Practical Paper

Investigations on reduction of colour from pulp and paper mill effluent by activated coconut jute carbon

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ABSTRACT

Coconut jute carbon, a waste by-product, was utilized in the production of activated carbon. The activated carbon was then evaluated for colour removal from pulp and paper mill wastewater. The activation of the coconut jute was evaluated using a fixed bed reactor involving carbonization and activation steps at temperatures of 650°C in the absence of air. The activation results showed that the maximum surface area of the activated coconut jute carbon (ACJC) was 94 $m^2 g^{-1}$. Adsorption equilibrium results of the pulp paper mill wastewater on the ACJC showed that a significant amount of colour reduction was achieved when the ACJC dose exceeded 8 to 12 $g l^{-1}$. Batch equilibrium data was used to develop adsorption isotherms for colour removal. Based on those isotherms, the amount of activated coconut jute carbon required to achieve colour removal can be predicted. Apart from reducing colour from the effluent, a waste disposal problem is also solved by utilizing this material as an adsorbent.

Key words | adsorption, activation, coconut jute carbon, equilibrium studies, isotherm

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NOMENCLATURE

b	Langmuir constant (l/CPU)
C_e	Equilibrium aqueous solution concentration (CPU)
C_0	Initial aqueous colour solution concentration (CPU)
k_{ad}	Rate constant of pseudo first-order kinetic model (min^{-1})
k	Freundlich adsorption isotherm constant ($mg\ g^{-1}$)
m	Mass of adsorbent (g)
n	Freundlich constant
q	Amount of colour adsorbed per unit mass of adsorbent at time t ($CPU\ g^{-1}$)
q_e	Amount of colour unit adsorbed per unit mass of adsorbent at equilibrium ($CPU\ g^{-1}$)
q_m	Maximum monolayer amount of adsorption Langmuir constant ($CPU\ g^{-1}$)
R^2	Correlation coefficient
t	Time (min)
CPU	Cobalt-platinum units

INTRODUCTION

The pulp and paper making industry is a very water-intensive industry and ranks third in the world, after the primary metals and the chemical industries, in terms of freshwater withdrawal. The effluent from the pulp and paper industry contains high concentrations of organic matter, non-biodegradable matter, suspended and dissolved solids, which pollute the surrounding surface and ground water (Join *et al.* 1996). If these effluents are not properly treated and allowed to pass into the environment, they are likely to affect aquatic and marine life and may also lead to many dreadful diseases (Rajannan & Oblisami 1979). Water bodies containing these pollutants are also hazardous to

human beings and animals. Various technologies have been reported in the literature for the treatment of pulp and paper mill effluent.

The major contaminants of a typical pulp and paper effluent are the presence of chemicals and colour. Biological treatment of effluent can lower the organic load (biodegradable matter) but these methods are ineffective for reduction of colour (Cecen *et al.* 1992; Saunamaki 1997). Colour in the effluent is mainly due to the lignin, which cannot be easily degraded to low molecular weight compounds. Discharge of coloured water affects the aesthetic value of receiving streams and retards the photosynthetic process. Various other technologies such as adding chemicals to the activated sludge process, coagulation (Othof & Eckenfeldev 1975), ozone treatment (Hostachy *et al.* 1997) and adsorption have been used for colour removal (Thompson *et al.* 2001). Activated carbon is one such adsorbent, which has shown good adsorption capacity in many studies. Activated carbon adsorption is considered very effective in the reduction of colour, adsorbable organic halides (AOX) and the non-biodegradable fraction of the pulp bleaching wastewater (Mall & Prasad 1998). However, this process has costs associated with the production of activated carbon (Shawwa *et al.* 2001).

Numerous studies have been reported in the literature on the removal of colour from wastewaters by activated carbons prepared from waste materials (Mall & Prasad 1998; Pala & Tokat 2002). An option for reduction of the cost associated with the production of activated carbon is by producing activated carbon from carbonaceous materials that are cheap and easily available in abundant quantities. Various low cost adsorbents such as chitin, chitosan, corn stalks, peat, rice husk and wood have been used by many workers for the removal of colour and chemical oxygen demand (COD) from pulp and paper mill effluent (Hall 1975; Poots *et al.* 1979; Mckay *et al.* 1980; George 1982; Gautam *et al.* 1987; Sarma & Sharma 1994; Annadurai & Krishan 1997).

Coconut husk is widely available in abundant quantities in India. Coconut husk carbon has been successfully used for the removal of phenols from industrial wastewater (Hitchcock *et al.* 1983) and arsenic from drinking water (Manju *et al.* 1998). The present study aims at determining the effects of different parameters on colour removal from pulp and paper mill effluent and optimizing these parameters. For this purpose, activated carbon prepared from coconut shell was used to assess the feasibility of the adsorbent under batch operation.

MATERIALS AND METHODS

All the reagents used were of AR grade. Double distilled water was used to prepare the chemicals used in the determination of colour. All measurements were carried out in triplicate at room temperature and the average value has been reported in this paper. All readings with an error greater than $\pm 5\%$ were repeated.

Pulp and paper mill effluent

Effluent was collected from a small paper mill located in western Uttar Pradesh (India). Samples were stored in airtight plastic containers (500 ml capacity) at a temperature below $2.0 \pm 0.5°C$ to avoid any change in the physicochemical or biological characteristics. Effluent was analysed for pH, electrical conductivity (EC) and total dissolved solids (TDS) at the sampling site itself immediately after the sampling whereas other physicochemical properties were determined by standard APHA methods (*Standard Methods* 1992) (Table 1). The pH of the effluent

Table 1 │ Physicochemical parameters of pulp and paper mill effluent

Parameter	Value
Colour	Dark brown
Total solids (mg l^{-1})	5,280
Total dissolved solids (mg l^{-1})	2,049
Total suspended solids (mg l^{-1})	3,264
pH	8.3
EC (m S/cm)	0.51
BOD (mg l^{-1})	1,680
COD (mg l^{-1})	3,560
Chloride (mg l^{-1})	422
Sulphate (mg l^{-1})	413

was measured using a pH meter (Elico, model LI-107, India) and was adjusted by using either diluted HCl (0.1 M) or NaOH (1N) solutions.

Preparation of adsorbents

Coconut jute coir was crushed to a finer fraction before converting it into carbon. Activated coconut jute carbon (ACJC) was prepared by treating four parts of adsorbent material with three parts by weight of concentrated sulphuric acid (H_2SO_4) and kept in an air oven maintained at 105°C for 24 hours. To remove the free acid the carbonized material was thoroughly washed with water and than dried at 105°C for 24 hours. The dried material was subjected to thermal activation at 650–700°C for a period of 15 minutes in the absence of air (nitrogen atmosphere). The material was further crushed and the particle size range 325–500 micron was used throughout the study. The surface area of the activated coconut jute carbon was determined by BET surface area analyser (Micromeritics, USA). Other properties such as particle size and moisture content were also evaluated (Table 2).

Determination of colour

Colour intensity of the pulp and paper mill effluent was measured using a Hitachi UV-2000 spectrophotometer at a wavelength of 465 nm. K_2PCl_6 (1.246 g) and cobaltous chloride (1 g) were dissolved in double distilled water in a 1-litre volumetric flask to make a colour standard solution of 500 cobaltous-platinum units (CPU). Further standard solutions of 10, 20, 50, 100 and 250 CPU were prepared by

diluting the stock standard solution for calibration. Pulp and paper mill effluent was diluted, as the concentration of colour of the effluent was very high.

Kinetics studies

Batch adsorption experiments were conducted at 30°C by agitating 0.6 g of ACJC with 100 ml of pulp and paper mill effluent at different pH (5.0 and 8.3) in plastic bottles in a mechanical shaker at 85 rpm. After predetermined time interval of 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 minutes, the adsorbent was removed from the solution and the residual colour concentration of the filtrate was determined by using a spectrophotometer at a wavelength of 465 nm.

Equilibrium study

For those samples with definite colour concentration (480 CPU and 1,000 CPU), 100 ml aliquots were taken in different conical flasks and various adsorbent doses ($0.1–1.2\,g\,100\,ml^{-1}$) were added to each flask. The system was equilibrated by shaking thoroughly on a mechanical shaker at a constant speed of 85 rpm. The suspension was filtered using Whatman No. 1 filter paper and the filtrate was analysed for residual colour concentration.

As initial solution pH and initial colour concentration affect the removal efficiency of the process, the effect of initial colour concentration (480–1,695 CPU) and pH (2.0–12.0) on the adsorption of colour from pulp and paper mill effluent by activated coconut jute carbon (ACJC) was also studied in a batch system.

RESULTS AND DISCUSSION

Characteristics of the paper and pulp mill effluent

Physicochemical analysis of the pulp and paper mill effluent was conducted by standard APHA methods and the results have been presented in Table 1. The effluent was dark brown in colour due to the presence of lignin and its derivatives. A pH of 8.3 was observed indicating its alkaline nature. The electrical conductivity of the effluent was high ($0.51\,m\,S\,cm^{-1}$) because of the high concentration of TDS

Table 2 │ Properties of activated coconut jute carbon (adsorbent)

Characteristic	Quantitative value
Surface area ($m^2\,g^{-1}$)	94
Pore volume (cc g^{-1})	0.15
Moisture content (%)	1.2 ± 0.1
Particle size (mesh)	325–500
Water-soluble matter (%)	4.25

$(3{,}264\,\mathrm{mg\,l^{-1}})$. Presence of chlorinated compounds, lignin and other oxygen requiring pollutants were found to be responsible for the high biochemical oxygen demand (BOD) $(1{,}680\,\mathrm{mg\,l^{-1}})$ and COD $(3{,}560\,\mathrm{mg\,l^{-1}})$. The chloride and sulphate content of the effluent was found to be $422\,\mathrm{mg\,l^{-1}}$ and $413\,\mathrm{mg\,l^{-1}}$, respectively.

Kinetics study

A steeply sloping curve for activated coconut jute carbon (Figure 1) indicates instantaneous sorption capacity up to 60 minutes $(>1{,}100\,\mathrm{CPU\,g^{-1}}$ of sorbent) with a sorbent dose of $0.6\,\mathrm{g\,100\,ml^{-1}}$ of effluent. Three distinct phases were observed in the plot in which the first phase (initial steep slope) indicates the instantaneous (overshoot phenomena) sorption of the coloured molecules within 30 min of contact time. This may be due to van der waals forces between coloured molecules and the surface of the ACJC sorbent. The second phase of the plot shows a gradual attainment of equilibrium indicating the utilization of all active sites on the sorbent surface. The third phase of the plots indicates attainment of equilibrium of the coloured molecules with the ACJC sorbent. From the above discussion, the sorption of coloured compounds over the activated coconut jute carbon is mainly due to physical forces involved. Percentage removal of colour was found to increase with time (Figure 1). A maximum of 90.1% colour removal was observed by ACJC in 100 minutes.

The adsorption rate constant (K_{ad}) for adsorption is determined from the following first order rate expression (Lagergren 1898):
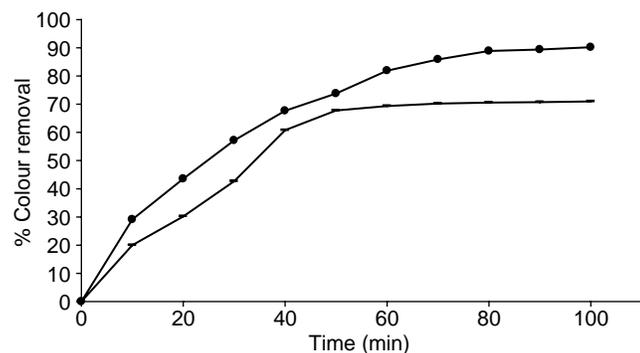
$$\log(q_e - q) = \log(q_e) - \left(\frac{K_{ad}}{2.303}\right)t \qquad (1)$$

Where q_e and q (both in CPU g^{-1} of sorbent) are the amount of colour adsorbed per unit mass of activated coconut jute carbon (ACJC) at equilibrium and at time t, respectively. k_{ad} is the first order rate constant $(\mathrm{min^{-1}})$. The value for k_{ad} was calculated from the slope of the linear plot of $\log(q_e\text{-}q)$ versus time (Figure 2). The rate constants for the initial colour concentration of 1,275 CPU at pH of 5.0 and 8.3 were found to be $0.073\,\mathrm{min^{-1}}$ and $0.055\,\mathrm{min^{-1}}$, respectively. The adsorption of colour followed the first order rate constant as there was not much variation between experimental and theoretical rate constants with an increase in initial colour concentration

Equilibrium study

To obtain information about the position of equilibrium between solute and sorbent, equilibrium studies were conducted by varying the adsorbent dose.

An increase in colour removal from 35% to 78.1% with an increase in adsorbent dose from 2 to $10\,\mathrm{g\,l^{-1}}$ was observed. An increase in uptake of colour with an increase in colour concentration is shown in Figure 4. The phenomenon of an increase in percentage colour removal with adsorbent dose up to certain level was also observed (Figure 3). This may be explained by the fact that with the increase in adsorbent dose more surfaces become available for the solutes to adsorb and this increases the rate of adsorption. Slow or constant removal beyond the $10\,\mathrm{g\,l^{-1}}$ equilibrium dose may be attributed to the attainment of equilibrium at the existing operating conditions.

Figure 1 | Effect of contact time on percentage colour adsorption on ACJC (pH: • 8.3, − 5.0, C_0 (CPU): 1,275, ACJC dose: $0.6\,\mathrm{g\,100\,ml^{-1}}$).
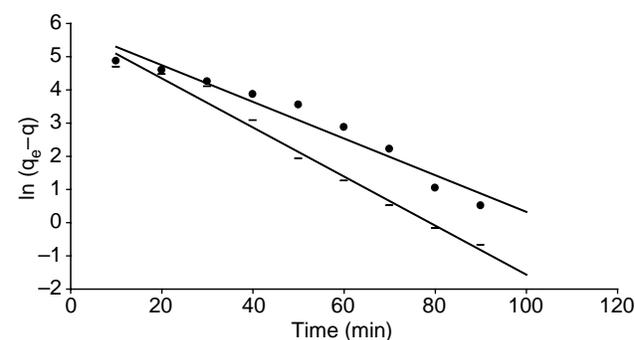

Figure 2 | Lagergren plot for adsorption of colour on ACJC (pH: • 8.3, − 5.0, C_0 CPU): 1,275).
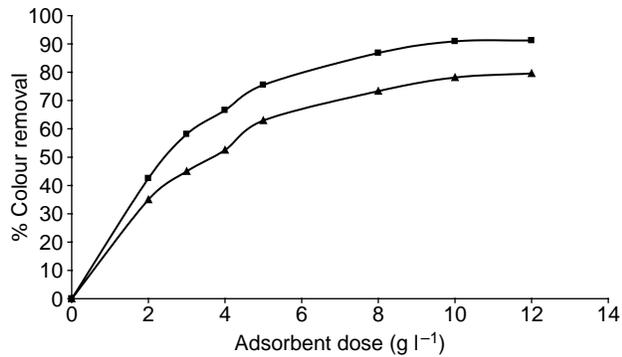
Figure 3 | Effect of adsorbent dose on percentage colour removal (C$_0$ (CPU): ■ 1,000 ▲ 480, pH 4.0).

Adsorption isotherm

To determine the functional form of the adsorption isotherm, the colour uptake (q$_e$) was plotted against the residual concentration (C$_e$). Figure 4 shows the adsorption capacity curve for colour removal onto activated coconut jute carbon. The curve obtained is concave to the concentration axis, which shows that the process is favourable. Uptake capacity increases with an increase in equilibrium concentration up to attainment of equilibrium after which no appreciable increase in sorption uptake was observed.

Adsorption isotherm data are quantified using empirical or theoretical equations since they describe the interactions between the adsorbate and adsorbent and so are critical in optimizing the use of adsorbent. A number of isotherm equations describe the adsorption process, such as Langmuir or Freundlich. Colour adsorption from pulp and paper mill effluent at different colour concentrations has been fitted to Langmuir and Freundlich isotherm models.
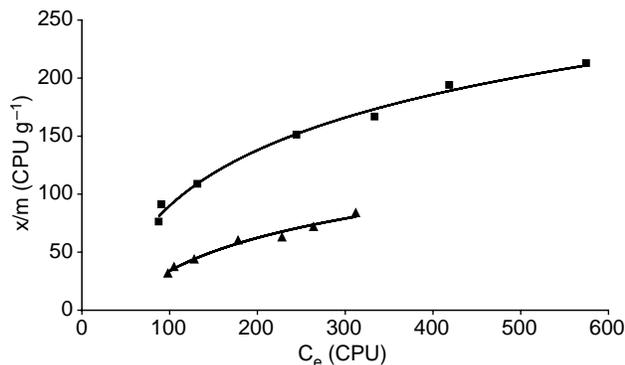
The Langmuir equation is the most popular of all the nonlinear isotherm expressions. It is a two-parameter equation. The equation is as given below:

$$q_e = \frac{bq_m C_e}{1 + bC_e} \qquad (2)$$

To obtain the parameters the linearized form of the above equation was used.

$$\frac{1}{q_e} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \qquad (3)$$

The value of the constant b and q$_m$ were obtained from the slope and intercept of the plot of 1/q$_e$ vs. 1/C$_e$ (Figure 5). Constants b and q$_m$ are related to energy of adsorption and adsorption capacity, respectively. The linear nature of the plot shows that the adsorption follows the Langmuir isotherm. The values of isotherm constants are tabulated in Table 3.

The Freundlich isotherm equation is one of the simplest for representing equilibrium data and is given as:

$$q_e = KC_e^{(1/n)} \qquad (4)$$

The above equation is linearized to determine the constants as given below:

$$\log(q_e) = \log(K) + \frac{1}{n}\log(C_e) \qquad (5)$$

Where K (mg g^{-1}) and n are Freundlich constants corresponding to adsorption capacity and adsorption intensity, respectively. The slope and intercept of a plot of log q$_e$ vs. log C$_e$ (Figure 6) gives the value of constants k and n. These values are also tabulated in Table 3.
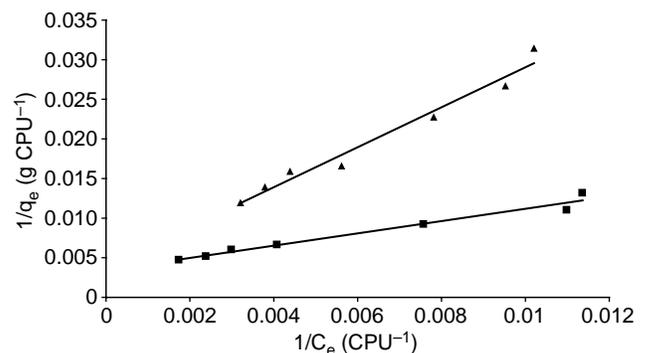

Figure 4 | Adsorption capacity curve of ACJC for adsorption of colour (C$_0$ (CPU): ■ 1,000 ▲ 480, pH 4.0).

Figure 5 | Langmuir plot for adsorption of colour on ACJC (C$_0$ (CPU): ■ 1, 000 ▲ 480, pH 4.0).

Table 3 │ Langmuir and Freundlich adsorption isotherm constants

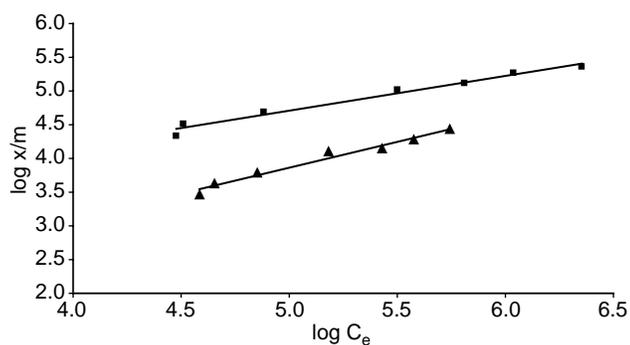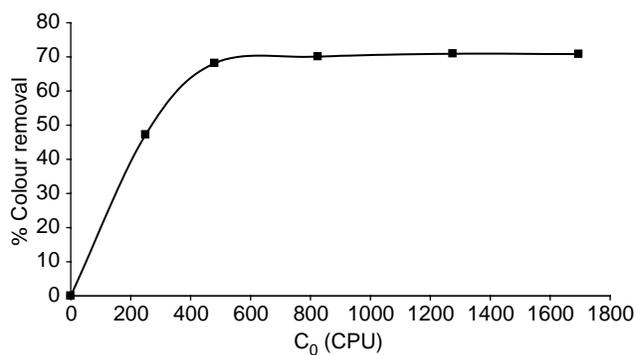| Initial colour concentration (CPU)	Langmuir isotherm constants			Freundlich constants	isotherm	
	b (l/CPU)	q_m (CPU g^{-1})	R^2	K	1/n	R^2
480	0.0015	263.15	0.9721	1.063	0.767	0.9714
1,000	0.0043	294.11	0.9703	134.33	0.516	0.9764

Effect of initial effluent pH

The effect of pH on the removal of colour from pulp and paper mill effluent is shown in Figure 7. For 1,275 CPU colour concentration, the percentage removal initially decreased from 90.5% to 86.6% when the pH was increased from 3.0 to 5.0, and then decreased suddenly to 30.8% at pH 8.0. The same trend was observed for initial colour concentration of 1,000 CPU, where a maximum removal of 79% was recorded at pH 2.0. Possible mechanisms of adsorption of colour on activated coconut jute carbon (ACJC) may be explained by either electrostatic interaction between the protonated groups of carbon and colour forming compounds or the chemical reaction between the adsorbate and adsorbent. At pH 2.0, significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and coloured molecule. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent does not favour the adsorption of coloured anions due to the electrostatic repulsion. Also, lower adsorption of colour at alkaline pH could be due to
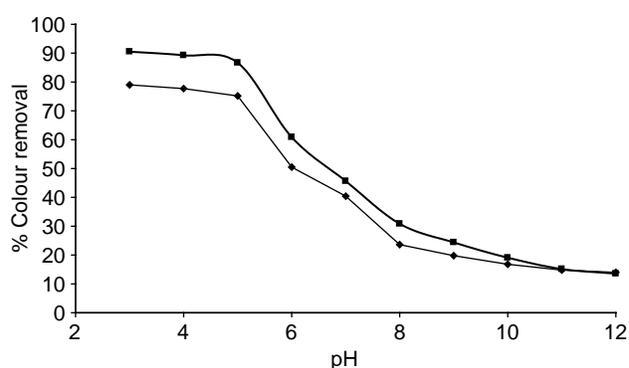
Figure 7 │ Effect of pH on adsorption of colour from pulp and paper mill effluent (C_0 (CPU): ■ 1,275 ◆ 1,000, ACJC dose (g l^{-1}): 6.0).

the presence of excess OH$^-$ ions competing with the coloured compounds for the adsorption sites (Figure 7).

The adsorption density (CPU g^{-1}) increased with the increase in effluent colour concentration; the percentage colour removal increased from 47.2% to 70.6% as the colour concentration was increased from 250 CPU to 825 CPU (Figure 8). It is clear that the removal of colour depends on the concentration of the colour. The removal curves are single, smooth and continuous leading to

Figure 6 │ Freundlich plot for adsorption of colour on ACJC (C_0 (CPU): ■ 1,000 ▲ 480, pH 4.0).

Figure 8 │ Effect of initial colour concentration on colour removal from pulp and paper mill effluent (pH: 4.0, ACJC dose (g l^{-1}): 6.0).

saturation. The proportional increase in colour uptake with initial colour concentration could be due to the presence of a greater number of coloured molecules available for adsorption. Once equilibrium is attained, no significant uptake was observed.

CONCLUSIONS

The present study showed that activated coconut jute carbon (ACJC) is effective for the removal of colour from pulp and paper mill effluent. Adsorption of colour was found to be dependent on adsorbent dose, initial colour concentration and solution pH. All adsorption data in the studied concentration range fitted well to both Langmuir and Freundlich adsorption models. Adsorption rate was found to be first order. A maximum adsorption capacity of 212.5 CPU g^{-1} of ACJC was observed at adsorbent dose of 2 g l^{-1} from a solution with initial colour concentration of 1,000 CPU. The ACJC adsorbent could be good alternative to expensive activated carbon, which could make the wastewater treatment process very economical. The water quality of the treated sample was found to be suitable for irrigation use or for direct discharge into the streams.

ACKNOWLEDGEMENTS

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