in acidic pH. The increase in contact time also resulted in increased dye removal. Over all, the adsorption of dye onto orange peels was influenced by initial dye concentration, pH, amount of adsorbent and contact time. Four grams of orange peel showed highest decolourisation after 200 min, and it was proportional to the contact time. The dye removal was the maximum at pH 2. Both Langmuir ($R^2 = 0.922$) and Freundlich ($R^2 = 0.999$) adsorption isotherms were calculated.

Keywords: Biosorption, Biosorbents, Industrial effluents, Pollution, Textile industry

Disposal of waste water is one of the major problems in textile industries along with other minor problems such as solid waste and resource waste management¹. Synthetic dyes employed in textile industries mainly affect the photosynthetic activity of plants and oxygen consumption of aquatic organisms². Component metals and chlorine present in certain synthetic dyes have lethal effects on some marine organisms. Dyes are carcinogenic, mutagenic, teratogenic and toxic which produce harmful effects in all living organisms including human beings. Removal of dye is a huge task, and that the textile wastewater must be treated before discharge^{3,4}. Different techniques, such as biological treatment, nanofiltration, oxidation process, ion exchange, ozonation, ultrafiltration and coagulation have been studied for the treatment of dyes from wastewater. However, these processes are expensive and ineffective to treat huge quantities of wastewater unlike adsorption which is proven to be one of the most effective techniques⁵⁻⁷.

Adsorption process is effective in removing colour and soluble organic pollutants including organic dyes. The most used adsorbent in removing colours is activated carbon. However, conventional activated

carbon that has been used today is expensive for a large scale of treatment^{8,9}. Recently, researchers have focused on the development of low cost adsorbent for a full scale treatment^{10,11}. Orange peel is a promising alternative low cost, natural adsorbent for removal of dyes. On the other hand, accumulation of orange peel waste in orange industries has been a issue as it occupies space and also causes pollution with phenolic compounds when dumped as waste. In this context, recycling of this solid waste for waste water treatment would not only be economical but also will help to solve solid waste disposal problems^{12,13}. Orange peel was previously investigated to adsorb methyl orange, methylene blue, rhodamine B, congo red, methyl violet, amido black, acid violet and direct red 23 and 80^{14,15}. Therefore, in the present work, we evaluated the possibility of using dried orange peel to develop a new low cost activated carbon and study its application to remove Bismarck brown which is currently among the widely used commercial dyes in the printing of cotton and mucilage glue fabrics as well as dyeing of silk and wool.

Materials and Methods

Characterization of orange peel

Orange peel was collected from local fruit juice shops and washed with tap water followed by

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washing with distilled water. After this, the clean orange peel biomass was oven dried at 105°C for 96 h. Characterization of orange peel was done using FTIR analysis (FTIR-4600, JASCO International Co., Ltd).

Preparation of activated carbon from orange peel biomass

The dried orange peel biomass was added in small portion to 98% of nitric acid and kept for 2 h and the resulting reaction mixture was cooled by adding cold water and filtered. The resulting material was heated in an oven at 150°C for 24 h.

Preparation of test solution and Determination of absorption maxima

Bismarck brown dye concentrations @100, 200, 300 and 400 ppm were prepared for 100 mL volume with distilled water. The dye solution was taken in a cuvette and placed in a colorimeter and absorbance value at each wavelength was observed using distilled water as blank. The wavelength which showed the maximum absorbance was chosen as the absorption maxima^{12,13}.

The carbon activated dried orange peel of about 0.2, 0.4, 0.6 and 0.8 g was introduced into the dye solutions. Initial absorbance was measured and the solutions were observed periodically for the absorbance values. The test samples were taken in a cuvette and placed in the colorimeter. The absorbance was noted periodically at an interval of 48 h at the wavelength of 450 nm which is the absorption maxima. The decolourisation activity was expressed in terms of percentage decolourisation as determined by monitoring the decrease in the absorbance at the absorption maxima of the dye^{12,13}. Decolourisation activity was calculated according to the following formula:

$$\text{Decolourisation activity (\%)} = \frac{(\text{Initial absorbance}) - (\text{Observed absorbance})}{\text{Initial absorbance}} \times 100$$

Isotherm and data analysis

Isotherm and data analysis

The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the "adsorption isotherm". Equilibrium isotherm equations are used to describe the experimental adsorption data. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid phase concentration was tested with the Langmuir¹⁶ and Freundlich¹⁷ isotherm equations. Linear regression was frequently used to determine the best fitting isotherm.

Langmuir isotherm

Langmuir isotherm model assumes uniform energies of adsorption on to the surface without transmigration of adsorbance in the plane of the surface. Therefore, the Langmuir isotherm model was chosen for the estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The Langmuir non-linear equation is commonly expressed as follows:

$$q_e = Q_0 b C_e / (1 + b C_e)$$

where q_e , equilibrium adsorption capacity (mg/g); C_e , equilibrium concentration of adsorbate (mg/L); Q_0 , Monolayer surface coverage (mg/g); b , the equilibrium adsorption constant (L/mg); Q_0 and b are the Langmuir constants related to capacity and energy of adsorption, respectively. The linear form of the Langmuir isotherm can be expressed as follows:

$$1/q_e = (1/Q_0) + (1/b Q_0 C_e)$$

Freundlich isotherm

The Freundlich isotherm model is the earliest known equation describing the adsorption process. The Freundlich non linear equation is expressed as follows:

$$q_e = K_f C_e^{1/n}$$

where, q_e , the amount of metal ions adsorbed per unit weight of adsorbents (mg/g); C_e , equilibrium concentration of adsorbate (mg/L); K_f and $1/n$ are the Freundlich constants that are dependent on several environmental factors.

The linear form of the Freundlich equation which is commonly used to describe the adsorption isotherm data is

$$\text{Log } (q_e) = \text{log } K_f + 1/n \text{ log } C_e$$

Results and Discussion

FTIR analysis of orange peel

The presence of characteristic peaks such as 3423.99 cm^{-1} , 1626.63 cm^{-1} , 916.986 cm^{-1} , 760.065 cm^{-1} , 723.17 cm^{-1} and 666.285 cm^{-1} , at three different ranges 3500-3300 cm^{-1} , 1650-1590 cm^{-1} , 900-650 cm^{-1} can be observed in FTIR analysis of orange peel (Fig. 1). They are a strong indication for the presence of N-H (amine group) in the sample. Broad weak peaks at 2396.12 cm^{-1} could indicate the presence of alkyne ($\text{C}\equiv\text{C}$) stretching in the sample. Broad medium multiple peaks around 1760 cm^{-1} and 1740 – 1715 cm^{-1} (1762.62 cm^{-1} and 1730.8 cm^{-1}) might reveal the C=O stretching due to carboxylic acid in monomer form,

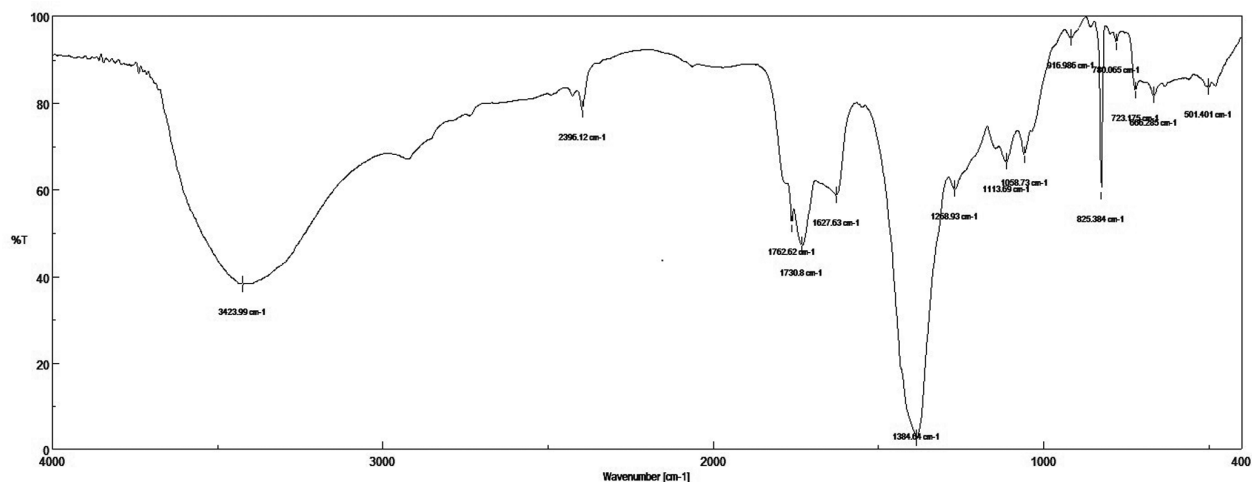


Fig. 1 — FTIR analysis of orange peel

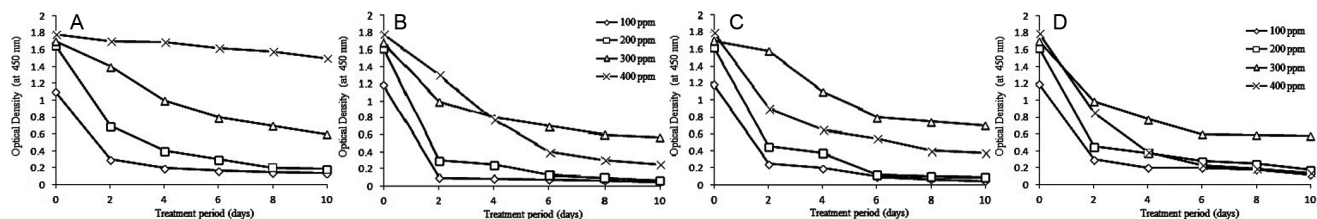


Fig. 2 — Biodecolourisation of bismarck brown using orange peel in different quantities (A-D) 0.2, 0.4, 0.6 and 0.8 g, respectively

and aldehyde or α,β -unsaturated ester functional groups. A weak peak at 1627.63 cm^{-1} could be due to C=C stretching of alkene or α,β -unsaturated ketone functional groups present in the sample. A sharp and narrow peak at 1384.64 cm^{-1} , lies within the range of characteristic frequencies $1390\text{--}1310\text{ cm}^{-1}$ exhibiting the presence of O-H bending in the phenol functional group in the sample. A range of narrow weak peaks at frequencies 1268.93 , 1113.69 , and 1058.73 cm^{-1} , are indicative of C-O stretching in various functional groups such as alkyl aryl ether, secondary and primary alcohol. Extensive C-H bending in monosubstituted and 1,2,4-trisubstituted carbon positions, can be inferred from the sharp peaks stretching from $900\text{--}700\text{ cm}^{-1}$ (760.065 cm^{-1} , 723.175 cm^{-1} respectively). Stretching in a halo compound containing bromine or iodine such as C-Br or C-I bond can also be detected to occur in through the two characteristic peaks at 666.285 and 501.401 cm^{-1} .

Effect of dose of adsorbent

Dosage of adsorbent is one of the important parameters in order to determine the adsorbent's capacity for a given amount of adsorbate at the operating conditions. In general, the increase in dye removal along with the increasing of adsorbent dose,

where the number of adsorption sites at the adsorbent surface will increase by increase of adsorbent dosage that will result in the increase of dye removal percentage^{18,19}. In the present work, in order to study the effect of initial concentration of adsorbent dose on the adsorption process, adsorbent adsorbate solution with different quantities of adsorbent (0.2, 0.4, 0.6 and 0.8 g/100 mL of orange peel) added to different initial dye concentrations (100, 200, 300 and 400 ppm of bismarck brown) were prepared and biodecolourisation activity was studied. From the results, it is noted that, the dye removal activity of orange peel varied depending upon the initial dye concentration, adsorbent dose and contact time (Fig. 2). It was evident that the amount of dye adsorption by orange peel decreased with the increase in initial Bismarck brown dye concentration. At the same time, increase in the adsorption with the increase of adsorbent dose was noticed. This is due to the increase in adsorbent surface area and availability of more adsorption sites. Heibati and coworkers²⁰ analysed the effect of adsorbent dose on the removal of acid red 18 (acid dye) by activated carbon from walnut (ACW) and poplar wood (ACP). The present results showed that the efficiency of dye removal

increased as the adsorbent dosage increased up to 0.4 g/100 mL and after that it remained almost constant with the increase in adsorbent dose. Amin¹⁵ reported similar trend with bagasse pith activated carbon removing reactive dye. The increase in dosage provides more sites for dye saturation during adsorption²¹. The present study revealed that using different doses of orange peel as adsorbent has a great potential in the removal of Bismarck Brown dye.

Effect of pH

The original pH of the dye concentration has a strong worthy impact on the adsorbent's surface characteristics as well as the degree at which the dye molecules ionize. Thus it becomes important to examine the impact that pH has on the adsorption process. Figure 3 shows the effect of initial pH on the amount of dye adsorbed by orange peel. In the trial, dye solutions in the pH range of 2, 4, 6, 8 and 10 have been studied. The pH of the dye solutions were changed to a desired value by using 0.1N sodium hydroxide (NaOH) and 0.1N hydrochloric acid (HCl) solution utilizing a pH meter. The result showed that the removal efficiency of dye is reasonably high in a low pH range and declined at higher pH. The higher adsorption at very acidic media could be due to the interactions between the positively charged dye cations with surface functional groups present in orange peels. On the contrary, at higher pH values, the adsorption decreased which may be because of the formation of soluble hydroxyl complexes. This shows a similar trend with bagasse fly ash and coir pith used as adsorbents for the removal dyes²². Amin¹⁵ studied the adsorption of reactive dyes on activated carbon from sugarcane bagasse at different pH and reported that pH is one of the significant factors that determine the percentage of dye removal.

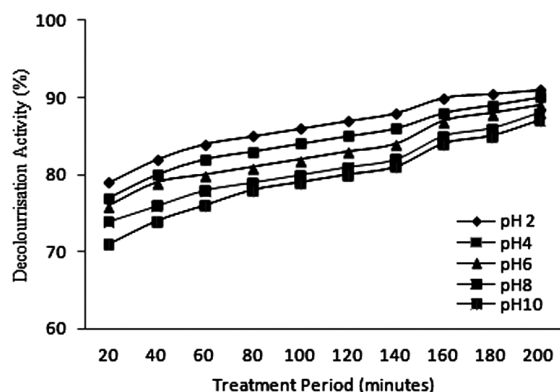


Fig. 3 — Effect of pH on the biodecolourisation activity of orange peel (0.4 g) on bismarck brown (100 ppm)

Effects of dye-adsorbent contact time

Generally, dye removal rate increases with an increase in contact time to a certain extent. Due to deposition of dyes on the available adsorption sites on adsorbent, any further increase in contact time will not increase the uptake⁵. At this point, the amount of dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of dye being adsorbed onto the adsorbent. The time to attain the state of equilibrium is the equilibrium time and the amount of dye adsorbed at the equilibrium time denotes the maximum adsorption capacity of the adsorbent under those operating conditions. El-Sayed & co-workers²³ reported contact time between adsorbent and adsorbate significantly affecting the capacity of dye removal. Table 1 shows that, there was an increase in removal efficiency with increase in contact time between adsorbate and adsorbent. From the result, it can be deduced that more time becomes available for the dye to make an attraction with orange peels. Under optimised conditions, the maximum adsorption (93%) for Bismarck brown dye was observed in the sample treated with orange peel. Hence from the observations, it can be inferred that over the period of experiment, the percentage removal of the dye increased steadily. The relation between N blue 106 dye with contact time was studied by Khaled & co-workers²⁴. Sometimes, the slow process in decolourisation activity was observed probably due to the slow pore diffusion of solution ion into adsorbent bulk.

Adsorption isotherm

Adsorption phenomenon can be represented through isotherms, that is, the amount of adsorbate on the adsorbent as a function of adsorbate concentration at a constant temperature. Amount of adsorbate adsorbed is normalized by adsorbent mass to allow comparison of various materials. Studies relating to equilibrium on adsorption process provide data on the capacity of the adsorbent. Also, an adsorption

Table 1 — Biodecolourisation activity of Orange peel (0.4g) on Bismarck Brown (100ppm)

Treatment period (min)	Biodecolourisation activity (%)
20	4.31
40	7.75
60	10.34
80	13.79
100	15.5
120	18.10
140	21.55
160	23.27
180	25.86
200	30.17

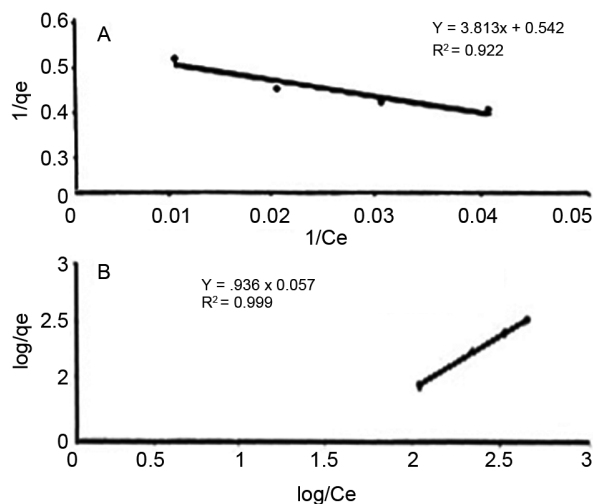


Fig. 4 — (A) Langmuir isotherm and (B) Freundlich isotherm for Bismarck brown treatment using orange peel

isotherm is characterized by some particular constant values that exhibit the properties of the surface and affinity of the adsorbent and can even be used to compare the adsorptive capacities of that particular adsorbent for various adsorbates²². The most common models at constant temperature for this sort of adsorption are Langmuir isotherm and Freundlich isotherm^{19,20}. In the present work, the isotherm studies were carried out for optimum condition, which was obtained (Fig. 4). The R^2 values suggest that the Langmuir isotherm (0.922) and Freundlich isotherm (0.999) provide good models for sorption.

Conclusion

From this study, it may be concluded that the removal of Bismarck brown dye from textile wastewater by adsorption on orange peels has been found to be useful for controlling water pollution due to dyes. From this experiment it is clear that the adsorption of dye onto orange peels is influenced by pH, amount of adsorbent and contact time. Orange peel (0.4 g) exhibited the highest activity of decolourisation after 200 min, and the activity increased with the increase in contact time. The activity decreased with the increase in initial dye concentration. The dye removal was highest at pH 2. Also, the adsorption of dye onto orange peels followed the Langmuir and Freundlich isotherm models.

Conflict of interest

Authors declare no competing interests

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