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Removal of Crystal Violet Dye from Aqueous Solution through Biosorption using *Lysiloma Latisiliquum* Seed Powder: Kinetics and Isotherms

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***Abstract*— In the present work Lysiloma latisiliquum (LL) seed powder, a low-cost horticultural by product, was employed as the adsorbent for the removal of cationic dye Crystal violet (CV) from aqueous solutions. Batch mode adsorption studies were performed under different trial conditions, such as contact time, initial dye concentration, pH, adsorbent dosage, and temperature to determine the potentiality of the adsorbent for the removal of CV from aqueous solutions. optimum absorption of CV was observed to be at pH of 6.0, for an equilibrium time of 50 min with an adsorbent dosage of 20 g/lit. Kinetic data were studied using pseudo first order and pseudo second order models. The test results demonstrated that the pseudo second order model fits well. Freundlich, Langmuir isotherm and Tempkin models were applied to the equilibrium data. The information fitted well with Freundlich model with a maximum adsorption capacity of 14.1442 mg/g.**

Keywords—Adsorption; Kinetics; Isotherms; Adsorption capacity.

I. INTRODUCTION

One of the prime concerns of global environmental pollution is the release of synthetic dyes into aquatic ecosystems by discharging effluents from industries like textile, paper, leather, printing, pigments, petroleum, food, cosmetics, solvent, plastic, rubber, pesticides etc. [1,2]. Dyes are composed of different chemical types: Azo, Anthraquinone, Triphenylmethane, Azine, Xanthene, Nitro, Nitroso etc. [3]. Dyes are usually made of complex aromatic molecular structures, making them environmentally more stable. Presence of dyes makes it difficult for light to penetrate through water and thus affects the aquatic life [4]. Also, biological degradation of dyes is a difficult task due to their complex structure. During the process of dyeing, almost 10-15% of all the dyes are directly lost to wastewater [5]. Dyes also rank as one of the most notorious organic contaminants that are released into the environment [6,7]. Therefore, the treatment of dye removal is of significant importance for the sake of environmental concern.

Several methods have been developed to treat waste water. Commonly used include: flocculation, coagulation, precipitation, biosorption, membrane filtration and electrochemical techniques [9]. But these methods also lack cost advantage and relative efficiency. Biosorption on the other hand found to be effective for its cost and effective removal of contaminants from waste water [10]. Throughout literature, we can find the following biomass that has been used for biosorption: peat [10], Pinus bark powder [11], tomato plant root and green carbon [12], deoiled soya [13], alligator weed, japonica, rice bran, wheat bran [14], skin almond waste [15]. Yet, still there is a need to develop biosorbents that can be available in the open source for a competitive price and should also prove reliable.

Crystal Violet (CV) belongs to the triphenylmethane group family and is used enormously in various fields. CV is a protein dye and hence is used in identifying bloody fingerprints. It is also used in textile operations and as an animal medicine as a biological stain [8]. The maximum absorption ranges from 589-594 nm [16]. The major utility of this dye is in the textile industry as a purple dye and also in the sectors of paints and printing inks [17]. Besides its uses, it has proven to be harmful for humans by direct inhalation and skin contact. It is also reported to cause cancer and severe eye irritation [18,19].

II. MATERIALS AND METHODS

1. Adsorbate:

The dye (Crystal Violet) was purchased from Avra Synthesis. Its molecular formula is $C_{25}H_{30}N_3Cl$ and has a molecular weight of 407.98. The maximum value of absorbance for Crystal Violet (CV) is 584nm. Dye solutions for this experiment were prepared by dissolving desired amount of Crystal Violet in distilled water without any further purification. The adjustment of pH of the solutions were performed using 0.1N NaOH and 0.1N HNO_3 and a pH meter.

2. Preparation of Biosorbent:

The seeds of *Lysiloma latisiliquum* are collected near Kolkata in West Bengal. At first, the plant is obtained in its native state and was then washed several times with distilled water to remove extra fine particles. Subsequently, it is dried in an oven drier at 65^0C for 72h. The dried plant is then powdered into fine particles with a household grinder. Only the leaf component of the plant is used. The powder obtained is then stored in a glass container for further purpose without any pre-treatment.

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3.Biosorption Studies:

The studies were performed in a batch process to obtain the equilibrium and rate data. The experiments were carried out in a 250mL conical flasks containing 100mL of dye solution of various concentrations: 20mg/L, 50mg/L, 100mg/L, 150mg/L and 1.0g of *Lysiloma latisiliquum* powder. These flasks were subjected to agitation at 180 constant rpm for equilibrium time. Also, the experiments were repeated for varying temperatures for 25, 30, 35, 40, 45 ^{0}C and for pH values ranging from 2-9. The studies of biosorption at different temperatures were carried out with help of an orbital shaker incubator. At the end, samples were centrifuged to separate the solid and liquid phases.

4. Analyses:

The final dye concentration remaining in the solution is measured using UV spectrometer. The amount of dye adsorbed per unit of adsorbent was obtained by the following equation:

$$q_e = \frac{C_i - C_e}{m} V$$

where C_i is the initial dye concentration (mg/L), C_e is the equilibrium due concentration in solution (mg/L), V is the volume of solution of solution (L) and m is mass of adsorbent in g.

The percent removal (%) of dye was calculated using the following equation:

$$\% = \frac{C_i - C_e}{C_i} \times 100$$

III. RESULTS AND DISCUSSIONS

1. Effect of Contact Time:

The effect of contact time on biosorption of colour was investigated by including known measure of Wild Tamarind Seeds powder (1g/100 mL) to a beaker containing 50 mg/L grouping of Crystal violet colour with a basic pH of 6 at a temperature of 303K. This arrangement is agitated in an Orbital Shaker at 180 rpm for 1min and after that subject to centrifugation. Post the agitation, the clear liquid is carefully decanted and subject it to analysis for residual dye concentration. Same strategy is repeated at various time interims: 1, 3, 5, 10, 20, 30, 40, 50, 60, 90, 120, 50 and 180 mins. From these interims, equilibrium time is determined. From Fig 1., the rate biosorption uncovered that it increments with increment in disturbance time and achieved balance at 50 mins and level of biosorption watched was 75.40%.

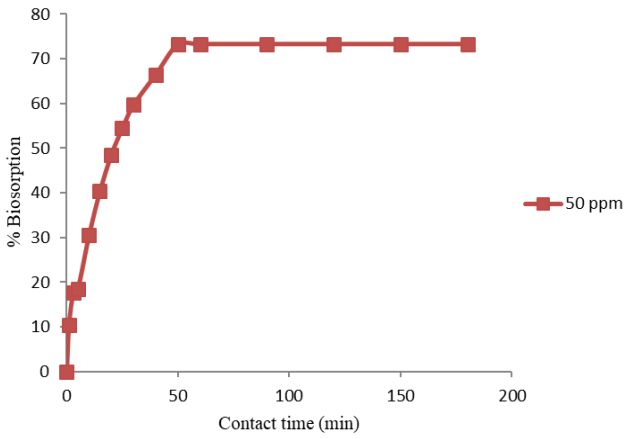

Fig 1. Effect of contact time on the adsorption of Crystal violet onto LL seeds (Experimental Data: Initial concentration = 50 mg/L, T=303K)

2. Effect of Initial Dye Concentration:

The impact of Initial concentration was estimated by varying concentrations of CV dye solution. For this, 20 mg/L, 50 mg/L, 100 mg/L, 150 mg/L initial concentration arrangements were taken for the test reason. The results obtained are shown in Fig. 2, demonstrates that dye uptake increased and % biosorption of CV on to LL seeds decrease with increase in initial dye concentration in the studied range. This increase in dye uptake (1.24 to 8.96 mg/g) is probably because of higher association between color particles and the biosorbent. Such behavior can be ascribed to the increase in the amount of biosorbate to the unchanging number to the accessible active sites on the biosorbent [20]. Equilibrium have been established at 50 minutes for all concentrations. Fig. 1 reveals that the bends are sharp and the straight leading to saturation, recommending the feasible monolayer coverage of the dyes on the carbon surface.

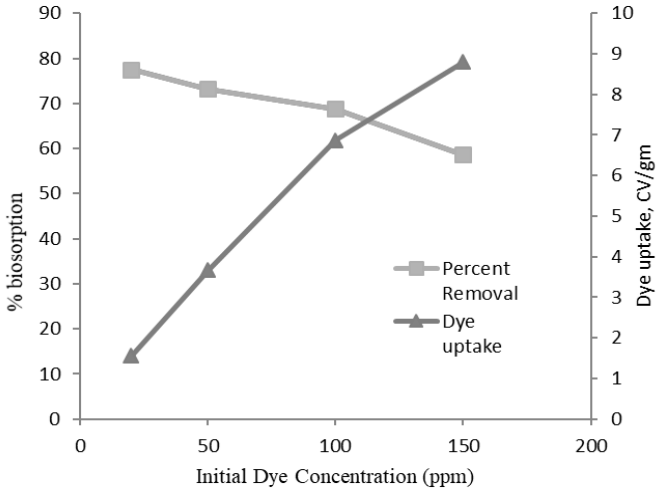

Fig. 2. Effect of initial concentration on the adsorption of Crystal violet onto LL seeds. (Experimental Data: Adsorbent Dosage = 1g/100 mL, Contact time = 50mins, T=303K).

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3. Effect of pH:

The pH of the solution effect the charge on the surface of adsorbent and degree of ionization of various components in the solution. The change in pH effect the adsorption procedure through the dissociation of functional groups onto the biosorbent surface dynamic sites. The adsorption of CV is examined in the pH ranges of 2-9. As pH is raised from 2 to 6, the biosorption limit of CV increased from 58.62 to 73.86% and later decreased from 6 to 9. Low pH reduces the biosorption of dye, due to competition with H^+ ions particles for active sites on the biosorbent surface. However, with increasing pH, this competition lower and dye ion will take over H^+ particles that was bounded to the biosorbent. This shows biosorption of CV is ideal in acidic medium. The outcomes are illustrated in Fig 3.

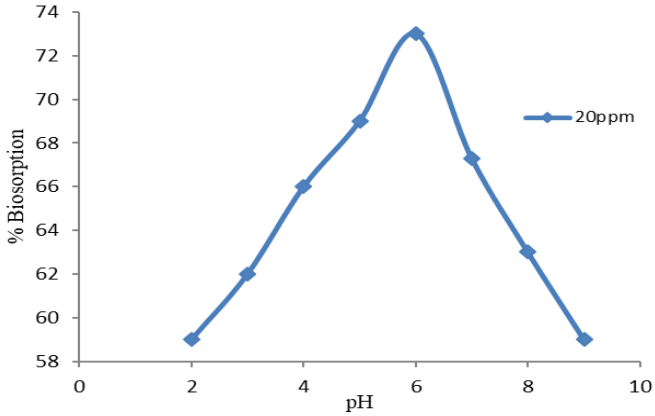

Fig. 3. Effect of pH on the adsorption of Crystal violet onto LL seeds (Experimental Data: Adsorbent Dosage = 1g/100 mL, initial concentration = 20mg/L, Contact time = 50 mins, T=303K).

4. Effect of Adsorbent Dosage:

The dosage of biosorbent is a fundamental parameter as it helps in deciding the adsorption limit of the biosorbent. Trial results are represented in Fig 4. The biosorption yield increased from 60.02% to 85.16%, when biosorbent dose was increased from 0.5g to 2.5g this fluctuation could be because of an increase in number of possible active sites and surface region of adsorbent. Increment in biosorbent mass from 2g to 2.5g demonstrated no appreciable improvement in biosorption yield. This might be attributed to a restricted aggregation of biomaterial, which at last outcomes in a decreased effective surface area for biosorption.

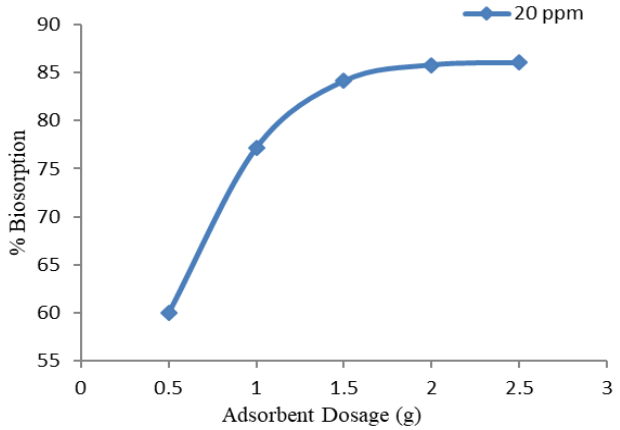

Fig. 4. Effect of Adsorbent Dosage on the adsorption of crystal violet onto LL seeds (Experimental data: Initial conc. = 20mg/L, Contact time = 50 mins, pH =6, T=303K).

5. Effect of Temperature:

Temperature is one of the prime components for governing the procedure of adsorption. Equilibrium capacity of the adsorbent is influenced by the adjustments in temperature. The adsorption rate constant for removal of CV with initial concentration of 20mg/L at pH 6 and temperatures 298K to 318K on *Lysiloma latisiliquum* seed powder has been considered for this reason. The discharge of CV increases from 70.02% to 85.65% by LL seeds powder with increase in temperature from 298K to 318K. The outcomes are illustrated in Fig 5. The increase in % biosorption might be because of increase in chemical interaction between dye ions.

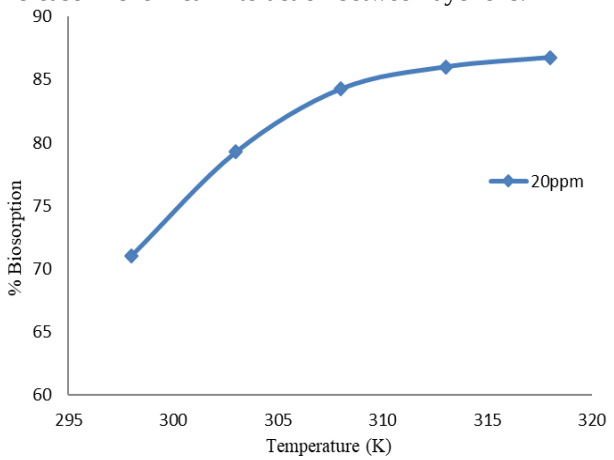

Fig. 5. Effect of Temperature on the adsorption of CV onto LL seeds (Experimental Data: Adsorbent Dosage = 2g/100 mL, initial conc = 20mg/L, Contact time = 50 mins, pH =6).

6. Biosorption Kinetics:

Studying of kinetics assumes an essential job as it helps us analyzing the reaction pathways and furthermore the mechanism included in it. Data on kinetics are required to get the ideal conditions for full-scale process. Kinetic studies were performed in conical flasks containing 100 mL CV concentration of 20 mg/L concentration. The conical flasks were shaken in an orbital shaker at constant rpm. Tests were taken at required intervals, centrifuged and analyzed for the residual CV concentrations. The Lagergren pseudo-first order rate condition and pseudo-second-order rate conditions were employed for displaying CV biosorption kinetics and kinetic information got were analyzed using regression coefficient (R^2).

The first-order rate expression of Lagergren supported solid capability is usually expressed as follows:

$$\frac{dq}{dt} = K_1(q_e - q)$$

After integrating and applying the boundary conditions, for q =0 at t = 0 and q = q at t = t, the integrated form of the above equation becomes

$$q = q_e(1 - e^{-Kt})$$

$$log\,(q_e - q) = log\,q_e - K_1 t/2.303$$

where q_e and q (both in mg/g) are respectively the amounts of dye adsorbed at equilibrium and 't' and K_1 (1/min) represents the rate consistent of biosorption.

The pseudo-second-order depends on the assumption that the adsorption procedure pursues second order chemisorption. This model can be expressed as:

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$$\frac{dq}{dt} = k_2(q_e - q)^2$$

$$q = \frac{k_2 q_e^2 t}{1 + k_2 q_2 t}$$

In linear form, this reduces to:

$$t/q = 1/K_2 q_e^2 + t/q_e$$

where k_2 (g/mg min) is the rate constant of pseudo-second-request adsorption.

The experiment data and correlation coefficients are given in Fig 6.1 and Fig 6.2. The table demonstrates that the correlation coefficients for the second order kinetics are more suitable than the first order kinetics. Consequently, from these we can say that the pseudo-second-order kinetics holds good than the Lagergren first order for the system studies in this work.

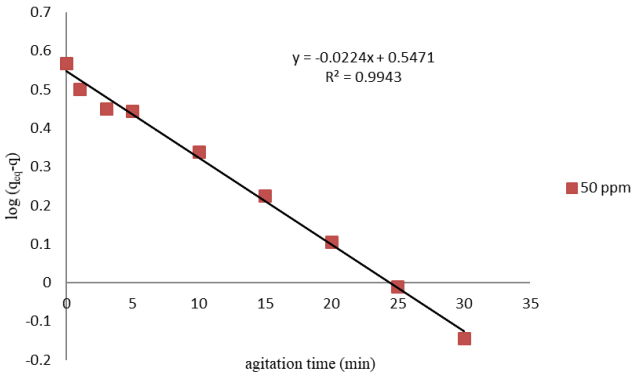

Fig 6.1. First order plots for the adsorption of CV onto LL seeds.

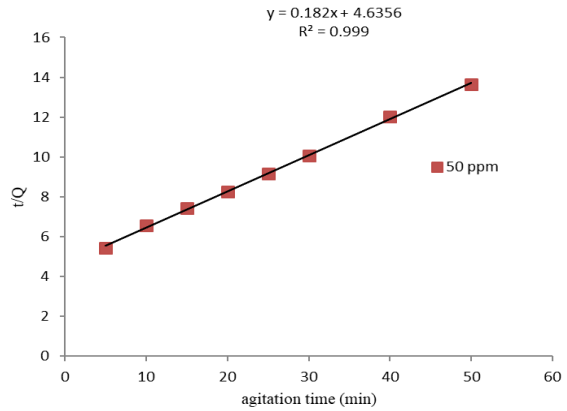

Fig 6.2. Pseudo second–order plots for the adsorption of CV onto LL seeds

TABLE I
Kinetic Parameters for adsorption of CV onto *Lysiloma latisiliquum* seed powder

Conc CV (mg/L)	q_e^{exp} (mg/g)	Pseudo-first-order			Pseudo-second-order		
		q_e^{cal}(mg/g)	K_1(min^{-1})	R^2	q_e^{cal}(mg/g)	K_2(min^{-1})	R^2
50	3.663	3.56	0.0895867	0.9943	4.95	0.0469	0.999

7. Biosorption Isotherms:

Adsorption is commonly demonstrated by isotherms as they relate the relative concentrations of solute adsorbed onto the solid (qe) and in solution (Ce). Throughout the literature, numerous models have been set up in order to get appropriate connections for the equilibrium curves. In this study, isotherms information was analyzed by using the three models: Langmuir, Freundlich and Temkin.

Biosorption isotherm studies were performed by contacting 1g of LL Seeds powder with 100 mL CV solutions of 20 mg/L concentration at pH 5 and temperature of 303K. The solution is agitated using orbital shaker at consistent rpm of 180 for equilibrium time. Whole method is repeated for temperatures in the range of 298K to 318K.

i) The Langmuir Model:

This model was proposed by Irving Langmuir in 1916 for the adsorption of species onto simple surfaces. It depends on the assumption that the sorption procedure is homogenous and monolayer with a fixed number of biosorption sites. The governing equation is as follows:

$$q_e = \frac{q_{max} K_a C_{eq}}{1 + K_a C_{eq}}$$

where q_{max} is the monolayer biosorption capacity (mg/g) and the Langmuir constant K_a is related to energy of biosorption. Linearized equation of Langmuir Model is:

$$C_{eq}/q_e = 1/q_{max} K_a + C_{eq}/q_{max}$$

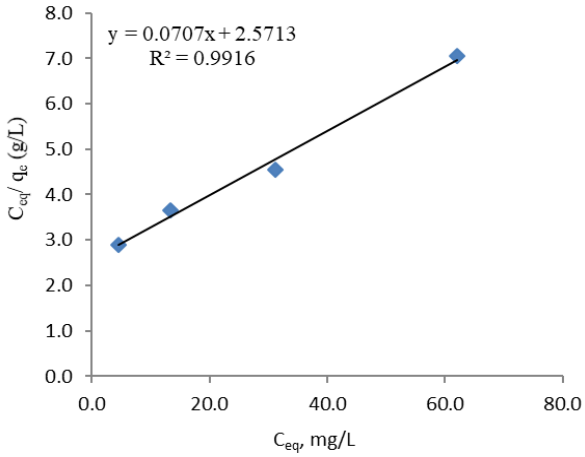

Fig. 7. Langmuir adsorption isotherm for the adsorption of CV onto LL seeds

ii) The Freundlich Model:

It was proposed by Boedecker in 1895 and later modified by Freundlich. It is an empirical equation based on sorption onto a heterogeneous surface. Its equation is:

$$q_e = KC_e^{\frac{1}{n}}$$

The linearized form is:

$$logq_e = logK + \frac{1}{n} logC_e$$

where 'q_e' is the equilibrium biosorption capacity (mg/g), C_e is the equilibrium concentration of the adsorbate within the solution. 'K' and 'n' are constants related to biosorption process such as biosorption capacity and intensity capacity.

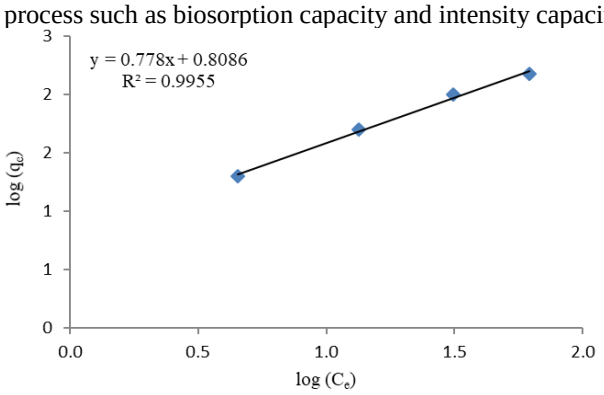

Fig. 8. Freundlich adsorption isotherm for the adsorption of CV onto LL seeds.

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iii) Tempkin Model:

It was proposed by Tempkin and Pyzhev. They explained that due to the interactions between adsorbate/biosorbent indirectly, the heat of biosorption of all the molecules in the layer will decrease linearly.

It's of the form:

$$q = \frac{RT}{b}\ln(A_T C_{eq})$$

where A_T (L/mg) and b are Temkin isotherm constants. 'T' is the absolute temperature in Kelvin and 'R' is the universal gas constant (J/mol. K). C_{eq} is the equilibrium concentration of the adsorbate.

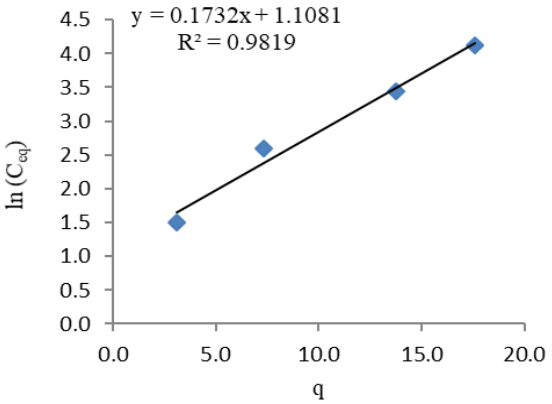

Fig. 9. Tempkin adsorption isotherm for the adsorption of CV onto LL seeds.

TABLE II
Isotherm Parameters

Isotherm	Parameter	Values
Langmuir	q_{max} (mg/g)	14.1442
	K_a	0.027
	R^2	0.9916
Freundlich	K	6.4357
	n	1.285
	R^2	0.9955
Tempkin	A_T (L/g)	1.69181
	B (KJ/mg)	14.54469
	R^2	0.9819

IV. CONCLUSION

Lysiloma latisiliquum seed powder was observed to be very effective for discharge of CV from aqueous solutions. The optimum pH for removal of CV was observed to be 6. The adsorptive removal of CV pursues Pseudo second order kinetics. Freundlich, Langmuir isotherm and Tempkin models were used to analyze equilibrium data. The Freundlich adsorption isotherm indicates best fit with maximum removal capacity of 14.1442 mg/g. The studies reveal that *Lysiloma latisiliquum* seed powder can be used as a potential adsorbent for removal of CV.

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