Influence of the Low Frequency Ultrasound on the Cadmium (II) Biosorption by an Ecofriendly Biocomposite (Extraction Solid Waste of *Ammi visnaga* / Calcium Alginate): Kinetic Modeling

L. Nouri Taiba, Y. Bouhamidi, F. Kaouah, Z. Bendjama, M. Trari

Abstract—In the present study, an ecofriendly biocomposite namely calcium alginate immobilized *Ammi Visnaga* (Khella) extraction waste (SWAV/CA) was prepared by electrostatic extrusion method and used on the cadmium biosorption from aqueous phase with and without the assistance of ultrasound in batch conditions. The influence of low frequency ultrasound (37 and 80 KHz) on the cadmium biosorption kinetics was studied. The obtained results show that the ultrasonic irradiation significantly enhances and improves the efficiency of the cadmium removal. The Pseudo first order, Pseudo-second-order, Intraparticle diffusion, and Elovich models were evaluated using the non-linear curve fitting analysis method. Modeling of kinetic results shows that biosorption process is best described by the pseudo-second order and Elovich, in both the absence and presence of ultrasound.

Keywords—Biocomposite, biosorption, cadmium, non-linear analysis, ultrasound.

I. INTRODUCTION

HEAVY metals pollution arising along with the rapid development of industry is becoming a serious threat for the aquatic environment over the last decades [1], [2]. Among the toxic metals, cadmium has attracted much attention because of its hazardous nature. It released in the aquatic medium through metal production, fertilizers, ceramic industries, electroplating, batteries and plastics manufacturing, accumulator manufacturing, smelting processes, mining processes, mineral processing, refining processes, alloy industries and paint pigments [3]. It has been classified as a human carcinogen [4], [5]. The World Health Organization has set 0.005 mg/L as the maximum cadmium (II) concentration in domestic water [6]-[8]. Ingestion of cadmium above the permissible limit causes testicular atrophy,

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hypertension, damage to kidneys and bones, anemia and itai-itai. In this respect, various techniques have been employed for the cadmium elimination from different environmental matrices, including physical, chemical, and biological process such as supported liquid membrane [9], liquid–liquid extraction [10], cementation [11], precipitation [12], ion exchange [13], and bioaccumulation [14]. Among them, the biosorption has been found to be an economically feasible alternative for metals removal utilizing naturally abundant, waste biomass of algae, moss, fungi or bacteria and biomass immobilized in a synthetic polymer matrix [15]. The biosorption has shown superiorities in low cost, high efficiency, wide adaptability, no secondary pollution, and stable performance especially for low metal concentration effluents. Polymers such as chitosan, agarose, and cellulose derived from microorganisms and plants are known to bind metal ions and could be used for their biosorption. In this investigation, we are interesting by sodium alginate which is an attractive biopolymer and has various applications in the field of water treatment. It is rich in carboxyl groups, the main functional groups involved in the heavy metal biosorption [16], [17]. Alginate gels in presence of divalent cations according to the Rees "egg-box" model [18].

The recent increase in the applications of ultrasound for benign environmental remediation has conducted many researchers to investigate the effects of ultrasound on sorption processes [19]-[22]. The process is based on the phenomenon of acoustic cavitation, involving the formation, growth, and sudden collapse of micro-bubbles in an irradiated liquid. Ultrasound causes the formation of cavitation bubbles leading to high localized temperatures and pressures. On the microscale, high bubble temperatures up to 5000 K and pressures up to 1000 atm have been estimated. These phenomena increase the rate of mass transfer near the surface as well as possibly thinning the film [23].

The primary objectives of this study are to investigate the cadmium biosorption from aqueous solution by an efficient biodegradable biocomposite beads (calcium alginate immobilized *Ammi visnaga* (Khella) extraction waste), in the absence and presence of ultrasound, and to clarify and explain the influence of low ultrasound frequency on the cadmium biosorption kinetics.

II. MATERIALS AND METHODS

A. Materials

All chemicals used in this study were of analytical grade. Sodium alginate and Calcium Chloride were purchased from Sigma Aldrich and used as received. Cd^{2+} solution of desired concentration was prepared by dissolving the appropriate amount of sulfate ($3CdSO_48H_2O$, Fluka) in distilled water.

B. AVEW (Ammi visnaga Extraction Waste) Biomass Preparation

The biomass used in the biocomposite preparation was obtained from the research center in analytical chemistryand physics (CRAPC, Algeria), as a solid waste of the *Ammi visnaga* extraction and used without further treatment. The biomass was washed repeatedly with distilled water until the washing water becomes colorless. The washed biomaterials were dried in an air oven at 80°C for 24 h. Then, the biomass was crushed, and sieved repeatedly to get a powder of 200 μm, the achieved biomaterial was stored in desiccators until use.

C. AVEW/CA Biocomposite Synthesis

The *AVEW/CA* biocomposite was prepared as described in [24]. Briefly, 4.34 g of sodium alginate was dissolved into 100 mL of distilled water to produce a viscous solution. 2.5 g of the biomass was added to 100 ml distilled water. Afterward, the biomass solution was carefully added into the sodium alginate solution and the mixed solution was ultrasonicated (frequency 37, power 880 w) for 30. The mixed solution was then injected through a peristaltic pump (Ismatec) and the resulting droplets were collected in a reservoir containing 1.99% of $CaCl_2$. The beads formed were stirred for 30 min and stored overnight in $CaCl_2$ solution at 4 °C. The wet beads were collected, washed, dried, and stored in a desiccator until use. The *AVEW/CA* biocomposite synthesis is shown in the experimental setup, Fig. 1.

D. Biosorption Procedures

Batch biosorption tests were conducted in the experimental setup shown in Fig. 2. Experiments were carried out in a 250 ml cylindrical jacketed glass vessel. The vessel was immersed in an ultrasonic cleaning bath (Elmasonic P70 H, indirect sonication). Indirect sonication means that the vessel was immersed in the ultrasonic bath and the mixture was sonicated. For direct sonication, the ultrasonic transducer was mounted at the bottom of the vessel. For all the experiments, a known weight of the biocomposite (0.1 g) was added to 100 mL of Cd^{2+} solution at a concentration of 100 mg/L and a pH that result from a dissolving cadmium sulfate in distilled water (pH ~ 5.3) without further adjustment. The temperature was maintained at 25°C and the solution was magnetically stirred at a constant speed (300 rpm) or sonicated at two frequencies (37 and 80 KHz) for 6 h. The reaction mixture was filtered through filter paper and the filtrate was analyzed for the remaining Cd^{2+} concentration by atomic biosorption spectrometry (SpectrAAvarian 110). The biosorption yield (Y %) is calculated from (1):

$$Y = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

where C_o is the initial concentration of Cd^{2+} and C_t the concentration at the time (t). The amount of cadmium biosorbed, q_t(mg/g), was obtained as (2):

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{2}$$

where C_o is the initial concentration of Cd^{2+} and C_t the concentration at the time (t). *V* is the volume of solution (L) and *W* is the biocomposite amount used (g). Each experiment was performed triplicate and the average values were presented. The maximum standard deviation was (± 2 %.) Preliminary experiments had shown that cadmium biosorption losses to the container walls and to the filter paper were negligible.
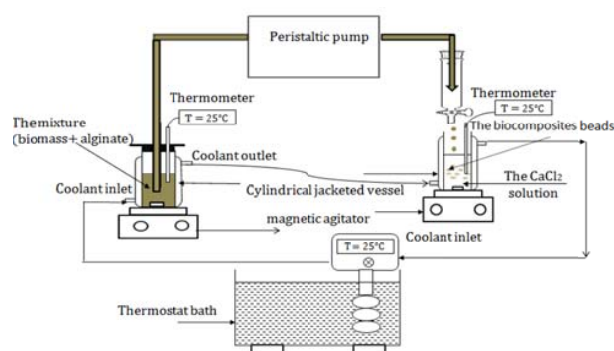

Fig. 1 Experimental setup for the biocomposite preparation

III. RESULTS AND DISCUSSION

A. Ultrasonic Frequency Effect

The ultrasonic frequency effect on the cadmium biosorption by the *AVEW/CA* biocomposite is shown in Fig. 3. From this figure, itis observed that the biosorption efficiency in the presence of 37 KHz ultrasound frequency is higher than that obtained by simple stirring and by sonication at 80 KHz frequency. The enhanced cadmium biosorption by 37 KHz ultrasonic frequency may be attributed to the extreme conditions generated during the violent collapse of cavitation bubbles. When the bubble is collapsing near the solid surface, symmetric cavitation is hindered and collapse occurs asymmetrically. The asymmetric collapse of bubbles in a heterogeneous system produces microjets with high velocity. Additionally, symmetric and asymmetric collapses generate shockwaves, which cause extremely turbulent flow at the liquid-solid interface, increasing the rate of mass transfer near the solid surface. Furthermore, the cavitation event also gives rise to acoustic micro streaming or formation of miniature eddies that enhance the mass and heat transfer at interfacial films surrounding nearby sorbent particles and within the pores. As a result, ultrasonication could produce not only high-speed microjets but also high-pressure shock waves and acoustic vortex micro streaming [19]-[22]. These actions lead to an improvement of the biosorption by an enhancement of

mass transfer across the boundary layer as well as into the pores. In addition, the cadmium amount biosorbed by the *AVEW/CA* biocomposite decreased with increasing acoustic frequency from 37 to 80 KHz, probably because more cavitation events occur and more ions are desorbed. Thus, it was concluded that high frequency of ultrasound leads to the

breaking of bonds formed between metal ions and the biocomposite surface. Therefore, an optimum acoustic frequency should be applied duringultrasonic irradiation in order to obtain higher biosorption capacities. Finally, the obtained results show that the biosorption efficiency values were in the order:37 kHz > 80 kHz> 300 rpm.
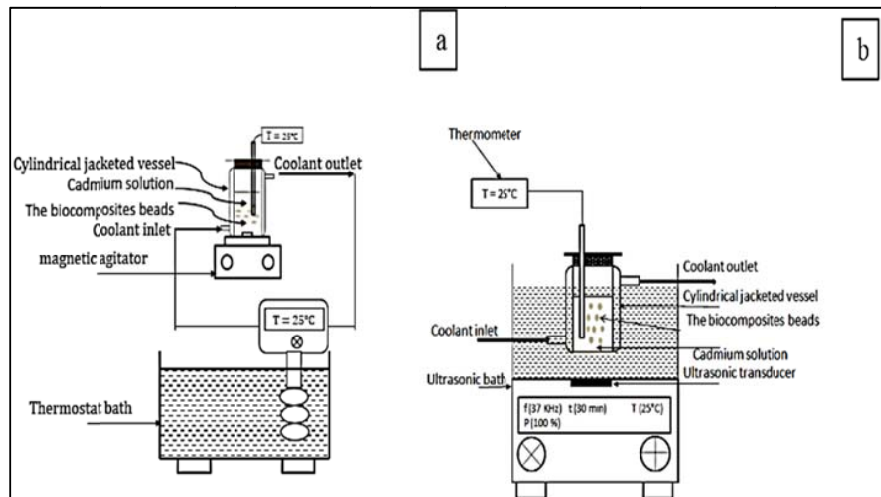

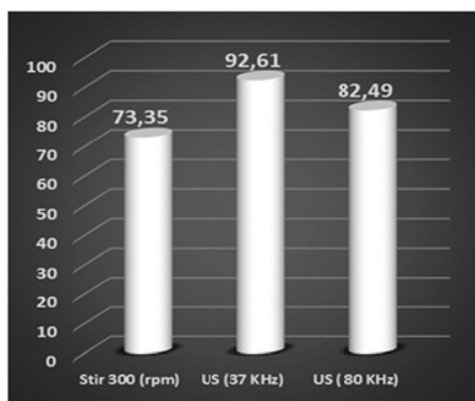Fig. 2 Experimental setup for the batch cadmium biosorption: (a) without ultrasound and (b) with ultrasound

Fig. 3 Effect of ultrasonic frequency on the cadmium biosorption by the beads biocomposite (conditions:100mL of cadmium solution, initial concentration 100mg/L, biocomposite mass:1.0 g, acoustic power 880 w, stirring speed 300 rpm, pH ~5.3, temperature 25 °C)

B.Cadmium Biosorption Kinetics

The cadmium biosorption kinetics by the *AVEW/CA*biocompositewasstudiedin the presence of both 37 and 80 kHz ultrasonic frequency at power intensity of (100%, 880 w), Fig. 2 (b) and in the absence of ultrasound (passive conditions) with simple magnetic stirring (300 rpm), Fig. 2 (a). The comparison of the kinetic curves shows that the cadmium biosorption in the conventional method and in the presence of 80 KHz ultrasound frequency reached equilibrium in about 360 min, while, in the presence of ultrasound (37 KHz) this time is reduced to about 300 min. In addition, at the beginning the cadmium biosorption rate in the presence of 37

KHz ultrasound frequency is higher than that obtained by the conventional method. The observed variation decreases with time for an ultrasonic frequency of 80 KHz. The shorter time to reach equilibrium and the faster rate of the cadmium removal in the presence of 37 KHz ultrasound frequency are attributed to the hydrodynamic phenomena effect due to the cavitation that gives a perfect mixing of the vessel content.
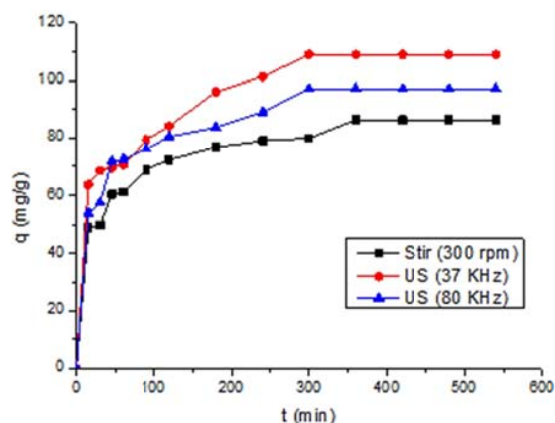

Fig. 4 Cadmium biosorption kinetics by (SWAV/CA) in the absence and presence of ultrasound (C_0) 100 mg/ L, (biocomposite dose) 1g/L, (T) 25 °C, (pH 5)

The mostly common kinetic models used to describe the experimental data using non-linear regression are pseudo-first-order, pseudo-second-order, Intra particle-diffusion, and Elovich [25], [26]. Fig. 5 shows Non Linear regression kinetic of Cd (II) on the *SWAV/CA* biocomposite by the four models.

The pseudo-first-order model is expressed in (3):

$$q_t = q_e(1 - e^{-k_1 t}) \qquad (3)$$

where q_t and q_e are the cadmium amount biosorbed (mg/ g) at time t (min) and at t_e (min) equilibrium, respectively, and k_1 (1/min) is the pseudo-first-order rate constant of biosorption process.

The pseudo-second-order model can be described in (4):

$$q = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \qquad (4)$$

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

The initial biosorption rate "h" (mg/g min) is given by (5):

$$h = k_2 q_e^2 \qquad (5)$$

To interpret the kinetics of chemisorption on highly heterogeneous sorbents the Elovich kinetic equation is often used. It can be presented by (6):

$$q_t = {}^1\!/_\beta \ln(\alpha\beta) + {}^1\!/_\beta \ln t \qquad (6)$$

where α and β are constants.

The intraparticle diffusion equation is written as:

$$q_t = k_i t^{0.5} + I \qquad (7)$$

where I is the intercept and k_i is the intraparticle diffusion rate constant (mg/g$\sqrt{min}$).

The uniformity between the experimental data and model predicted values are expressed by the determination coefficients (R^2), average percentage errors (APE) and deviation percentage values.

The average percentage errors (APE) are calculated as (8):

$$APE(\%) = \left(\frac{\sum_{i=1}^{N}|((q_e)exp - (q_e)cal|/(q_e)exp)}{N}\right) * 100 \qquad (8)$$

where the subscripts 'exp' and 'cal' show the experimental and calculated values and N is the number of experimental data.

The deviation percentage was calculated as (9):

$$Deviation(\%) = ((q_e)exp - (q_e)cal)/(q_e)exp) * 100 \qquad (9)$$
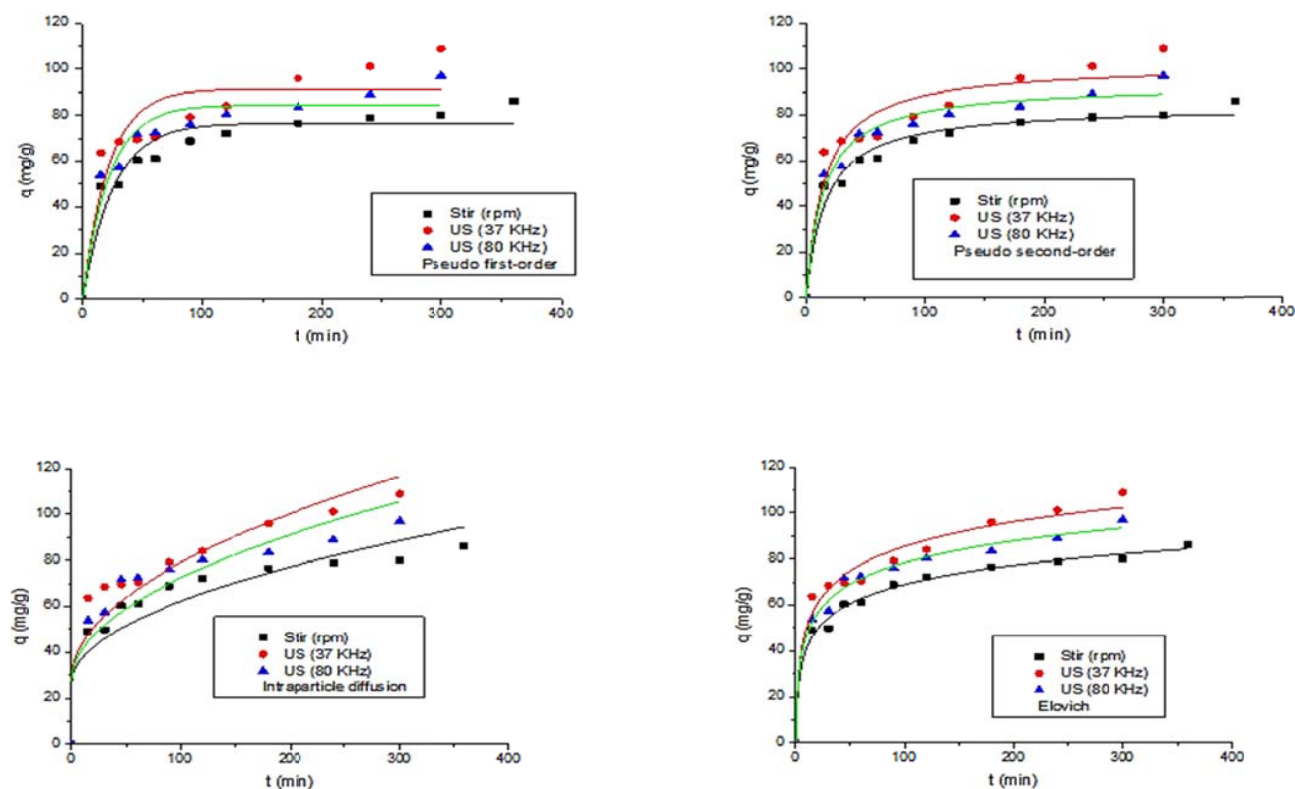

Fig. 5 Different biosorption non-linear regression kinetic models applied to the cadmium biosorption data by (SWAV/CA) biocomposite in the absence and presence of ultrasound

The parameters of the pseudo first and second order models and the determination coefficients (R^2), APE, deviation percentage values are summarized in Table I. The determination coefficient values were found to be in the range 0.8289 to 0.9221 for the pseudo first order and deviation percentage varies between +0.116% and +0.260% and the mean APE was 5.93%. Moreover, the variations between the calculated q_e and experimental q_e were very large. Even

though pseudo second order model shows correlation coefficients more or equal to 0.9164 but the maximum deviation varies from −2.80% to +18.33% and the mean APE was 3.06%. Moreover, the variations between the calculated q_e and experimental q_e were minimal. Therefore, it can be concluded that the pseudo-second-order kinetic model provided a better correlation for the biosorption of cadmium by *SWAV/CA* biocomposite in the absence and presence of ultrasound compared to the pseudo-first-order model. So, from pseudosecond order model, it is observed that the initial biosorption rate "h" value increase by decreasing ultrasonic frequency from 80 to 37 KHz and its values are in the order: 300 rpm <80 kHz<37 kHz.

TABLE I
KINETIC MODEL CONSTANTS AND CORRELATION COEFFICIENTS OF PSEUDO FIRST AND SECOND ORDER FOR CD BIOSORPTION ONTO SWAV/CA BIOCOMPOSITE IN THE ABSENCE AND PRESENCE OF ULTRASOUND

Kinetic parameters	Stirring 300 rpm	Ultrasound frequency 80 KHz	Ultrasound frequency 37 KHz
q_e (exp) (mg/g)	86.30	97.05	108.95
Pseudo First-order $q_t = q_e(1 - e^{-k_1 t})$			
q_e(cal) (mg/g)	76.66	71.75	91.36
K_1 (1/min)	0.040	0.046	0.047
R^2	0.9105	0.9221	0.8289
APE (%)	3.72	8.69	5.38
Deviation (%)	0.1116	0.2607	0.1615
Pseudo Second-order $q = \dfrac{k_2 q_e^2 t}{1 + k_2 q_e t}$			
q_e(cal) (mg/g)	83.88	79.25	101.96
K_1 (g/mg min)	$7.28\ 10^{-4}$	$8.85\ 10^{-4}$	$6.40\ 10^{-4}$
h (mg/g min)	5.13	5.37	6.65
R^2	0.9678	0.9699	0.9164
APE (%)	0.93	6.11	2.14
Deviation (%)	2.800	18.3393	6.4138

Since neither the pseudo-first-order nor the pseudo-second order model can identify the diffusion mechanism, the kinetic results were further analyzed by the intraparticle diffusion (Table II).The intraparticle diffusion equation did not provide a suitable fitting to the experimental data, giving values for the determination coefficients (R^2)less than 0.8142,for all the studied cases. This result indicates that intraparticle diffusion is not the rate controlling mechanism.

Further, the kinetics data were fitted to the Elovich equation and the coefficients α and β are listed in Table II. The Elovich equation assumes that the solid surface active sites are heterogeneous in nature and therefore, exhibit different activation energies for chemisorptions [25]. This model provide an adequate description of the kinetic data in the absence and presence of ultrasound with (means AEP <2.19%, R^2> 0.9713).

TABLE II
KINETIC MODEL CONSTANTS AND CORRELATION COEFFICIENTS OF THE INTRAPARTICLE DIFFUSION AND ELOVICH MODELS FOR CD BIOSORPTION ONTO BIOCOMPOSITE SWAV/CA IN THE ABSENCE AND PRESENCE OF ULTRASOUND

Parameters	Stirring 300 rpm	Ultrasound frequency 80 KHz	Ultrasound frequency 37 KHz
q_e (exp) (mg/g)	86.30	97.05	108.95
Intra-particle diffusion $q_t = k_i t^{0.5} + I$			
q_e(calc) (mg/g)	94.550	96.109	116.598
K_i (g/mg min)	3.5935	3.8454	5.1243
I (mg/ g $\sqrt{min}$)	26.367	23.1475	27.843
R^2	0.7671	0.7712	0.8142
APE (%)	3.1868	0.3231	2.3399
Deviation (%)	-0.0956	0.0096	-0.0701
Elovich $q_t = {}^1/_\beta \ln(\alpha\beta) + {}^1/_\beta \ln t$			
q_e(cal) (mg/g)	84.3742	108.2395	102.4375
α (mg /g min)	3.0324	3.0956	2.5503
β (g /mg)	0.0829	0.0648	0.0648
R^2	0.9911	0.9890	0.9713
APE (%)	0.7438	3.8432	1.9925
Deviation (%)	0.0223	-0.1153	0.0598

IV. CONCLUSION

The present work shows that the *SWAV/CA* biocomposite bead was successfully used as a biosorbent for Cd (II) removal from aqueous solutions in the absence and presence of ultrasound at low frequency. Both the rate and the amount of cadmium biosorption were significantly increased from 86.30 to 108.95 mg/g in the absence and presence of the ultrasonic field, respectively. The kinetic fitting data demonstrate that the biosorption can be predicted by pseudosecond-order and Elovich models. The results of the present investigation indicate that the ultrasonic low frequency played a key role in the removal of cadmium.

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