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COLOR POLLUTION CONTROL IN TEXTILE DYEING INDUSTRY EFFLUENTS USING TANNERY SLUDGE DERIVED ACTIVATED CARBON

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ABSTRACT. Effective treatment of dyestuff containing textile dyeing industry effluents require advanced treatment technologies such as adsorption for the removal of dyestuffs. Powdered commercial coal based activated carbon has been the most widely used adsorbent for the removal of dyestuffs from dyeing industry effluents. As an alternative to commercial coal based activated carbon, activated carbon prepared from dried tannery sludge was used as an adsorbent for dyestuff removal from simulated textile dying industry effluent in this study. The color removal performance of tannery sludge derived activated carbon and commercial coal based activated carbon has been investigated using parameters such as adsorbent dosage, initial dye concentration, pH and temperature. It was found that tannery sludge derived activated carbon exhibits dye removal efficiency that is about 80–90 % of that observed with commercial coal based activated carbon. The amount of dye adsorbed on to tannery sludge derived activated carbon is lower compared with commercial activated carbon at equilibrium and dye adsorption capacity increased with increase of initial dye concentration and temperature, and deceasing pH. It was found that the Langmuir isotherm appears to fit the isotherm data better than the Freundlich isotherm. The leachate of heavy metals from tannery sludge derived activated carbon to the environment is very low, which are within the standard limit of industrial effluent and leachable substances.

KEY WORDS: Adsorption, Tannery sludge derived activated carbon, Commercial coal based activated carbon, Adsorption isotherms, TCLP

INTRODUCTION

Textile dyeing is a process in which clothing material is imparted the desired color(s)/shades by applying colorants (dyes) and host of organic/inorganic chemicals in aqueous media often at elevated temperatures and pressures in stages. In the textile dyeing process in addition to dyes large quantity of other organic/inorganic chemicals like electrolytes, carriers, leveling agents, promoting agents, chelating agents, emulsifying oils, softening agents etc. are also added. About 10 to 20 % of the dye remains in the dye bath and is discharged along with other residual chemicals as exhausted dye bath waste. The exhausted dye bath wastes still contain significant quantities of coloring matter and impart color to the receiving water bodies. In addition to imparting color dye baths also contribute to organic and inorganic load of the receiving streams. Dye bath wastes are typically characterized by residual color, alkaline pH (mostly), excess TDS content, high COD but relatively low BOD values.

Coloration or discoloration of receiving water detracts attention, affects the appearance from aesthetic point of view and is dissented by public on presumption that the color is indicative of the pollution. Dyes are recognized as micro-toxicants and their acute and short-term effects have long been recognized. The complex organic framework of dyes and presence of heavy metals induce chronic toxicity and they may be mutagenic, teratogenic and carcinogenic. Many investigators reported several cases of tumors, cancer and effect on liver and kidney after long-term exposure. The most obvious impact of the discharge of dye colored effluent is the persisting nature of the color, which is stable and fast, difficult to degrade, toxic and inhibitory, and render the receiving water unfit for its intended use [1, 2].

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Various physical, chemical, physico-chemical and bio-chemical processes like sedimentation, equalization, neutralization, flotation, chemical oxidation/reduction, chemical precipitation, coagulation and flocculation, adsorption, ion exchange, reverse osmosis, electrochemical coagulation, etc. have been investigated for treatment of dye effluents [3-9]. Among all these processes, the adsorptive process is a sludge free process, and using activated carbon as a sorbent is found to be effective in removal of dye color and is firmly established as most reliable one [10].

Coal based activated carbon has been widely used as an adsorbent for the removal of various pollutants due to its high adsorption capacity [11-15]. However it has relatively high operational cost and problems of regeneration [16]. Therefore a number of non-conventional, low cost adsorbents have been tried for dye removal. These include bottom ash [17], fly ash [18, 19], coir pith [20], cassava peel [21], cotton [22], orange peel [23], bagasse fly ash [24], cellulose-based wastes [25], sewage sludge [26, 27], kaolinite [28], zeolite [29], wheat straw [30], sawdust [31, 32], char fines [33], oil shale and olive mill waste [34]. The adsorption process would provide an attractive technology, if the adsorbents were inexpensive and ready for use. Utilization of industrial solid waste for the treatment of wastewater is a win-win strategy because it not only converts the wastes in to useful materials but it also, alleviates the disposal problems. Further more it is not necessary to regenerate these cheap substitutes.

In this study, an activated carbon was prepared from dried tannery sludge, and studied for its potential use as an adsorbent for color removal from simulated cotton textile dyeing industry effluent with different parameters such as adsorbent dosage, initial pH, contact time, temperature and initial dye concentration. The color removal efficiency of commercial coal based activated carbon (CAC) was also investigated and compared with the performance of tannery sludge derived activated carbon (TSC). The Langmuir and Freundlich isotherm models were used to represent the equilibrium data. The toxicity characteristics leaching protocol (TCLP) was used to study the leachability of toxic metals from tannery sludge derived activated carbon, to assess its applicability from environmental safety point of view.

EXPERIMENTAL

The dried and dewatered tannery sludge collected from sludge drying beds of a common effluent treatment for tannery effluents, Chennai, Tamil Nadu, India, was used for making the activated carbon using the procedure shown in Figure 1. The pyrolysis of the sludge was carried out in a muffle furnace in the absence of oxygen. The activation of pyrolized sludge was performed by impregnating 10 g of pyrolized sludge sample in to 25 mL of activating agent solution ($ZnCl_2$ (3 M)) for 24 hours at room temperature. Later activating agent was drained and the wet activated carbon was dried at 105 ^{0}C for 24 hours. Before utilizing for adsorption studies, activated carbon sample was washed with distilled water to remove residual activating agents and dried at 105 ^{0}C in a hot air over for 24 hours. Characteristics of tannery sludge derived activated carbon in comparison with locally available commercial coal based activated carbon are presented in Table 1.

The simulated cotton textile dyeing industry effluent was prepared using Procion Brilliant Blue M-R (Figure 2) and other auxiliary chemicals as per the procedure suggested by Sreedhar Reddy *et al.*, [35]. According to the information obtained from the local dyeing industries, usually 20 % of the dyestuffs (hydrolyzed and/or unfixed form) and 100 % of all assisting chemicals remain in the exhausted dye bath. Laboratory prepared dye-bath was suitably diluted to simulate the actual field conditions. The Composition of suitably diluted exhausted dye-bath is presented in Table 2.

Table 1. Properties of activated carbons used in the investigation.

Activated carbon	Apparent density (g/L)	Iodine number	Surface area (m^2/g activated carbon)
Tannery sludge derived	788.5	998.431	999.03
Commercial coal based	291.7	1249.753	1083.42

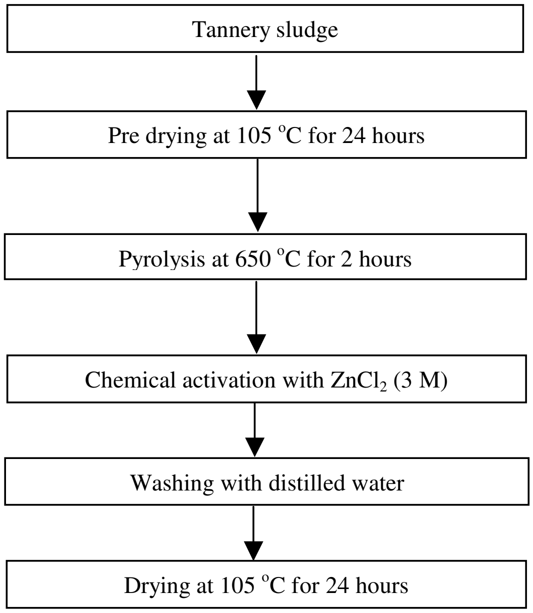

Figure 1. Schematic process flow diagram of activated carbon preparation from tannery sludge [27].

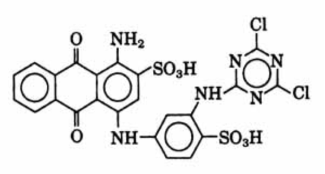

Figure 2. Chemical structure of Procion Brilliant Blue M-R.

Adsorption experiments were carried out by shaking 1.0 g tannery sludge derived activated carbon samples with 100 mL aqueous solution of simulated cotton textile dyeing effluent of desired concentrations at various initial dye concentrations and contact periods, pHs (3-11), and temperatures (25 and 40 ^{0}C) for 1 h (the time required for equilibrium to be reached between dyes adsorbed and dyes in solution). An incubator type shaker bath (Lab Net Scientific, India) was used to keep the temperature constant. The initial concentration of dye was varied from 120 mg/L to 40 mg/L and the adsorbent dosage is varied from 1 g/L to 10 g/L. All adsorption experiments were performed at 25 ^{0}C and pH 7.0 of dye solution except those in which the effects temperature and pH were investigated. The pH of the solution was adjusted with NaOH or HCl solution by using a pH meter. The pH meter was standardized with standard buffers before every measurement. At the end of the adsorption period, the solution was centrifuged for 15 min at 3000 rpm and then the concentrations of the residual dye (C_e) was determined with the aid of a Ultra-violet Visible Spectrophotometer (Spectronic, India) by measuring absorbance at λ_{max} of 602 nm. Blanks containing no dyes were used for each series of experiments. Each experimental data was an average of two independent adsorption tests. The amounts of dyes adsorbed were calculated from the concentrations in solutions before and after adsorption. The data obtained from the adsorption tests were then used to calculate the adsorption capacity, q_t (mg/g), of the adsorbent by a mass-balance relationship, which represents the amount of adsorbed dye per amount of dry adsorbent,

$$q_t = \frac{(C_o - C_t)V}{W} \qquad (1)$$

where C_o and C_t are the concentrations of dye in solution (mg/L) at time t = 0 and t, respectively, V the volume of the solution (liters), and W is the weight of the dry adsorbent used (g). The leaching characterization of tannery sludge derived activated carbon was evaluated using TCLP by suspending one gram of activated carbon in 20 mL of distilled water for 24 hours in an incubator shaker (Lab net scientific) at a rolling speed of 50 rpm. Later, distilled water was separated from the activated carbon using Whatman No. 40 filter paper and analyzed for heavy metals like chromium, cadmium, nickel and zinc using an atomic adsorption spectrophotometer as per the procedures suggested in standard methods for the examination of water and wastewater [36].

Table 2. Characteristics and composition of simulated cotton textile dyeing industry effluent.

No	Parameter	Concentration
1	Dye (Procion Brilliant Blue M-R)	120
2	pH	8.0
3	Total solids	7500
4	Total suspended solids	320
5	Total dissolved solids	7180
6	BOD_5 at 20 ^{0}C	560
7	COD	3200
8	Chlorides (as Cl^-)	3800
9	Sodium (as Na^+)	7900

All the values except pH are in mg/L.

RESULTS AND DISCUSSION

Effect of pH

Figure 3 shows the effect of pH on adsorption by TSC and CAC. Evidently pH significantly affected the extent of adsorption of dye over both the adsorbents. It was observed that the dye uptake by TSC and CAC was higher at lower pH. At lower pH the surface of the adsorbents becomes positively charged and this would facilitate sorption of the color cation probably by exchange sorption [37]. The variances in solid phase aggregation of dye on activated carbon is probably due to interactions between the cationic groups on the dye molecule and the carboxyl, carbonyl, lactonic and quinone (acidic) and basic functional groups within the activated carbon structure [38]. Maximum uptake of dye was observed at pH 3.0 on GAC and CAC. At an adsorbent loading of 1 g/L the amount of dye adsorbed on TSC and CAC increased from 10 to 30 mg/g and from 12 to 40 mg/g, respectively, with a decrease in pH from 11 to 3.

Effect of adsorbent dosage

Figure 4 shows the adsorption of dye from simulated textile dyeing industry effluent as a function of dosage of tannery sludge derived activated carbon and commercial activated carbon.

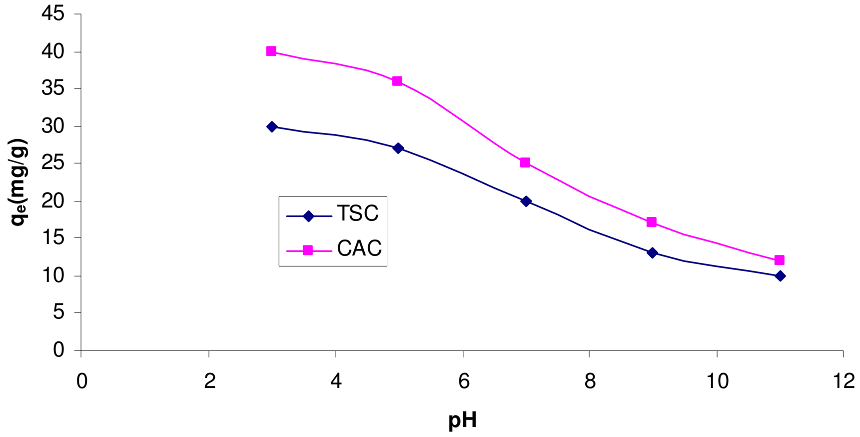

Figure 3. Effect of pH on adsorption capacities of tannery sludge derived and commercial activated carbons.

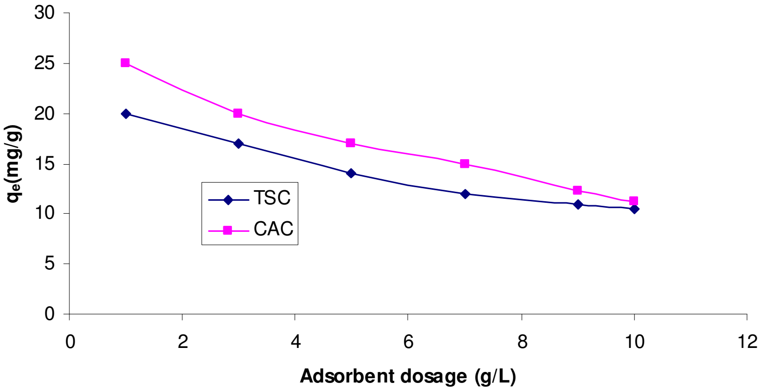

Figure 4. Effect of adsorbent dosage on adsorption capacities of tannery sludge derived and commercial activated carbons at equilibrium.

It is apparent that by increasing the adsorbent dose, the percentage dye removal increases, but adsorption density, the amount adsorbed per unit mass, decreases. It is readily understood that the number of available adsorption sites increases by increasing the adsorbent dose and it, therefore, results in the increase of percentage of dye adsorbed. The decrease in adsorption density with increase in the adsorbent dose is mainly because of unsaturation of adsorption sites through the adsorption process [37, 39]. Another reason may be due to the inter particle interaction, such as aggregation, resulting from high adsorbent dose. Such aggregation would lead to decrease in total surface area of the adsorbent and on increase in diffusional path length [37].

Effect of contact time and initial dye concentration

Effects of contact time and initial dye concentration on adsorption of dye from simulate textile dyeing effluent by commercial activated carbon and tannery sludge derived activated carbon are presented in Figure 5 and 6. The amount of dye adsorbed increased with increase in contact time and almost reached equilibrium in 60 min for initial dye concentrations 40, 80, and 120 mg/L used in this study. The equilibrium time is independent of initial dye concentration. But in the first 30 min, the initial rate of adsorption was greater for higher initial dye concentration, because the diffusion of dye molecules through the solution to the surface of adsorbents is affected by an increase in the dye concentration.

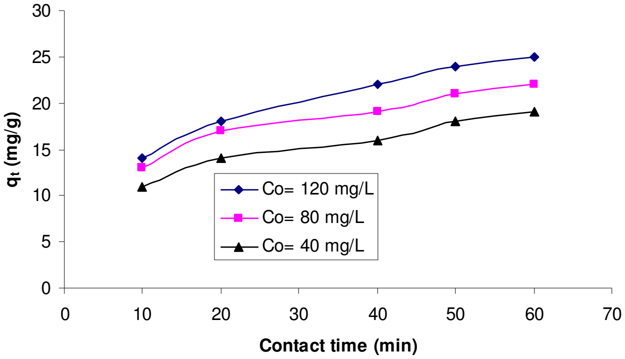

Figure 5. Effect of initial dye concentration and contact time on adsorption capacity of commercial activated carbon.

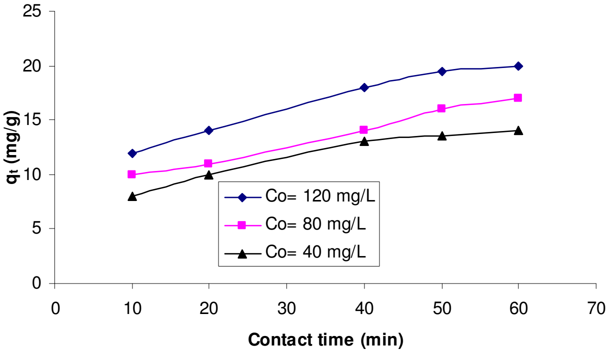

Figure 6. Effect of initial dye concentration and contact time on adsorption capacity of tannery sludge derived activated carbon.

An increase of the dye concentration accelerates the diffusion of dyes from the dye solution on to adsorbents due to the increase in the driving force of the concentration gradient [40, 41]. Hence, the amount of dye adsorbed at equilibrium increased from 14 to 20 mg/g for tannery sludge derived activated carbon and from 19 to 25 mg/g for commercial activated carbon, as the initial dye concentration was increased from 40 to 120 mg/L.

Effect of temperature

It has been believed that the temperature generally has two major effects on the adsorption process. Increasing the temperature will increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [42]. Figure 7 shows the effect of temperature on adsorption capacities of tannery sludge derived and commercial activated carbons.

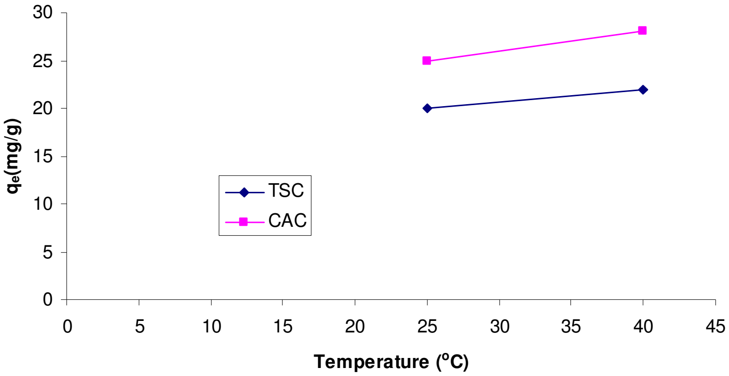

Figure 7. Effect of temperature on adsorption capacities of tannery sludge derived and commercial activated carbons.

It is seen that higher temperature will result in an increase in dye adsorption on tannery sludge derived and commercial activated carbons suggesting that the dye adsorption is an endothermic process. For tannery sludge derived activated carbon, the adsorption capacity at equilibrium is improved from 20 mg/g to 22 mg/g as the temperature of the experimentation is changed from 25 ^{0}C to 40 ^{0}C. However, for commercial activated carbon, the adsorption capacity at equilibrium is increased from 25 mg/g to 28 mg/g for the change in experimentation temperature from 25 ^{0}C to 40 ^{0}C.

Adsorption isotherms

The distribution of dye between the adsorbent and dye solution, when the system is at equilibrium, is important to obtain the capacity of the tannery sludge derived and commercial activated carbons. Table 3 summarizes the Q_0 and K_L values for the Langmuir isotherm, the K_f and n values for the Freundlich isotherm and the correlation coefficients for the two isotherms. The Langmuir isotherm is represented by the following equation [43]:

$$C_e/q_e = 1/Q_o K_L + C_e/Q_O \quad (2)$$

where q_e and C_e are defined as the amount of dye adsorbed (mg g^{-1}) and equilibrium liquid-phase concentration (mg/L), respectively. K_L is a direct measure of the intensity of the sorption (l mg^{-1}), and Q_0 is a constant related to the area occupied by a monolayer of adsorbate, reflecting the maximum adsorption capacity (mg g^{-1}). From the data of C_e/q_e vs C_e, Q_0 and K_L can be determined from the slope and intercept. The essential characteristics of Langmuir equation can be expressed in terms of a dimensionless separation factor R_L, which is defined by McKay *et al.* [44], as

$$R_L = 1/1 + K_L C_O \tag{3}$$

where C_0 is any adsorbate concentration at which the adsorption is carried out. Favorable adsorption is indicated by $0 < R_L < 1$ [44]. The Langmuir isotherm constants were found to be $Q_0 = 24.4$ mg g^{-1}, $K_L = 0.034$ L mg^{-1} for tannery sludge derived activated carbon ($R^2 = 0.973$), and $Q_0 = 27.24$ mg g^{-1}, $K_L = 0.068$ L mg^{-1} for commercial activated carbon ($R^2 = 0.9753$).

The R_L values for tannery sludge derived activated carbon were found to be between 0.59 and 0.196 for dye concentrations of 20, 40, 60, 80,100 and 120 mg L^{-1} (data not shown in Table 3) and for the commercial activated carbon R_L value is in between 0.42 and 0.109 for above said dye concentrations. The R_L values between 0.59 and 0.196 show favorable adsorption of textile dyes on to tannery sludge derived activated carbon. The Freundlich isotherm, as an empirical equation has been shown to be satisfactory for low adsorbate concentrations. The Freundlich equation was linearized as follows:

$$\text{Log}\,(X/M) = \log K_f + 1/n \log C_e \tag{4}$$

where K_f and n are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity, respectively. Values of K_f and n were calculated from the intercept and slope of the plots of log (X/M) versus log (C_e). From the slope and intercept of the best-fit lines, the following Freundlich isotherm constants were found for tannery sludge derived activated carbon and commercial activated carbon. $K_f = 3.88$ mg g^{-1}, n = 2.91 for tannery sludge derived activated carbon ($R^2 = 0.932$) and, $K_f = 5.86$ mg g^{-1}, n = 3.23 for commercial activated carbon ($R^2 = 0.9689$). The Freundlich exponent n for tannery sludge derived and commercial activated is in between 1 and 10 indicates favorable adsorption [45].

Table 3. Summary of the isotherm constants and correlation coefficients for Freundlich and Langmuir isotherms.

Adsorbent	Freundlich isotherm			Langmuir isotherm		
	K_f	n	R^2	Q_o (mg/g)	K_L (L/mg)	R^2
Tannery sludge derived	3.88	2.91	0.932	24.4	0.034	0.9473
Commercial activated carbon	5.86	3.23	0.9689	27.24	0.068	0.9753

Leachate testing of tannery sludge derived activated carbon

The results of TCLP leaching test are presented in Table 4. Tannery sludge derived activated carbon generated leachate with values lower than the United States Environmental Protection Agency (EPA) requirements for the disposal of hazardous metals [46]. This is mainly due to the conversion of metals in the raw sludge to metal oxides during the pyrolysis. The results of TCLP tests indicated that activated carbons derived from tannery sludge are non-hazardous.

Table 4. TCLP of activated carbon derived from tannery sludge: contents of metals in leachate.

Elements	Concentration in leachate (mg/L)	EPA regulatory level (mg/L)
Chromium	0.007	0.5
Nickel	0.003	-
Zinc	3.526	25
Cadmium	0.035	1.0

CONCLUSIONS

The results of the present investigation show that tannery sludge derived activated carbon has considerable potential for the removal of color from textile dying industry effluents over a wide range of concentrations. The adsorbed amount of dye increased as the surface area increased with an increasing adsorbent mass. The surface charge on the adsorbent and the solution pH play a significant role in influencing the capacity of an adsorbent towards dye ions. A decrease in the pH of solution leads to a significant increase in the adsorption capacities of dye on to commercial coal based activated carbon and tannery sludge derived activated carbon. The adsorbed amounts of dye increased with increase in contact time and reached the equilibrium in 60 min. The equilibrium time is independent of initial dye concentration. The equilibrium data have been analyzed using Langmuir and Freundlich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined from graphs of their linear equations. It was found that the Langmuir isotherm appears to fit the isotherm data better than the Freundlich isotherm. The results of TCLP tests indicate that tannery sludge derived activated carbons generates leachate with values lower than the environmental protection agency (EPA) requirements for trace metals for disposal of hazardous materials and are considered as non-hazardous.

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