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Comparative Studies In Batch Reactor on Removal of Hexavalent Chromium Using *Tabebuia Aurea* , *Allium Cepa, Hibiscus Rosa-Sinensis, Delonix Regia* And *Saraca Indica* Leaves As A Biosorbent By Using Immobilization/Non-Immobilization Technique

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Abstract

This study reports the results on the performance of biosorbent materials such *as Tabebuia aurea, Allium cepa, Hibiscus rosa-sinensis, Delonix regia* and *Saraca indica* in removal of hexavalent chromium. The experiments were carried out in batch reactor with continues mixing at 75 rpm, the concentration ranging from 30 mg/l to 150 mg/l and 1 g of about 1.676 mm mesh size adsorbent was used. The adsorption process follows Pseudo-first-order, Pseudo-second-order, Elovich model, Intra-Particle diffusion model as well as isotherms such as Freundlich , Langmuir, Temkin isotherm, Dubinin-Radushkevich model. The systematic characterization of samples was performed using FT-IR. Regression coefficient R_1 of first order reaction kinetics was much better for Ia, IIIa, Va than IIa, IVa . The results indicated that the adsorption kinetics of chromium (VI) followed the first order kinetic model well, were as for immobilized leave samples (I_i,II_i,III_i,V_i) shows best fit except IV the adsorption kinetics of chromium (VI) followed the first order kinetic model well. The correlation coefficients (R^2) for the intraparticle diffusion model for *Tabebuia aurea* was 0.824, *Hibiscus rosa-sinensis* was 0.961, *Delonix regia* was 0.566 , *S. indica* was 0.747, *A. cepa* was 0.806.

Keywords: Hexavalent chromium, FT-IR, Isotherms, Kinetic models, Intra-particle diffusion model

Introduction

Chromium is a toxic metal are introduced into natural water by means of industrial wastes. They cause severe environmental and public health problems [15][16]. The major sources are from leather tanning, textile dyeing, electroplating and metal finishing industries[2]. Nearly 9,420,000 m^3 of wastewater was discharged from tannery industries annually [5][6][17].Lot of leather tanneries were located in Vellore, Ambur, Vaniyambadi, Erode areas in Tamilnadu, India. Repetitive use of contaminated water leads to various biological disorder such as mutation, cancer and also causes liver damage. Physical and chemical process have been in process for the treatment of Cr(VI) contaminated wastewater [7][9][13][18]. Due to high cost these process are not adaptable in large scale process [14] [10][12]. One of the cheapest processes for treating chromium industrial effluent is adsorption and this method is more economic when compared to all other physical and chemical process. According to Blacksmith Institute Research, about125 million people are affected b industrial pollution worldwide and it also stated that 30,000 are exposed to above the standards. Tamilnadu one of the leading leather producer in India. In which 6000 tanneries are involved in the chrome tanning process [18]. Cr in sea water range from 0.2-50µg/l were as in air it range from $5x10^{-6}$-$1.2x10^{-3}$ µg /m^3. [17]

Experimental

Material and Methods

Adsorbate

A stock solution of chromium (VI) was prepared (1000 mg/l) by dissolving required amount of potassium dichromate ($K_2Cr_2O_7$) in distilled water. The stock solution was diluted with distilled water to obtain desired concentration ranging from 30 to 150 mg/l.

Adsorbents

Adsorbent (I_a) Tabebuia aurea leaves were collected at Coimbatore Institute of Technology campus, Coimbatore.

Adsorbent (II_a) Allium cepa (Monocotyledon) was collected from local market at Hosur, Krishnagiri district, Tamil nadu.

Adsorbent (III_a) Hibiscus rosa-sinensis leaves were collected at Coimbatore Institute of Technology campus, Coimbatore.

Adsorbent (IV_a) Delonix regia leaves were collected at Coimbatore Institute of Technology campus, Coimbatore.

Adsorbent (V_a) Saraca indica leaves were collected at Coimbatore Institute of Technology campus, Coimbatore.

Adsorbent I_a-V_a was washed thoroughly in running water to remove impurities and any adhering particles. The leaves were dried at room temperature for 20 days until it became crisp. The dried leaves were crushed and blended to powder (preethi mixer) about 1.676 mm mesh size particle were taken for the study. The adsorbents was stored in an airtight container for further use.1g of each adsorbents (I_a-V_a) were added to the concentration ranging from 30 mg/L to 150 mg/l. Experiments were carried out with continues mixing at 75 rpm. The removal of Cr(VI) concentration were analyzed using Atomic Absorption Spectroscopy(AAS).

Immobilized adsorbents

Sodium alginate + adsorbent
↓
Calcium chloride
↓
Calcium alginate beads entrapped with adsorbents.

The adsorbents I_a, II_a, III_a, IV_a, V_a were immobilized by dissolving 1g of adsorbents with 10 ml of 5% sodium alginate solution And the mixture was added drop wise to the prepared 100 ml of 0.2M calcium chloride solution using 1 ml micropipette. The beads were allowed in calcium chloride solution for 20 min to deplete the excess calcium, excess calcium chloride on the surface of the beads were removed by washing with distilled water and named it as I_i, II_i, III_i, IV_i, V_i Approximately 1g of each immobilized adsorbents (Ii-Vi) were added to the concentration ranging from 30 mg/L to 150 mg/l. Experiments were carried out with continues mixing at 75 rpm. The removal of Cr(VI) concentration were analyzed using Atomic Absorption Spectroscopy (AAS).

Adsorption Isotherms and Kinetics

The adsorption isotherms and kinetic models were done according to the following models: Freundlich model, Langmuir model, Temkin model, Dubinin–Radushkevich Model, Pseudo-first order, Pseudo-second order, Elovich Model and Intra-particle diffusion model.

FT-IR analysis

FT-IR analysis was done for the leave samples (I_a-V_a) before and after treatment. Similarly FT-IR analysis was done for the immobilized leave samples (I_i-V_i) before and after treatment.

Results and Discussion

A comparative study was made on the adsorption experiments carried out by the leave samples and immobilized leave samples (*T. aurea, A. cepa, H. rosa-sinensis, D. regia and S. indica*)

Adsorption isotherm and kinetic models

The experimental data of adsorption of hexavalent chromium by beads (immobilized leave) followed isotherm in the order (Table 1)

Table 1: Isothermal studies for non-immobilized leave samples (I_a-V_a)

Isotherms	**Parameters**	**Non-immobilized leaves**				
		Tabebuia aurea **I_i**	***Allium cepa*** **II_i**	***Hibiscus rosa-sinensis*** **III_i**	***Delonix regia*** **IV_i**	***Saraca indica*** **V_i**
Langmuir isotherm	**q_{max} (mg/g)**	1.223	1.349	15.625	83.33	16.129
	b (L/mg)	0.2518	0.385	0.080	0.00783	0.034
	R^2	0.966	0.944	0.969	0.908	0.892
Freundlich isotherm	**N**	8.33	4	2.617	2.688	2.55
	K_F (mg/g) (L/g)$^{1/n}$	1.018	1.325	1.554	1.700	1.355
	R^2	0.802	0.812	0.846	0.569	0.966
Dubinin–Radushkevich	**q_m (mg/g)**	1048.37	1.351	11.24	25.89	5.37
	K_{DR}(mol^{2}J^2)	12512	109.4	2.962	1162	437.5
	R^2	0.864	0.003	0.79	0.751	0.665
	E (kJ/mol)	0.006	0.020	0.410	0.020	0.033
Temkin Isotherm	**A (L/min)**	1.223	1.000	1.0512	2.883	1.051
	B (L/min)	4.375	1.953	7.077	13.16	7.077
	b_T	70.312	157.51	43.46	23.37	43.46
	R^2	0.828	0.953	0.925	0.942	0.932

(I_i) : D-R > Temkin > Freundlich > Langmuir
(II_i) : Temkin > Langmuir > Freundlich > D-R
(III_i) : Temkin > Freundlich > D-R > Langmuir
(IV_i) : Freundlich > D-R > Temkin > Langmuir
(V_i) : Langmuir > Temkin > D-R > Freundlich

The experimental data of adsorption of hexavalent chromium for the leave samples which are not immobilized followed isotherm in the order (Table 2)

Table 2: Isothermal studies for immobilized leave samples (I_i–V_i)

Isotherms	**Parameters**	**Immobilized leaves (beads)**				
		Tabebuia aurea **I_i**	***Allium cepa*** **II_i**	***Hibiscus rosa-sinensis*** **III_i**	***Delonix regia*** **IV_i**	***Saraca indica*** **V_i**
Langmuir isotherm	**q_{max} (mg/g)**	4.385	3.623	16.393	1.515	13.157
	b (L/mg)	0.0131	0.069	0.0187	2.898	0.040
	R^2	0.481	0.944	0.836	0.559	0.934
Freundlich isotherm	**N**	0.896	2.5188	2.150	1.277	2.262
	K_F (mg/g) (L/g)$^{1/n}$	5.027	1.117	1.085	1.001	1.016
	R^2	0.845	0.937	0.917	0.987	0.896

Dubinin–Radushkevich	**q_m (mg/g)**	5.87	1.531	4.19	6.06	9.40
	K_{DR}(mol^{2}J^2)	10225	266.6	1070	158.4	1282
	R^2	0.921	0.690	0.807	0.779	0.824
	E (kJ/mol)	0.0069	0.043	0.02	0.056	0.019
Temkin Isotherm	**A (L/min)**	1.010	1.0049	1.0049	1.00	1.034
	B (L/min)	1.886	0.829	3.272	0.073	3.107
	b_T	163.10	371.07	94.015	4213.94	99.00
	R^2	0.990	0.989	0.948	0.392	0.868

(I_a) : Langmuir > D-R > Temkin > Freundlich
(II_a) : Langmuir > Temkin > Freundlich > D-R
(III_a) : Langmuir > Temkin > Freundlich > D-R
(IV_a) : Langmuir > Temkin > D-R > Freundlich
(V_a) : Freundlich > Temkin > Langmuir > D-R

In D-R isothermal model both immobilized (I_i to V_i) and non-immobilized (I_a to V_a) the mean energy of adsorption (E) values shown in the Table 3 is less than 8 KJ/mol, then it was concluded that it follows physical adsorption[9,10]. In order to define the adsorption kinetics of heavy meal ions the kinetic parameters for the adsorption process were studied. Linear plot 1/qt vs 1/t indicates the applicability of the first order kinetics and good agreement with experimental data. Regression coefficient R_1 of first order reaction kinetics was better for I_a, III_a,V_a than II_a, Iv_a (Table 4) The results indicated that the adsorption kinetics of chromium (VI) followed the first order kinetic model well. Were as for immobilized leave samples (I_i, II_i, III_i, V_i) shows best fit except IV_i the adsorption kinetics of chromium (VI) followed the first order kinetic model well.

Table 3: Kinetic studies for non-immobilized leave samples (I_a –V_a)

Models	**Parameters**	**Non-Immobilized Leaves**				
		Tabebuia aurea **I_a**	***Allium cepa*** **II_a**	***Hibiscus rosa-sinensis*** **III_a**	***Delonix regia*** **IV_a**	***Saraca indica*** **V_a**
Pseudo first order model	**q_e (mg/g)**	5.408	3.303	3.472	9.12	3.691
	K_1 (min^{-1})	0.023	0.0138	0.0161	0.034	0.0161
	R^2	0.914	0.915	0.908	0.957	0.963
Pseudo second order model	**q_e (mg/g)**	5.617	19.60	30.30	30.30	29.41
	K_2 (g/mg/min)	9.6×10^{-4}	7.5×10^{-5}	1.27×10^{-4}	1.31×10^{-4}	1.5×10^{-4}
	R^2	0.323	0.083	0.484	0.774	0.581

Table 4: Kinetic studies for immobilized leave samples (I_i –V_i)

Models	**Parameters**	**Immobilized leaves (beads)**				
		Tabebuia aurea **I_i**	***Allium cepa*** **II_i**	***Hibiscus rosa-sinensis*** **III_i**	***Delonix regia*** **IV_i**	***Saraca indica*** **V_i**
Pseudo first order model	**q_e (mg/g)**	2.20	2.04	3.640	8.08	2.44
	K_1 (min^{-1})	0.092	0.092	0.161	0.23	0.138
	R^2	0.982	0.996	0.913	0.955	0.946
Pseudo second order model	**q_e (mg/g)**	7.75	8.695	28.57	200	17.24
	K_2 (g/mg/min)	0.00027	0.00055	0.00020	3.6×10^{-6}	0.00058
	R^2	0.441	0.991	0.828	0.004	0.676
The Intra-Particle Diffusion	**R^2**	0.824	0.806	0.961	0.566	0.747

Table 5: FT-IR absorption bands and the possible functional groups

WAVE NUMBER cm^{-1}		**FUNCTIONAL GROUPS**
Before treatment	**After treatment**	
-	3332	OH Stretch
2361(narrow)	2361(broad)	OH –Carboxylic acid
-	2115 (2200-2000)	Inorganic ions
-	1836	Aromatic ring
3620-3540(narrow)	3620-3540 (broad)	Tertiary alcohol, OH Stretch
-	1740	C=O-Aldehyde group
-	1642	NO_2
2332	2332	H_3O
1693	1693	Primary Amides
1461	1464	carboxyl group
670(narrow band)	670(broad band)	C-S Stretch,Phenyl derivatives
-	3300-3400	OH Stretch
3620-3540	-	Tertiary alcohol, OH Stretch
2362(narrow)	2362(broad)	OH –Carboxylic acid
1740	1740	C=O-Aldehyde group
1516 (narrow)	1516(broad)	N=O Nitro (R-NO_2)
1426	1426	C-H bend
1014	-	C-O
670	-	C-S Stretch , Phenyl derivatives

According to intraparticle diffusion model, the plot of uptake, qt versus the square root of time should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intra-particle diffusion is the rate-controlling step[16,].When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further show that the intra-particle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously. The correlation coefficients (R^2) for the intraparticle diffusion model for *Tabebuia aurea* was 0.824, *Hibiscus rosa-sinensis* was 0.961, *Delonix regia* was 0.566 , *S.indica* was 0.747, *A.cepa* was 0.806

FT-IR Analysis

The changes in surface functional groups in the biosorbents during the biosorption process are studied by the FTIR technology. Figure 1-4 shows the infrared spectra of before and after the biosorption of Hexavalent chromium of leave sample (I_a-V_a) and (I_i-V_i).The broad region around 3400 cm^{-1} can be assigned to –OH stretch and amine groups. The absorbance peak at 2363 cm^{-1} could be the H_3O+, respectively. The peaks at 1427–1466 cm^{-1} represent the carboxylate salt COO–M, where M denotes to the metal cations such as Na^+, K^+, Ca^{2+} and Mg^{2+} that may naturally exist in the leaf samples. FTIR analysis of samples shows the peak at 3620-3540 cm^{-1} were as after treatment the peak is shifted to 3300-3400 cm^{-1}, 1014 cm^{-1} and 670 cm^{-1} have not appeared in the after sample of *T.aurea.* The IR spectra before and after the Cr(VI) binding shows that Phenyl derivatives, carboxylic and alcohol group may also involved in binding of chromium. The shift of 1516 cm^{-1} to 1547 cm^{-1} indicates that, the amino group is one of the important functional groups in the binding of Cr. Aldehyde groups and alcohol groups are responsible for removal of chromium.

Conclusions

In this study, leave samples with and without immobilization were used for the removal of Hexavalent chromium from aqueous solutions. The kinetic studies showed that Pseudo first order rate equation was able to provide a realistic description of adsorption kinetics of hexavalent chromium. Langmuir, Dubinin-Radushkevich (D-R), Temkin, Freundlich equations were used to describe the adsorption of hexavalent chromium onto I_i to V_i and I_a to V_a. Hence the choice of immobilized adsorbent will be based on the specific application and economic consideration. The experimental results and comparative studies made would be useful for the effective application to treat industrial effluent.

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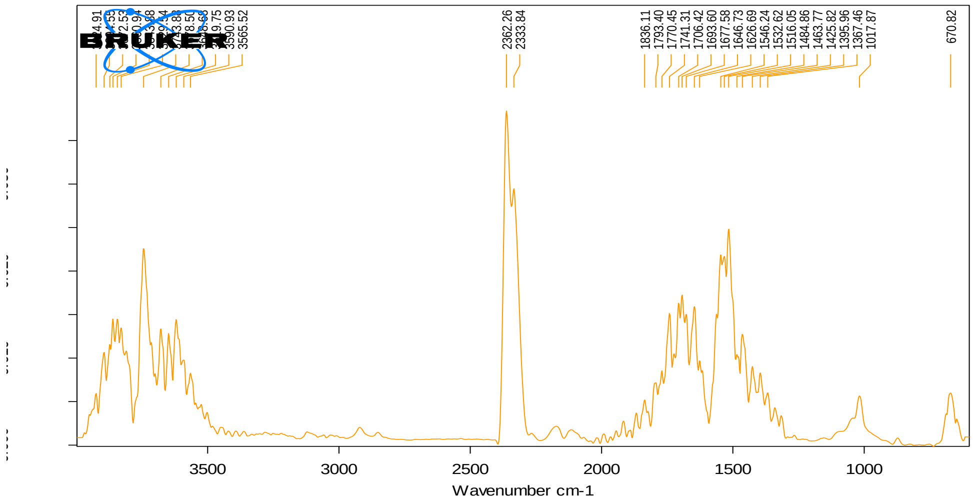

Figure 1: FT-IR analysis of leave samples (I_a-V_a) before treatment

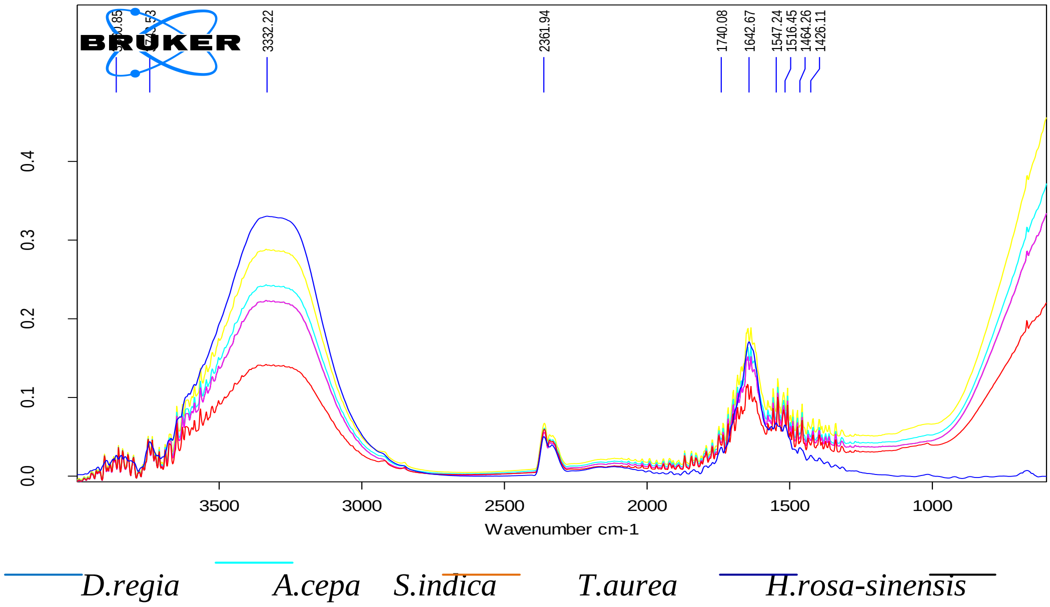

Figure 2: FT-IR analysis of leave samples (I_a-V_a) after treatment

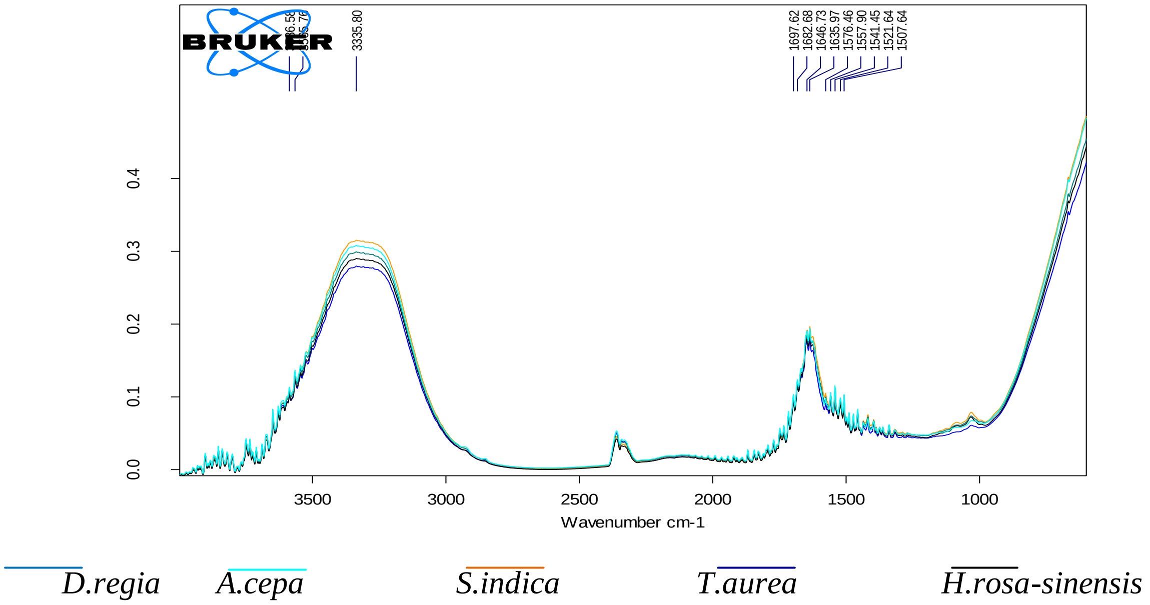

Figure 3: FT-IR analysis of leave samples (I_i-V_i) before treatment

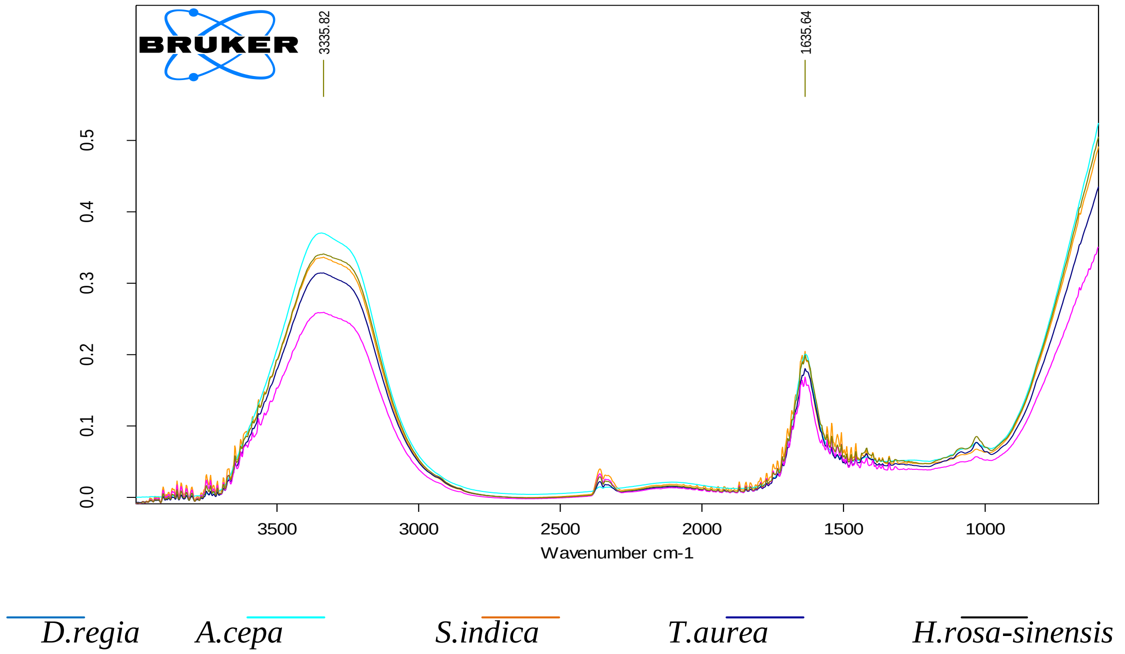

Figure 4: FT-IR analysis of leave samples (I_i-V_i) after treatment

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