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Response surface methodology for prediction of Pb(II) adsorption characteristics

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Abstract : In the present investigation a half-fraction central composite design had been applied for prediction of Pb(II) adsorption capacity on the surface of microwave assisted activated carbon. For this purpose, five input variables such as, solution pH, initial concentration, adsorbent concentration, temperature, contact time and one output variable, Pb(II) adsorption capacity had taken into consideration. The optimum adsorption condition was found to be pH: 6, initial concentration: 120 mg/L, adsorbent concentration: 1.5 g/L, temperature: 20 °C, time: 80 min.

Keywords : Response surface methodology; Central composite design; Statistical modeling; Activated carbon; Optimization.

INTRODUCTION

Lead is a primary contaminant generally present in the effluents of lead battery industry, lead wire and pipe industry, dye manufacturing industry, printing industry and metal recycling industry[7]. Classically, lead intoxication occurres due to long exposure to high levels of lead present in various Pb(II) salts and organic lead compounds. Regulations regarding restricted use of lead have greatly reduced lead exposure in some developed countries but lead is still widely used in many developing countries. According to the Environmental Protection Agency (EPA) and World Health Organization (WHO), the permissible limits of lead for drinking water are 50 and 10 µg/L respectively whereas; the EPA standard for lead in wastewater is 500 µg/L[5]. Therefore, removal of lead ions from different industrial waste water has become very important. Many convention techniques such as, adsorption, membrane separation, ion exchange, nano-filtration are available for removal of Pb(II) micriowave assisted activated carbon. Therefore, in the present research, an activated carbon was prepared by carbonization of Acacia Auriculiformis scrap wood followed by micro-wave activation. The adsorption characteristics of Pb(II) had been modeled by using response surface methodology.

EXPERIMENTAL

Materials

Lead nitrate was procured from Loba Chemie

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Private Limited, Mumbai, India. The hydrochloric acid (35% pure), sodium hydroxide and the commercial activated carbon were procured from Merck Specialities Private Limited, Mumbai, India. All the chemicals used in the present study were of analytical grade.

(a) Experimental set up

The batch adsorption study was carried out in a mechanical shaker-incubator (Thermocon, India). The shaker is equipped with a digital temperature controller-cum- indicator and rpm indicator. A timer is also attached with the shaker.

(b) Procedure

The kinetic study was carried out by adding 0.1 g of adsorbent into a series of 250 mL conical flasks containing 100 mL solution of Pb(II) and were shaken in a mechanical shaker-incubator (Thermocon, India). The samples were withdrawn from the flasks at fixed interval of time and were filtered. Then the samples were analyzed for determining the residual Pb(II) concentration in the solution.

(c) Analysis of Pb(II)

The concentration of Pb(II) in solution was measured by using an atomic-absorption spectrophotometer (AAS) (Perkin Elmer Analyst 300, USA). The AAS reports the concentration of a metal in ppm (mg/L). Prior to the analysis, the instrument was calibrated by using some standard solutions of known metal concentrations. The absorbance of these solutions was measured to establish a relation between the measured absorbance and the metal concentration.

RESULTS AND DISCUSSIONS

Statistical modeling by CCD

The Pb(II) adsorption process was successfully optimized by using central composite design (CCD). In the present study, solution pH (x_1), adsorbent concentration (x_2, g/L), initial adsorbate concentration (x_3, mg/L), contact time (x_4, min) and temperature (x_5, °C) were selected as the input variables whereas the amount of Pb(II) adsorbed Y (mg/g) was selected as the output variable based on the literature and batch adsorption study discussed in the previous sections of this chapter. The average particle size and agitation speed were kept constant at 105.5 μm and 200 rpm respectively. The statistical analysis of the developed model was statistically performed by using Design expert software (Stat-Ease, Inc., version 8.0.7.1, Minneapolis, USA). The input parameters along with their respective levels are shown in TABLE 1. Each experimental parameter was coded at five levels: –α, –1, 0, +1 and +α. The ranges of the each experimental parameter are shown in TABLE 1.

TABLE 1: The range and levels of the input variables

Input variables	Ranges and levels				
	-α	-1	0	+1	+α
Solution pH (x_1)	4	5	6	7	8
Adsorbent concentration, (g/L) (x_2)	1.0	1.5	2	2.5	3.0
Initial concentration, (mg/L) (x_3)	80	100	120	140	160
Contact time, (min) (x_4)	15	40	65	90	115
Temperature, (°C) (x_5)	10	20	30	40	50

In the present study, the central composite design was developed for five factorial designs which consisted of thirty two experimental runs with six replicates at the center points as shown in TABLE 2.

The model equation and analysis of variance (ANOVA)

The analysis of variance (ANOVA) for Pb(II) adsorption along with the model F-value and the probability value is shown in TABLE 3. It is observed from TABLE 3 that the model is statistically significant with F-value of 228 and probability value of <0.0001. The value of the regression coefficient (R^2) for the model is found to be 0.998 which is quite close to unity. Therefore, the developed model is able to predict the response variable successfully. The value of adjusted determination coefficient ("Adj R-Squared" = 0. 993) signifies that only 0.7% of the total variable is not described by the model. The predicted determination coefficient ("Pred R-Squared" = 0.939) is found to be very close to the adjusted determination coefficient which indicates a high significance of the developed model. Besides, the values of the coefficient of variation (CV) and standard deviation have also been shown in TABLE 3 which signifies a good precision and reliability of the experiments[1].

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TABLE 2 : Complete design matrix with the response variable for Pb(II) adsorption

Run	x_1	x_2 (g/L)	x_3 (mg/L)	x_4 (min)	x_5 (°C)	Y (mg/g)
1	6	2	160	65	30	61.54
2	7	2.5	100	90	20	39.79
3	6	2	120	65	10	59.81
4	6	2	120	65	30	59.88
5	5	1.5	140	40	20	63.91
6	6	1	120	65	30	61.37
7	6	2	120	65	30	59.88
8	7	2.5	140	90	40	35.02
9	7	2.5	140	40	20	55.81
10	7	2.5	100	40	40	39.79
11	8	2	120	65	30	59.88
12	6	2	80	65	30	38.21
13	6	3	120	65	30	39.04
14	5	1.5	100	40	40	12.06
15	5	2.5	140	40	40	19.49
16	7	1.5	100	40	20	66.60
17	6	2	120	65	30	59.88
18	6	2	120	65	30	59.88
19	5	2.5	140	90	20	34.44
20	5	1.5	140	90	40	41.12
21	5	2.5	100	40	20	11.89
22	6	2	120	65	30	59.88
23	6	2	120	65	50	5.05
24	5	2.5	100	90	40	15.78
25	7	1.5	140	90	20	85.75
26	7	1.5	100	90	40	17.12
27	4	2	120	65	30	29.34
28	5	1.5	100	90	20	40.71
29	7	1.5	140	40	40	20.12
30	6	2	120	115	30	42.53
31	6	2	120	15	30	35.45
32	6	2	120	65	30	59.88

TABLE 3 : The ANOVA for Pb(II) adsorption

Sources of variations	Sum of squares	Degrees of freedom	Mean square	F value	Probability
Model	12209.22	20	610.46	228	< 0.0001
Residual	29.45	11	2.68		
Error	0	5	0		

Standard Deviation = 1.64; CV = 3.76; R^2 = 0.998; Adj-R^2 = 0.993; Pred-R^2 = 0.939

After performing the ANOVA, a regression equation for the quadratic model was obtained. The regression equation which correlates the input and output variables in terms of coded variables is as follows:

$$Y = 60.17 + 7.57x_1 - 5.84x_2 + 6.61x_3 + 1.43x_4 - 12.83x_5 + 3.56x_1x_2 - 2.82x_1x_3 - 1.83x_1x_4 - 4.59\,x_1x_5 - 2.31x_2x_3 - 1.50x_2x_4 + 8.42x_2x_5 + 3.37x_3x_4 - 3.12x_3x_5 - 0.94x_4x_5 - 4.11x_12 - 2.71x_2^2 - 2.79x_3^2 - 5.51x_4^2 - 7.15x_5^2 \quad (1)$$

This second-order full polynomial equation represents an empirical relationship between the amount of Pb(II) adsorbed and the solution pH, initial adsorbate concentrations, adsorbent concentration, contact time and temperature. In the present study, a second-order response surface model was studied to predict the Pb(II) adsorption characteristics. The results of the regression analysis obtained from ANOVA are shown in TABLE 4. The significance of each coefficient was estimated through the determination of p-values as shown in TABLE 4. The model terms with a probability of F-statistics value less than 0.0500 are found to have sinificant effects at 95% confidence level[2].

In the present study, the first-order main effect ($p<0.0001$) and the square effect ($p<0.0001$) of solution pH, adsorbent concentration, initial concentration

TABLE 4 : The results of regression analysis for Pb(II) adsorption

Model term	Regression coefficient	Standard error	p-value
Intercept	60.17	0.65	-
x_1	7.57	0.33	< 0.0001
x_2	-5.84	0.33	< 0.0001
x_3	6.61	0.33	< 0.0001
x_4	1.43	0.33	0.0113
x_5	-12.83	0.33	< 0.0001
x_1x_2	3.56	0.41	< 0.0001
x_1 x_3	-2.82	0.41	< 0.0001
x_1 x_4	-1.83	0.41	0.0009
x_1 x_5	-4.59	0.41	< 0.0001
x_2 x_3	-2.31	0.41	0.0002
x_2 x_4	-1.5	0.41	0.0038
x_2 x_5	8.42	0.41	< 0.0001
x_3 x_4	3.37	0.41	< 0.0001
x_3 x_5	-3.12	0.41	< 0.0001
x_4x_5	0.94	0.41	0.0415
x_1^2	-4.11	0.3	< 0.0001
x_2^2	-2.71	0.3	< 0.0001
x_3^2	-2.79	0.3	< 0.0001
x_4^2	-5.51	0.3	< 0.0001
x_5^2	-7.15	0.3	< 0.0001

and temperature have significant effect on Pb(II) adsorption. This signifies that small change in these parameters can affect Pb(II) adsorption to a larger extent.

In case of contact time, the square effect ($p<0.0001$) is much more significant than its first-order main effect ($p = 0.0113$). It is evident from this result that a small change in contact time can cause large variation in Pb(II) uptake as with progresses of time the rate of adsorption increases.

The combined effects of pH and adsorbent concentration, pH and initial concentration, pH and time, pH and temperature, adsorbent concentration and initial concentration, adsorbent concentration and time, adsorbent concentration and temperature, initial concentration and time, initial concentration and temperature, time and temperature are found to have significant effects of Pb(II) adsorption.

Effects of experimental parameters on Pb(II) adsorption

The effects of various experimental parameters such as solution pH, adsorbent concentration, initial Pb(II) concentration, contact time and temperature on the adsorption of Pb(II) were studied in detail. The combined effect of solution pH and initial adsorbate concentration on Pb(II) adsorption is shown through surface plot (Figure 1). It is observed that the Pb(II) adsorption increases with increase in solution pH and initial concentration. The adsorption of Pb(II) favors at comparatively higher pH values because of decrease in competition between positively charged Pb(II) ions and hydrogen ions (H^+).

Conversely, at lower solution pH, the adsorption of Pb(II) ions decreases due to excessive protonation of the activated carbon surface[3]. The Pb(II) adsorption is found to increase with increase in initial concentrations because of high concentration gradient between the bulk liquid and the adsorbent surface[9].

The combined effect of solution pH and adsorbent concentration on adsorption of Pb(II) is shown through contour plot (Figure 2). It is easily observed from Figure 2, that with increase in adsorbent concentration, the adsorption capacity decreases as the adsorption capacity is expressed as the amount of pollutant adsorbed per gram of adsorbent. It may also happen due to overcrowding of the adsorbent particles. At higher adsorbent concentration, conglomeration of adsorbent particles can also happen due to decrease in the effective surface area[8].

The combined effect of initial adsorbate concentration and contact time on Pb(II) adsorption is shown in Figure 3.

It is observed from Figure 3 that the Pb(II) adsorption increases with increase in contact time. Initially, a large number of vacant surface sites are available on the activated carbon surface and with the progresses of time the vacant sites are being occupied by the adsorbate molecules. Therefore, the adsorption process becomes slower and it finally reaches to equilibrium[6].

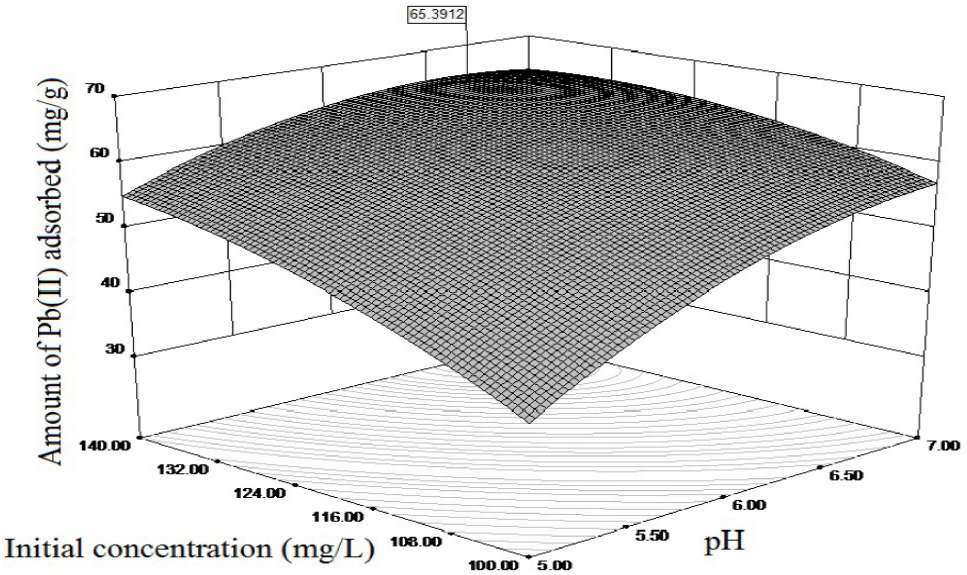

Figure 1 : Effect of pH and initial adsorbate concentration on the adsorption of Pb(II)

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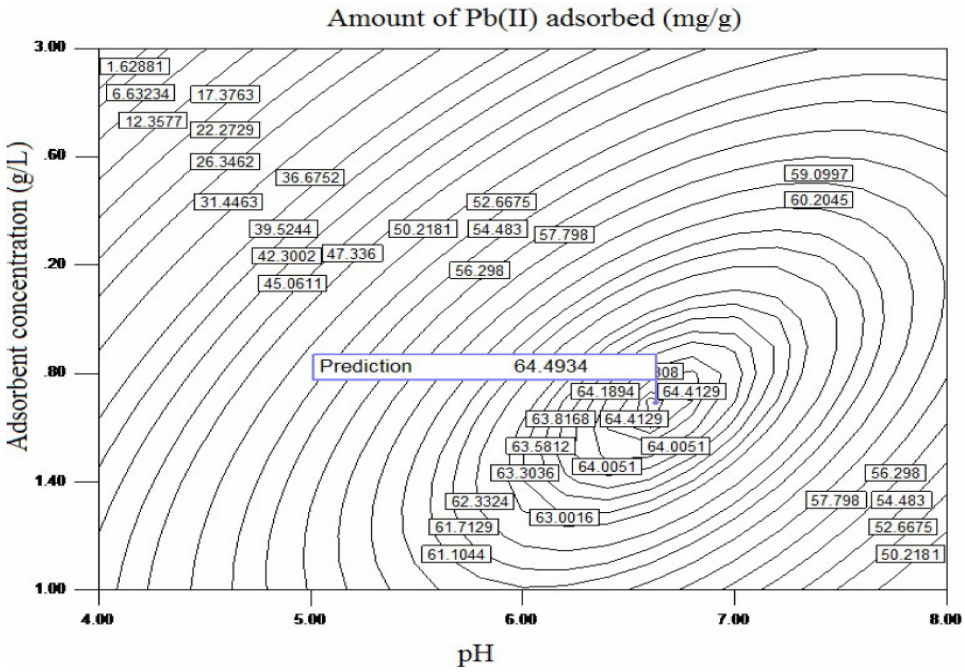

Figure 2 : Effect of pH and adsorbent concentration on the adsorption of Pb(II)

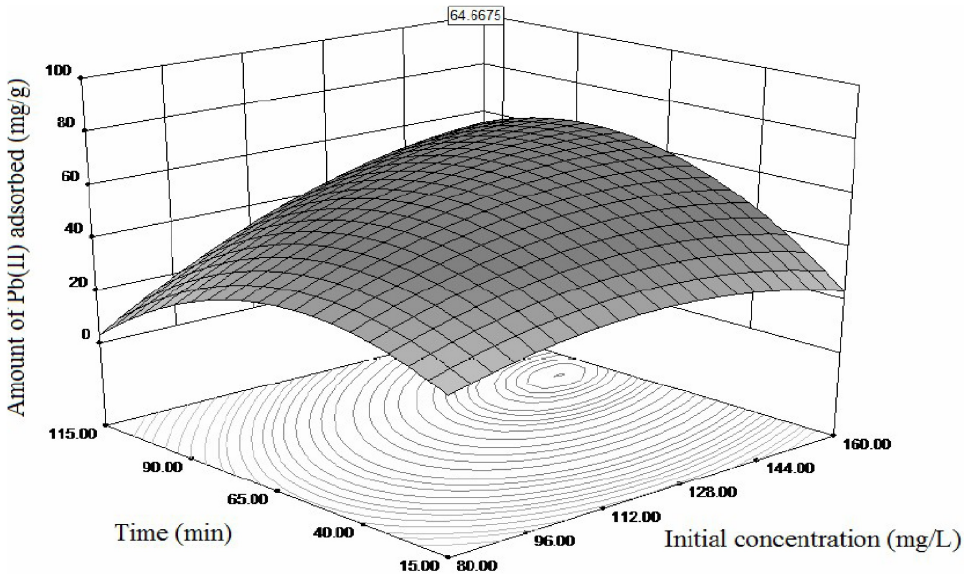

Figure 3 : Effect of initial adsorbate concentration and time on the adsorption of Pb(II)

The combined effect of adsorbate concentration and temperature on adsorption of Pb(II) is shown in Figure 4.

It is further noticed from Figure 5, that the maximum amount of Pb(II) adsorption (72.90 mg/g) is achieved with an initial concentration of 138 mg/L and 20 °C approximately. Besides, amount of Pb(II) adsorbed per unit mass of activated carbon is found to decrease with increase in temperature. This may happen due to weakened force of physical attraction between the adsorbate molecule and the adsorbent surface at higher temperature[4].

Comparison of experimental and model predicted values of response variable

The experimental and model predicted values of the response variable were compared. The plot between experimental (actual) and predicted values of amount of Pb(II) adsorbed is shown in Figure 5. It is noted from Figure 5 that both the values are in reasonable agreement with each other. It implies that a good correlation between input and output variables could

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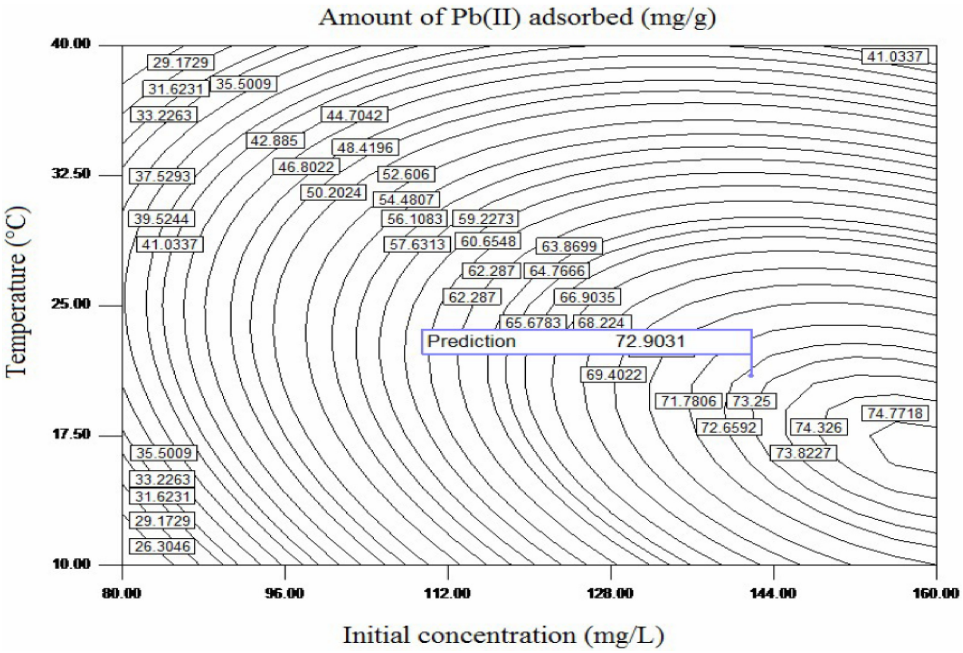

Figure 4 : Effect of initial concentration and temperature on the adsorption of Pb(II)

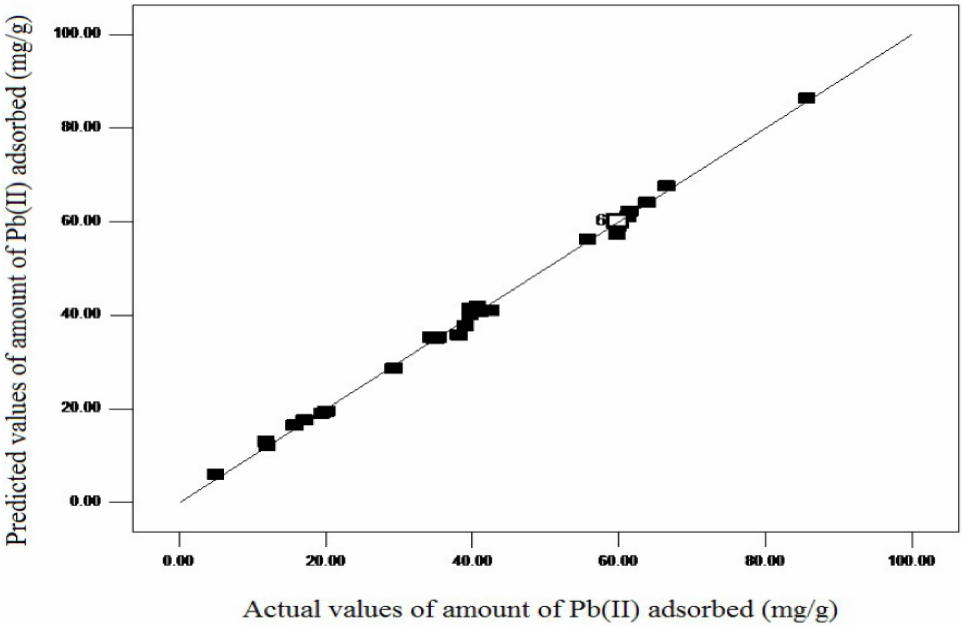

Figure 5 : Comparison of actual and predicted amount of Pb(II) adsorbed

be drawn by the model developed.

Optimization of process variables

The numerical optimization was applied to optimize the Pb(II) adsorption process and the optimum values of various parameters are provided in TABLE 5.

The model predicted value of Pb(II) adsorption capacity at this optimum condition was found to be 76.60 mg/g. A desirability value of 0.963 was obtained after optimizing the process parameters. The experimental value of lead adsorption capacity at this optimum condition was determined and the value was found to be 81.03 mg/g.

TABLE 5 : The optimum values of the experimental parameters

Parameters	Optimum values
Solution pH	6
Initial concentration (mg/L)	120
Adsorbent concentration (g/L)	1.5
Contact time (min)	80
Temperature (° C)	20

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CONCLUSION

The batch adsorption study of Pb(II) was carried out by using micro-wave assisted activated carbon. The residual Pb(II) concentrations, at the end of the batch studies, were found to be below the ISI specified permissible limit (0.1 mg/L). The adsorption process was successfully optimized by using a central-composite design (CCD) and the optimum process condition was found to be at a pH of 6, initial concentration of 120 mg/L, adsorbent concentration of 1.5 g/L, contact time of 80 min and temperature of 20 °C. It was observed that the experimental and predicted values of Pb(II) adsorption capacity were in well agreement with each other.

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