



Efficacy of orange peel in the decolourization of the commercial auramine yellow dye used in textile industry

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Auramine yellow dye used in textile industry was treated with different quantities of carbon activated dried orange peel for ten days. 0.2, 0.4, 0.6 and 0.8 g quantities of orange peel were tested with 100, 200, 300 and 400 ppm of auramine yellow dye. Increase in orange peel quantity and treatment period caused an increase in the activity of decolourization. Decolourization was the maximum at pH2. Orange peel of 0.6 g quantity performed better and the isotherm models could explain the biosorption process.

Keywords: Adsorption Isotherms, Biosorbents, Colour removal, Textile dyes

Due to human activities and industrialization, our environment is contaminated through waste disposal. Textile industries are one among them which release a huge amount of wastewater^{1,2}. This waste water contains a significant level of dyes along with high COD, BOD, pH, Colour and heavy metals. Dyes are the most important component used in textile industries. Dyes contain organic and inorganic chemical substances along with toxic heavy metals. Dyeing and subsequent rinsing steps contribute much to wastewater generation in textile industries. As dyes are almost invariably toxic, their removal from the effluent stream is ecologically necessary. Generally, dyes pose the greatest problem in terms of colour. Reactive dyes possess substituted aromatic and heterocyclic groups. Since the reactive dyes are highly soluble in water, untreated disposal of these coloured compounds into the receiving aquatic systems causes damage not only to aquatic life but also to human beings. In man, it causes severe health hazards like cancer, tumour and allergic reactions. Hence, it is very essential to degrade the dye and remove its colour³⁻⁸.

Several physico-chemical methods are employed for the treatment of wastewater. Various techniques including adsorption, filtration, ion-exchange, coagulation, flocculation, reverse osmosis, and electro dialysis are used for the removal of dyes from the wastewater. Most of these methods are expensive and

also produce secondary sludge. So, finding out of suitable treatment strategies is very much needed at present. Biodecolourization provides the opportunity for dye degradation which is also eco-friendly and cost-effective. Living organisms and their products are very much useful in this context⁹⁻¹⁵. *Citrus sinensis* (L.) is used in the production of orange oil. Activated carbon prepared from the orange peel which is a biowaste from industries was tested as an adsorbent in a few research studies^{16,17}. The present work focuses on decolourization of the dye solutions employing activated carbon from dried orange peel which is a biodegradable adsorbent and the most abundant waste from local juice shops.

Materials and Methods

Biomass

Orange peel was collected from local fruit juice shops and washed with tap water followed by washing with distilled water. After this, the clean orange peel biomass was oven-dried at 105°C for 96 h.

Preparation of Activated Carbon from Orange Peel Biomass

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

Preparation of Test Concentrations

100, 200, 300, and 400 ppm of auramine yellow dye concentrations were prepared for 100 mL volume with distilled water.

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Determination of Absorption Maxima

100 ppm dye concentration was taken in a cuvette, placed in a colorimeter and absorbance value at each wavelength was observed using distilled water as blank. The wavelength which exhibited the maximum absorbance was chosen as the absorption maxima.

Decolourisation Study

The carbon activated dried orange peel of about 0.2, 0.4, 0.6, and 0.8 g quantities were introduced into the selected dye concentrations. Initial absorbance was measured and the solutions were observed periodically for the absorbance values.

Estimation of Absorbance

The test samples were taken from each concentration 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 of auramine yellow.

Influence of pH

The influence of pH on the biodecolourisation activity of the selected quantity of orange peel (0.6 g/100 mL) on 100 ppm of auramine yellow was tested at different pH levels such as 2, 4, 6, 8 and 10 at various treatment periods.

Decolourisation Assay

The decolourisation activity can be expressed in terms of percentage decolourisation as determined by monitoring the decrease in the absorbance at the absorption maxima of the dye. 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

The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is represented in 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^{18,19}. The correlation with the amount of adsorption and the liquid phase concentration was tested with the Langmuir and Freundlich isotherm equations. Linear regression is 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 adsorbate 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 adsorbent (mg/g); C_e – equilibrium concentration of adsorbate (mg/L); K_f and $1/n$ are the Freundlich constants which depend on several environmental factors.

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

$$\log (q_e) = \log K_f + 1/n \log C_e$$

Results and Discussion

Decolourization is the result of two mechanisms, adsorption and ion exchange, and is influenced by many factors. The dye removal activity of orange peel varied depending upon the initial dye concentration, adsorbent dose, and contact time. It was evident that the amount of dye adsorption by orange peel decreased with the increase in initial auramine yellow dye concentration. At the same time, an increase in the adsorption with the increase of adsorbent dose was noticed. This is due to the increase in adsorbent

surface area and the availability of more adsorption sites²⁰⁻²². Subramanian and Ponnusamy²³ reported that the increase in dye removal with increasing adsorbent dose was due to the split in the concentration gradient between solute concentrations on the surface of the adsorbent. At lower dye concentration, the ratio of dyes to the available surface area was low and subsequently the fractional adsorption became independent of initial dye concentration. The adsorption sites available are very less at high concentrations. So, the percentage of dye removal is always based on concentration.

In the present study, a rapid decolourisation was found at the initial stages of the adsorption, and equilibrium was attained from fifth day onwards. Generally an increase in biosorbent quantity resulted in an increase in decolourisation. Decolourisation was faster in lower concentrations of auramine yellow (Fig. 1). Such uptakes specify a high degree of affinity towards the dye molecules through chemisorption²⁴. The minimum colour removal efficiency obtained on tenth day indicates that the aggregation of dye molecules decreased with an increase in contact time and made it almost impossible to diffuse deeper into the adsorbent structure at the highest energy sites²⁵.

The pH plays a significant role in decolourisation process and mainly on the adsorption capacity. Variation in solution pH leads to a change in the degree of ionization and the surface properties of the adsorbent²⁶. The results revealed that the percentage of decolourisation decreased with an increase in pH. The maximum decolourisation activity was noted at pH 2 (Table 1). This confirms that the alkaline pH was unfavourable for dye decolourisation by orange peel which was attributed to the anion exchange reaction between the dye and surface-active groups on the adsorbent²⁷. Malik²⁸ and Mohamed²⁹ reported that at low pH, the active sites of the adsorbent will be largely protonated and the H⁺ ion creates an electrostatic attraction between the adsorbent and the dye molecules which leads to maximum colour removal. At pH above 4, the degree of protonation on the surface sites will be less which results in the decrease in diffusion and adsorption thereby due to electrostatic repulsion^{30,31}. Furthermore, lower adsorption of the dyes in an alkaline medium can also be attributed to the competition from excess hydroxide ions (OH⁻) with the anionic dye molecules for the adsorption sites. In this study, the adsorption was

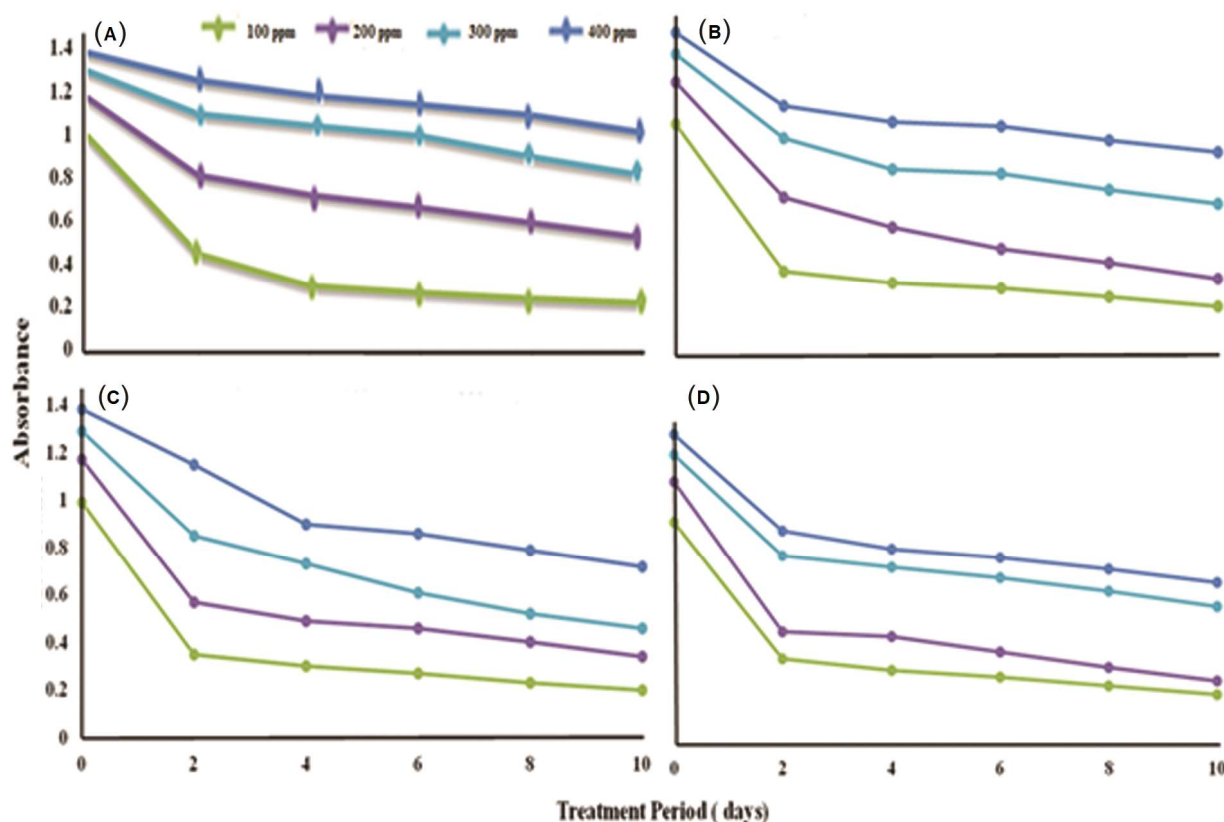


Fig. 1 — Biodecolourization of auramine yellow using orange peel in different quantities (A) 0.2 g; (B) 0.4 g; (C) 0.6 g; and (D) 0.8 g

Table 1 — Effect of pH on the Biodecolourization activity of Orange peel (0.6 g/100 mL) on 100 ppm Auramine Yellow dye

Treatment Period (in min)	Biodecolourization activity (%)				
	pH 2	pH 4	pH 6	pH 8	pH 10
20	79.79	73.73	69.69	63.63	47.47
40	80.80	75.75	70.70	65.65	48.48
60	82.82	76.76	72.72	68.68	50.50
80	84.84	78.78	73.73	70.70	51.51
100	85.85	79.79	75.75	71.71	54.54
120	88.88	81.81	78.78	73.73	56.56
140	89.89	82.82	80.80	76.76	58.58
160	90.90	85.85	83.83	78.78	61.61
180	92.92	86.86	85.85	79.79	64.64
200	94.94	88.88	87.87	81.81	66.66

favourable in acidic pH. This is attributed to the increase in H^+ concentration leading to the formation of aqua complexes thereby retarding the dye sorption (Table 1). Thus the optimum conditions for removal of auramine yellow from an aqueous solution by orange peel were successfully identified. Under optimised conditions, the maximum adsorption (95%) for auramine yellow dye was achieved in the sample treated with orange peel (0.6 g/100 mL).

Langmuir and Freundlich isotherms were selected to investigate the interaction between adsorbate molecules and the adsorbent surface. It is understood that the formation of a monolayer on the surface of adsorbent is mainly due to one to one interaction between the dye molecule and adsorption site. The intermolecular forces gradually reduce when there is an increase in the distance. It is also assumed that the adsorbent surface is homogeneous in character and possesses identical and energetically equivalent adsorption sites^{32,33}. The Langmuir isotherm was found to be linear over the entire concentration range with a good linear correlation coefficient ($R^2 = 0.9229$) showing that the Langmuir equation represents the best fit of experimental data than the other isotherm equations (Fig. 2).

The Langmuir isotherm is based on the assumption that the coverage of adsorbate molecules at the outer surface of the adsorbent occurs in a monolayer and the adsorbent surface is homogeneous. The Freundlich isotherm assumes that the adsorption occurs on a heterogeneous surface³⁴. The slope and the intercept correspond to the Freundlich constants ($1/n$) and k_f , respectively. The plot of $\log q_e$ and $\log C_e$ yielded a straight line (Fig. 3) and the correlation coefficient (R^2) was 0.9998.

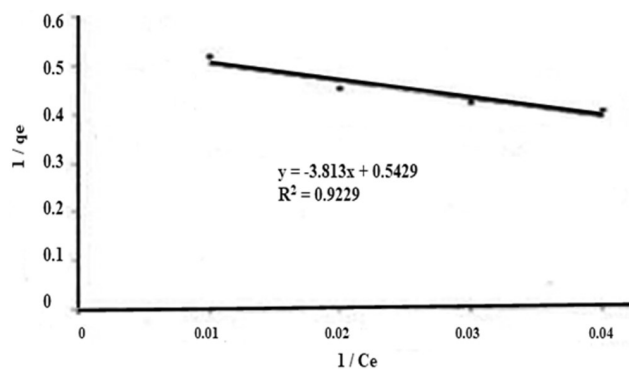


Fig. 2 — Langmuir isotherm for auramine yellow treatment using orange peel

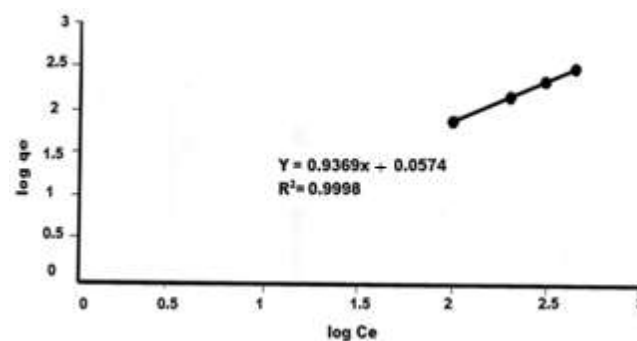


Fig. 3 — Freundlich isotherm for auramine yellow treatment using orange peel

Conclusion

Orange peel was able to decolourise auramine yellow dye by 95% in 200 min at pH 2. Increase in pH of the dye solutions caused a decline in decolourisation activity. Among the tested quantities of orange peel, optimum activity was observed for 0.6g/100 mL.

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Conflict of interest

All authors declare no conflict of interest.

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