Investigation of Phenol Adsorption Characteristics by Chemically Treated Ganga Soil

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Abstract: In this study, chemically modified natural clay was employed to remove phenol from its aqueous solution. The effects of various parameters on phenol adsorption were investigated through batch adsorption in order to find out the phenol adsorption characteristics onto the surface of modified adsorbent. The adsorption of phenol was found to increase at lower solution pH and comparatively lower temperature. The adsorption was also found to increase with increase in initial concentration and contact time but decrease in adsorbent dose. The maximum adsorption capacity of 87.08 mg/g was found at a solution pH of 3, initial concentration of 100 mg/L, adsorbent dose of 1 g/L and temperature of 30 °C. The adsorption capacity was found to increase with decreasing temperature indicating exothermic nature of the adsorption process. The Adsorption characteristics was correlated by Langmuir, Freundlich and Tempkin isotherms at three different temperature and Langmuir isotherm exhibited a better fit to the experimental data. The kinetics of the adsorption process was also studied by using pseudo-first-order, pseudo second-order, intra-particle and Elovich model at three different temperatures and concentrations. It was found that pseudo-second-order kinetic was well correlated with the given experimental data. The thermodynamic study of phenol adsorption also confirmed the exothermic nature of the adsorption process.

Keywords: Adsorption, Adsorbent, Phenol, Kinetics, Equilibrium.

I. INTRODUCTION

Owing to its inherent toxicity and good solubility, phenols are considered to be one of the potential organic pollutants being discharged into the environment causing severe carcinogenic and mutagenic effects to living organisms as they generally get accumulated in animal and human tissues [1]. Phenolic pollutants are mainly emerged from in the outlets of fine chemical plants such as paints, pesticides, steel plant, coal conversion, petrochemical, polymeric resins, and petroleum and petrochemical industries. The tolerance limit of the phenol contents in the drinking water should not exceed 0.002 mg/L as per the Indian standard [2]. Because of its numerous inimical effects, the eradication of phenol from industrial wastewaters prior releasing to water bodies has become essential [3]. Several physicochemical methods, such as reverse osmosis and ultrafiltration, oxidation, reduction, precipitation, adsorption electrodialysis etc are employed among which adsorption appears to be the most pronounced technique as it is able to remove micropollutants [4-7]. The adsorption emerges to be the most prominent technique for the water reuse in terms of the cost effectiveness, high efficacy, versatility, flexibility, and simplicity of the design, ease of operation and insensitivity to toxic pollutants. It also does not lead to the formation of the harmful substances. [8]. In the present study, a low-cost adsorbent, chemically modified natural clay was used to remove phenol from its aqueous solution through batch adsorption study and the effects of different parameters were investigated upon phenol adsorption.

II. EXPERIMENTAL

A. *Preparation of Adsorbent*

In the present study, the adsorbent was prepared through chemical treatment by using zinc acetate dihydrate (98% pure) of natural soil collected from the local basin of the Ganges. The impregnation ratio of soil to zinc acetate dehydrate was 1:2. The soil was impregnated for 12 hours followed by subsequent washing with distilled water and then dried in a hot air oven at 105 °C for 30 min. All the reagents are used are of analytical grade and was supplied by Merck Specialist Pvt. Ltd., Mumbai, India. The detailed preparation method was also described in a previous research work by Bhar et al., 2017 [9].

B. *Adsorption experiments*

In this study, the batch adsorption experiments were conducted by adding 0.1g of adsorbent in 100 mL solution and contacted it for a predetermined time intervals. The aliquots of the samples were withdrawn at a predetermined time intervals and analysed in a UV-Vis Spectrophotometer (Chemito, Spectrascan 200) at 270 nm to determine the residual phenol concentration in the solution. For this purpose, the solution pH was varied from 2 - 8, the initial concentration of phenol solutions from 60 - 120 mg/L, adsorbent dose from 1 - 2 g/L, contact time from 5 - 120 min and temperature from 10 - 50 °C. The reproducibility of the experiments was tested under identical experimental conditions and the reproducibility was found to fall within 95% confidence range.

C. *Equilibrium Study*

The equilibrium study was carried out by varying the adsorbate initial concentrations from 30 - 200 mg/L with an adsorbent dose of 1 g/L. The solutions were shaken for 3 hours and then filtered and analysed in order to determine the residual adsorbate concentrations. Various isotherms such as Langmuir, Freundlich, and Tempkin were investigated in order to find out the equilibrium characteristics. The Langmuir isotherm can be expressed as:

$$q_e = \frac{K_l Q_m C_e}{1 + K_l C_e} \qquad (1)$$

where q_e is equilibrium uptake (mg/g), K_l is the Langmuir constant related to the energy of adsorption (L /mg), C_e is the solution concentration at equilibrium (mg/L) and Q_m is the monolayer adsorption capacity (mg/g).

The non-ideal sorption characteristics were investigated through Freundlich isotherm given by Eqn. (2)

$$q_e = K_F (C_e)^{1/n} \qquad (2)$$

where, K_F is a rough indicator of the adsorption capacity (L/g), and 1/n is the adsorption intensity. In general, with the increase of the adsorption capacity, the K_F value increases.

The heat of adsorption and interaction between adsorbent-adsorbate molecules were well predicted by Tempkin isotherm given by Eqn. (3).

$$q_e = B_1 \ln k_T + B_1 \ln C_e \qquad (3)$$

where k_T is the equilibrium binding constant which is corresponding to maximum binding energy (L/g) and B_1 corresponds to the heat of adsorption.

D. *Kinetic Study*

The kinetic study was carried out by varying the initial concentration of phenol solution from 60 - 120 mg/L at 30 °C. Different kinetic models such as pseudo first-order, pseudo-second order, intra-particle, and Elovich were fitted to the experimental data. The pseudo-first-order kinetics can be expressed as:

$$\frac{dq_t}{dt} = k_f (q_e - q_t) \qquad (4)$$

where q_t is the amount of adsorbate adsorbed at time t (mg/g), q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), k_f is the rate constant of pseudo-first-order model (min^{-1}), and t is the time (min). After integrating the above equation becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303} t \qquad (5)$$

This is the linearized form of the first order kinetic model [10].

The second order kinetics is given as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t) \qquad (6)$$

The equation corresponding to the pseudo-second-order kinetic model is given bellow [11]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

Where, k_2 is the equilibrium rate constant of the pseudo-second-order adsorption (g /mg- min).
The kinetic data were also fitted to Elovich and Intra-Particle diffusion model [12]. The amount of adsorption and desorption of a substance is given by Elovich model as follows:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad (8)$$

Where, α is the initial adsorption rate constant (mg/g-min) and β is the desorption constant (g/mg). The value of β also corresponds to the extent of surface coverage and activation energy for chemisorptions. The effect of pore diffusion on the adsorption process was determined by intra-particle diffusion model. The diffusion of adsorbate molecule involves several steps including transportation of the adsorbate molecules from the bulk liquid phase to the solid adsorbent surface and the diffusion of the adsorbate molecules in the pore interior of the adsorbent particles. The intra-particle diffusion model which can be represented as:

$$q_t = k_i t^{0.5} + I \qquad (9)$$

Where k_i is the rate constant of intraparticle transport (mg/g-h$^{1/2}$). Here, the values of I relates to the thickness of boundary layer where, larger the intercept, greater is the boundary layer effect.

E. Thermodynamic study

The endothermic or exothermic nature of the adsorption process was analysed through thermodynamic study. Here, different thermodynamic parameters such as changes in Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) at standard state were determined. Enthalpy represents total energy of the system including internal energy. If a change in enthalpy (ΔH) is positive, then the system is said to be endothermic in nature, but if the change in enthalpy (ΔH) is negative then the system is of exothermic in nature [13]. The disorder or randomness of the process is determined by entropy change (ΔS) and negative value of (ΔS) designates the decreased randomness of the process. The spontaneous nature of the adsorption process can be determined from the change in enthalpy (ΔH) and entropy (ΔS) can be determined from Vant Hoff equation [14]. The Vant Hoff equation can be expressed as follows:

$$\ln K_l = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (10)$$

Where K_l is the Langnuir constant (L/mg). The ΔH and ΔS are the enthalpy (kJ/mol) and entropy (J/mol-K) respectively. Besides, the Gibb's free energy (ΔG) can be obtained from Eqn. (11)

$$\Delta G = \Delta H - T\Delta S \qquad (11)$$

Where T is the absolute temperature (K) and ΔG is the Gibb's free energy (kJ/mol). A

III.RESULTS AND DISCUSSIONS

F. Effect of pH

The adsorption of phenol onto the surface of natural clay was found to be affected by solution pH. The effect of pH on the adsorption of phenol is shown in Fig. 1. It can be seen from Fig. 1 that the adsorption capacity of phenol does not change significantly with solution pH. The adsorption capacity (q_t) changes from 71.94 to 70.48 mg/g due to the change of pH in the range of 2.0 to 8.0 and the highest adsorption capacity was found at pH 3. This is due to the amphoteric property of adsorbent, and variation of pH of phenol [15].
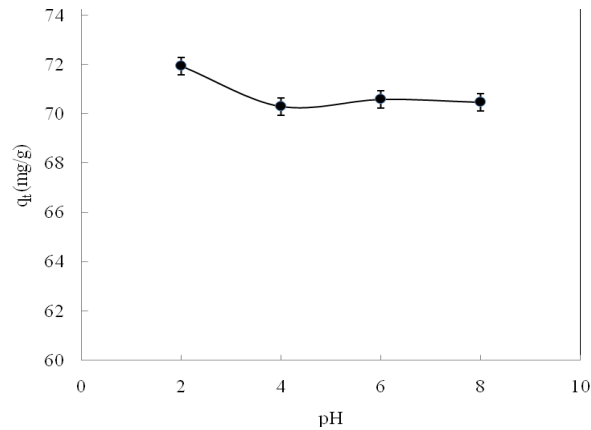
Fig. 1 Effect of pH on phenol adsorption

G. Effect of Initial concentration and contact time

The effect of initial concentration and contact time on phenol removal was studied by varying the initial phenol concentration from 60 – 120 mg/L and contact time from 5 – 120 minutes whereas the solution pH, temperature, and adsorbent dose were maintained at 3, 30 °C and 1 g/L respectively. The effect of adsorbent dose is shown in Fig. 2. It can be depicted from Fig. 2 that with an increase in initial concentration from 60 – 120 mg/L, the adsorption capacity increases from 50.65 - 107.15 mg/g. The probable reason may be a high rate of adsorption due to the higher driving force of mass transfer. Initially, more vacant sites are presents on the adsorbent surface which with passage of time gets saturated with phenol molecule resulting into lower adsorption capacity [16]
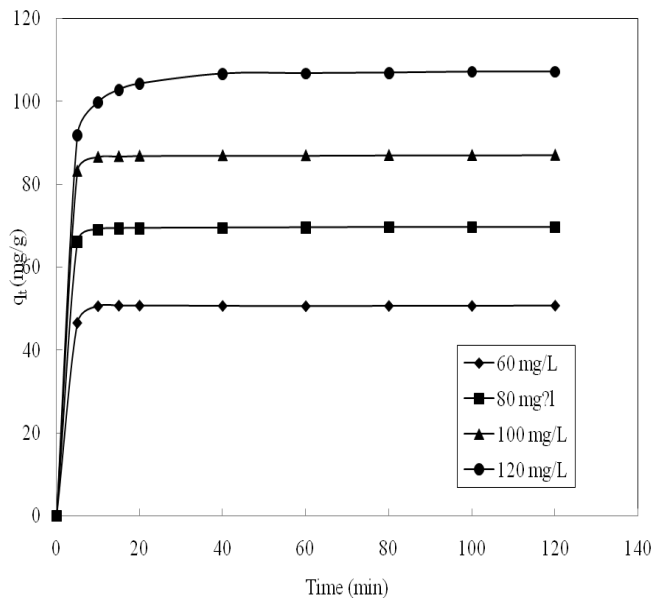

Fig. 2 Effect of initial concentration and contact on phenol adsorption

H. Effect of Adsorbent dose

In the present study, the adsorbent dose was varied from 1 to 2 g/L in order to study the effect of adsorbent dose on phenol removal. The other experimental conditions were maintained as solution pH: 3 and initial concentration: 100 mg/L and contact time: 120 min. The effect is shown in Fig. 3 where it can be seen that with an increase in adsorbent dose, a substantial decrease in adsorption capacity occurs from 87.08 to 39.78 mg/g. This phenomenon can be explained in the vicinity of the numerical relationship between adsorbent capacity (q_t) and adsorbent does. As the value of adsorbent dose increases the adsorption capacity decreases significantly [17].
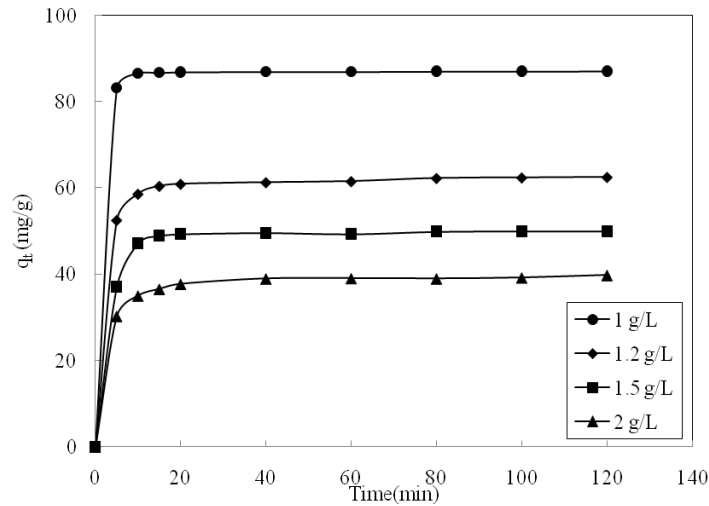
Fig.3 Effect of adsorbent dose on phenol adsorption

I. Effect of Temperature

The temperature effect on phenol adsorption was studied by varying the temperature from 30 -50 °C at a solution pH of 3, an initial adsorbent concentration of 100 mg/L and an adsorbent dose of 1 g/L. The temperature effect is shown in Fig. 4. It is observed from Fig. 4 that with decrease in temperature from 30 to 50 °C the adsorption capacity is decreased from 87.08 to 75.18 mg/g. The possible reason maybe at higher temperature the destruction of active sites on adsorbent surface takes place which leads to lower binding force between phenol molecules and the adsorbent surface [18].
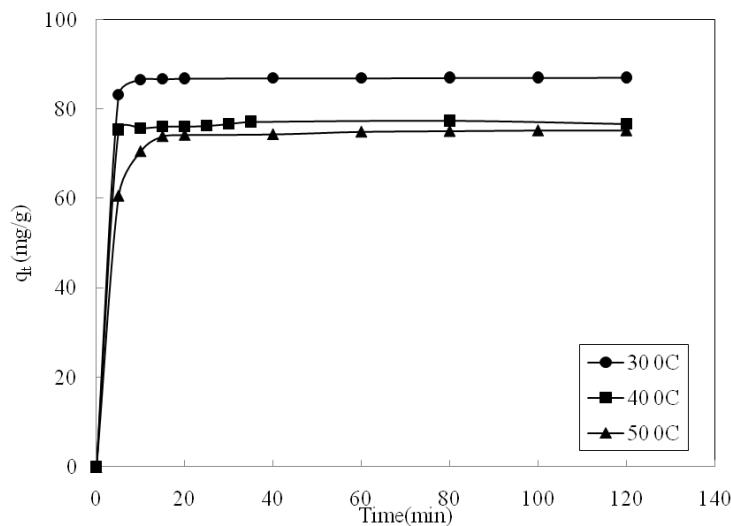

Fig. 4 Effect of temperature on phenol adsorption

J. Isotherm study for phenol adsorption

The adsorption characteristics of phenol were studied by using three different isotherms such as Langmuir, Freundlich, and Tempkin at three different temperatures varying from 30 to 50 °C. The values of the isotherm parameters at three different temperatures are shown in Table 1. It can be seen from Table 1 that Langmuir isotherm exhibits a better fit to the experimental data at three different temperatures with the highest regression coefficient ($R^2 = 0.998$) value and minimum chi-squared value ($\chi^2 = 2.594$). The monolayer equilibrium adsorption capacity was found to decrease from 237.653 to 176.052 mg/g as the temperature was increased from 30 to 50 °C. Similar trend was also observed by Calvete et al., (2010) [19].

TABLE I
EQUILIBRIUM MODEL CONSTANT AT DIFFERENT TEMPERATURES

Langmuir (30 °C)		Freundlich (30 °C)		Tempkin (30 °C)	
K_l (L/mg)	0.059	1/n	0.524	B (J/mol)	51.775
Q_m (mg/g)	237.653	K_F (L/g)	25.366	k_T (L/g)	0.596
R^2	0.993	R^2	0.961	R^2	0.990
χ^2	20.087	χ^2	129.024	χ^2	30.535
Langmuir (40 °C)		Freundlich (40 °C)		Tempkin (40 °C)	

K_l (L/mg)	0.051	1/n	0.462	B (J/mol)	38.049
Q_m (mg/g)	173.906	K_F (L/g)	20.601	k_T (L/g)	0.522
R^2	0.998	R^2	0.978	R^2	0.999
χ^2	2.929	χ^2	49.423	χ^2	1.951
Langmuir (50 °C)		Freundlich (50 °C)		Tempkin (50 °C)	
K_l (L/mg)	0.049	1/n	0.461	B (J/mol)	39.133
Q_m (mg/g)	176.052	K_F (L/g)	20.374	k_T (L/g)	0.472
R^2	0.998	R^2	0.967	R^2	0.997
χ^2	2.594	χ^2	76.536	χ^2	5.701

The experimental data were fitted to various isotherms such as, Langmuir, Freundlich and Tempkin at 30 °C as shown in Fig. 5. It can be clearly observed from Fig. 5 that Langmuir isotherm fits better with the experimental data in compare to other isotherms.
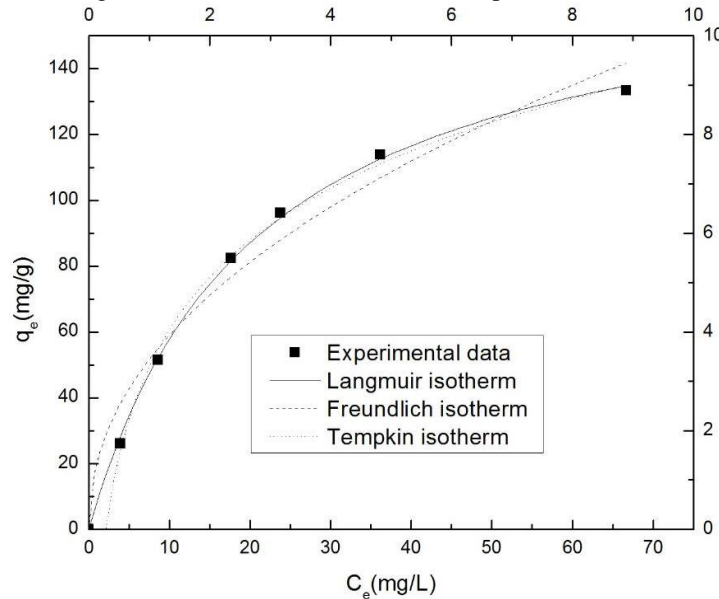

Fig. 5 Equilibrium study for phenol adsorption

K. Kinetic study of phenol adsorption

In this investigation pseudo second order kinetic model, the intra-particle diffusion model and the Elovich model were studied at different initial concentrations (60 - 120 mg/L) and temperatures (30 -50 °C). The values of the model parameter evaluated at different experimental conditions are shown in Table 2. It can be seen from Table 2 that pseudo second order kinetic model shows a better fit with the experimental data in compared to pseudo-first order kinetic model with a higher highest regression coefficient ($R^2 = 0.998$). The similar characteristics were also observed by Shirzad-Siboni et al., (2013) [20]. In order to investigate the diffusion mechanism of phenol molecules onto the surface of chemically modified natural clay the intra-particle diffusion model was investigated at various experimental conditions. It is noted that higher values of intra-particle diffusion rate constants (k_i) are obtained at the initial period of time due to comparatively larger concentration gradient and availability of the vacant pores Vargas et al., 2012 [21]. The value of the rate constant (k_i) is found to increase with an increase in initial phenol concentrations. The similar trend was also observed in the previous literature [22]. Elovich model was also investigated at different experimental conditions and the parameters values are shown in Table II.

TABLE II
KINETIC MODEL CONSTANTS AT DIFFERENT INITIAL CONCENTRATIONS

Model	Initial concentration (C_0, mg/L)			
	60	**80**	**100**	**120**
Pseudo-first-order				
q_e (mg/g)	44.473	52.917	65.554	72.794
k_1 (min^{-1})	0.355	0.359	0.326	0.175
R^2	0.977	0.925	0.898	0.869
Pseudo-second-order				
q_e (mg/g)	52.631	71.428	86.956	111.111
k_1 (min^{-1})	0.180	0.196	0.132	0.016
R^2	0.999	0.999	0.999	0.999
Elovich				

α (mg/g-min)	96420.78	2.719	3.9×10^{10}	60.580
β (g/mg)	0.249	0.014	0.296	0.021
R^2	0.887	0.999	0.890	0.850
Intra-particle diffusion				
k_i (mg/g-min$^{0.5}$)	16.863	23.265	29.193	
I	1.991	3.196	4.063	
R^2	0.953	0.938	0.936	

The pseudo first order and pseudo second order kinetic models were investigated at three different temperatures as shown in table III. It is observed form table three that experimental data are fitted well with pseudo second order kinetics.

TABLE IIII

KINETIC MODEL CONSTANTS AT DIFFERENT TEMPERATURES

Model	30	40	50
Pseudo-first-order			
q_e (mg/g)	65.554	50.373	65.554
k_1 (min^{-1})	0.326	0.291	0.326
R^2	0.898	0.766	0.898
Pseudo-second-order			
q_e (mg/g)	86.956	76.923	86.956
k_1 (min^{-1})	0.132	0.141	0.132
R^2	0.999	0.999	0.999

L. Evaluation of thermodynamic parameters

The phenol adsorption capacity was studied onto the surface of chemically modified natural clay at three different temperatures ranging from 303 to 323 K and the equilibrium constant for Langmuir isotherm amount was evaluated at these temperatures. The values of enthalpy, entropy and Gibb's free energy were calculated from the slope and intercept of the plot of ln K versus 1/T. The parameter values are presented in Table III. It is observed from Table III that the value of enthalpy is negative for this adsorption process indicating exothermic nature of adsorption. The negative value of ΔS shows the decreased randomness of the solid-solution interface during the adsorption of phenol on the adsorbent surface. The values of Gibb's free energy lie between 71 to 80 kJ/kmol indicating the chemisorptions process [23]. A typical value of ΔG lies between 0 and - 20 kJ/mol indicates physical adsorption whereas, the chemisorptions is characterized by a ΔG value of - 80 to - 400 kJ/mol. Chemisorption involves the sharing or transferring of charges from the adsorbent surface to the adsorbate molecules [24].

TABLE IIIII

KINETIC MODEL CONSTANTS AT DIFFERENT INITIAL CONCENTRATIONS

Temperature (K)	ΔG (kJ/mol)	ΔS (J/mol-K)	ΔH (kJ/mol)
303	71.29721	-48.7367	-7599
313	77.44208		
323	80.99058		

CONCLUSIONS

In this investigation, the adsorption characteristics of surface modified natural clay were studied for phenol adsorption. Batch adoption study was employed to investigate the effect of various parameters such as pH, initial concentration, adsorbent dose and temperature. An increase in adoption efficacy was observed at lower solution pH (3) and lower temperature (30°C). The phenol adsorption was also found to increase with an increase in initial concentration and contact time. The experimental data were fitted to pseudo first-order, pseudo second-order, intra-particle and Elovich model and pseudo-second-order kinetic model exhibited better fit to the experimental data. The decrease in adsorption capacity with an increase in temperature indicates the exothermic nature of the adsorption process which is further confirmed by the negative value of enthalpy. Various isotherms were also studied and the adsorption characteristics were successfully predicted by Langmuir isotherm with a monolayer adsorption capacity of 237.653 mg/g.

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