Response surface methodology for cobalt removal from aqueous solutions using Isparta pumice and zeolite 4A adsorbents

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Abstract. In this study, the adsorption of non-radioactive cobalt ions from aqueous solutions onto Isparta pumice and zeolite 4A sorbents was investigated. Both adsorbent materials have been activated at 873 K for 2 h prior to adsorption experiments in batch mode. The maximum removal efficiencies of 90% and 99% have been obtained experimentally using Isparta pumice and zeolite 4A, respectively. In addition, the experiments with radioactive ⁶⁰Co were performed to test zeolite ability to remove radioactive compounds. Likewise, the response surface methodology (RSM) has been applied to develop the predictive regression models to describe the adsorption of cobalt and radiocobalt ions onto zeolite 4A and Isparta pumice. The results indicated that zeolite 4A as well as Isparta pumice could be used as the efficient sorption materials for cobalt and radiocobalt ions removal.

Key words: zeolite • Isparta pumice • adsorption • radioactive waste • cobalt ions • response surface methodology

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Introduction

Heavy metals are toxic pollutants ceaselessly released into the aquatic environment as a result of urbanization, developing of industry and agricultural activities [9]. They do not undergo biodegradation being predisposed to accumulate into the organisms and entering into the food chains [21]. As regards radioactive wastes, these types of pollutants include a variety of radionuclides and appear in a variety of physical and chemical forms. One of the common radionuclides present in radioactive wastes deriving from production and application of radioisotopes is 60Co. 60Co is an artificial isotope produced in nuclear reactors by irradiation of stable ⁵⁹Co, and applied in industry and medicine – in cancer therapy as a "cobalt bomb". The radioactive cobalt is also released from nuclear reactors as a corrosion and activation product and it is one of the main impurities in reactor waters. Treatment of liquid wastes is required to produce a waste product suitable for long-term storage and disposal [18]. The applying of adsorption techniques for removal of heavy metals and radionuclides from waste waters, as an alternative method of treatment, is of great interest. Therefore, the investigation and comparison of different sorbent materials is also very important.

Pumice is a volcanic rock, which can have acidic or basic character. The structure of pumice, a shapeless aluminosilicate, consists of linked tetrahedral SiO₄ units. Because of its microporous structure, pumice has a high specific surface area. Significant internal porosity makes it useful for drinking water treatment. It is considered as an effective sorbent in the processes applied for water and wastewater purification to remove such pollutants like phenols [1], pesticides [2] or bacterial toxins [8]. Pumice has been found to be efficient for the elimination of phosphate ion [17], metal ions [23], and as a support material for metal catalysts [6]. Possessing high silica content (generally 60-75% SiO₂), pumice stone is a valuable scouring, scrubbing, and polishing material. It has been applied as supplementary and polishing material in the textile and chemical industries. Pumice stone is also used in construction sector as a lightweight aggregate in precast masonry units, poured concrete and plaster [14].

Zeolites are aluminosilicate crystalline compounds owning microporous and ion exchange properties suitable for a wide range of applications in catalysis and separation of liquid mixtures [10]. They have cavities and channels that can host cations, water and other molecules. Zeolite can be used to adsorb a variety of substances. They are very effective desiccants and they can remove water to very low partial pressures. They are used to remove volatile organic chemicals from air streams, separate isomers and mixtures of gases [5, 7, 19]. Zeolite structure is constructed of tetrahedral SiO₄ and AlO₄ units bridged by oxygen atoms generating secondary building units. The ion exchange method is preferred for the removal of radioisotopes when liquid nuclear effluents are being treated by zeolite [16].

Conventional methods of adsorption process investigation by changing one variable and maintaining other factors at constant levels does not describe properly the combined effect of all factors employed. This classical technique involves many experimental runs, which are time-consuming ignores interaction effects between the considered operating parameters of the process, and leads to a low efficiency in optimization. These restrictions of the classical method can be prevented by applying the response surface methodology (RSM) that involves statistical design of experiments in which all factors are varied together over a set of experimental runs [3, 13, 15, 22]. RSM has been implemented successfully in several scientific and technical fields such as applied chemistry and physics, chemical engineering, environmental protection. In adsorption science, small numbers of studies are carried out using RSM. The main objective of RSM is to settle optimum operational conditions of the system or to determine a region that satisfies the operating specifications [15]. The implementation of statistical experimental design techniques in adsorption process development can result in enhanced product yields, diminished process variability, closer confirmation of the output response to target requirements, and overall costs [4, 20, 22].

In this study, the adsorption of cobalt ions from aqueous solutions on zeolite 4A and Isparta pumice was investigated. The experiments were supplemented by testing the possibility of removal of the ⁶⁰Co radionuclide from water by zeolite 4A sorbent. The experimental design and response surface methodology (RSM) was applied as an efficient approach for establishing

empirical models used for prediction of adsorption processes.

Present experiments were carried out with model water-cobalt solutions that avoided all the problems related to dealing with radioactive wastes which are more complex systems taking into account their origin and various types created. The aims of the experiments included: studying the possibility of application of statistical methods with RSM technique for evaluation of removal of metals (e.g. Co^{2+} ions) from water solutions via adsorption, and for examination the same method of statistical design for elimination of radionuclide such as 60Co. The studies on non-radioactive Co2+ ions removal were carried out also as preliminary tests with radioactive solutions of 60Co to minimize radiation exposure for the researchers. In the first case, the metal concentration and adsorbent dosage were selected as input parameters, for the second – the specific radioactivity of the solution and adsorbent amount. Another important parameter, worthy of considering was pH of the initial solution. However, to reduce the number of the variables and quantity of experiments two input factors were taken into account in the experiments that were carried out in stable pH conditions.

Experimental

Pumice samples (Isparta) were obtained from Suleyman Demirel University, Pumice Research and Implementation Center, Isparta, Turkey. The chemical composition of pumice powder samples determined by XRF is given elsewhere [23]. Prior to use in the experiments, pumice samples were crushed to get powder.

A commercial molecular sieve, i.e. zeolite 4Å, provided by Sigma-Aldrich was another sorbent used in this study. Molecular formula of 4A zeolite is $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot xH_2O$.

As a source of cobalt ions, cobalt (II) chloride hexahydrate CoCl₂·6H₂O (puriss) ($M_W = 237.93$ g/mol) provided by Sigma-Aldrich was used for preparing aqueous solutions.

Both sorbent samples (i.e. Isparta pumice and 4A) were activated at 873 K for 2 h prior to adding them into the aqueous solutions. Batch adsorption experiments have been carried out by mixing the activated powders of sorbents with synthetic waste water solution of different initial cobalt concentrations. Samples were mixed for 24 h to reach the equilibrium state using an orbital shaker. The shaking speed was set up at 320 rpm to maintain the sorbent particles in suspension for all experiments. Afterwards, the suspensions were filtrated using a syringe filter (Whatman Syringe Filter 25 mm diameter, 0.2 µm pore size). The resulted filtrate was analyzed for cobalt concentration via the UV-Vis spectrometry method. In this respect, the concentrations of cobalt ions in the filtrate solutions were measured by an analytical kit (HACH Permachem Reagents), based on the measurement of color intensity (absorbance reading at a 620 nm wavelength) of the complex form in aqueous solution. The reproducibility of the concentration measurement was within a maximum deviation of 5% in all cases studied. By means of direct reading spectrophotometer UV-Vis (HACHDR/2000), the absorbance was recorded.

The amount of metal adsorbed, $q \pmod{g}$, can be calculated from the equation

(1)
$$q = \frac{(C_0 - C_f) \cdot V}{M}$$

where: C_0 is the initial concentration of cobalt in solution (mg/L); C_f is the final concentration of cobalt after adsorption (mg/L); V is the volume of cobalt solution (L); M is the weight of pumice used (g). The maximum q (mg/g) values obtained in the valid region of experimetns were 138.7 mg/g and 9.9 mg/g for zeolite 4A and Isparta pumice, respectively.

As a response of interest, in the present studies the removal efficiency was applied that can be expressed as a rejection factor Y(%) of cobalt ions or decontamination factor (DF) in the case of radioactive solutions [11, 12].

The removal efficiency of cobalt ions from aqueous solution by adsorption was determined as follows:

(2)
$$Y = \left(1 - \frac{C_f}{C_0}\right) \times 100$$

where C_0 is the initial concentration of cobalt in solution (mg/L) and C_f is the final concentration of cobalt after adsorption (mg/L).

For the adsorption experiments with radionuclides ⁶⁰Co, the radioactivity measurements were taken using a Polon Warszawa Analyzer (A-22p HT Power supply ZW N-21M HT Control 0/2000V). A volume of 10-ml sample was used for all liquid radioactivity measurements. For these experiments, the decontamination factor was ascertained as:

$$DF = A_0 / A_f$$

where A_0 is the initial activity of cobalt solution (Bq/L) and A_f is the final activity of solution (Bq/L) after adsorption.

All experiments with non-radioactive and radioactive solutions were carried out at room temperature and for a fixed pH of 5.70 ± 0.20 .

Results and discussion

Adsorption studies dealing with non-radioactive solutions

The investigations of adsorption processes were carried out using the central composite design of experiments. The experimental data collected according to experimental designs were applied for statistical modeling using the response surface methodological approach. The response surface methodology (RSM) is generally used to improve and optimize the performance of a system that is the subject to a set of controllable input variables called also design variables or "factors". The first step in RSM involves determining an appropriate functional form to explain the relationship between the "response" of interest (in the present case the removal efficiency) and controllable input variables ("factors"). The most commonly used functional form in RSM is the polynomial regression model. For the experiments with non-radioactive solutions, the RSM tool has been

applied to develop the polynomial regression models between the removal efficiency (metal uptake efficiency) and the experimental factors. The most important factors that influence the removal efficiency (response) are the initial concentration of cobalt ions in aqueous solutions (C_0 , mg/l) and the sorbent dose (SD, % w/v). Note that the sorbent dose of SD = 0.5% w/v means 0.5 g of the sorbent per 100 mL solution. For statistical calculations, the actual values of factors were coded according to Eq. (3) [15, 16].

(4)
$$x_i = \frac{z_i - z_i^0}{h_i} \quad \forall i = 1, n$$

where: z – denotes the actual value of design variable; z^0 is the center point of design variable (actual value); h is the interval of variation; x is the coded level of design variable (dimensionless value) and n is the number of variables (in our case n = 2). Thus, each variable consists of three different coded levels from low (-1), to medium (0) and to high (+1).

For the case of 2 design variables ("factors"), the regression model of second-order with the interaction given by RSM can be written in a general form as follows:

(5)
$$\tilde{Y} = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2$$

where the regression coefficients that represent the components of the column matrix $\beta = [\beta_0\beta_1\beta_2\beta_{11}\beta_{22}\beta_{12}]^T$ were computed by means of regression analysis as [15, 16]:

(6)
$$\beta = (X^{\mathrm{T}} \cdot X)^{-1} \cdot X^{\mathrm{T}} \cdot Y$$

where: β – denotes the column matrix of the regression coefficients; *X* is the matrix of coded variables; *Y* is the column matrix of experimental values of response (removal efficiency).

The experimental designs used for investigation of adsorption processes with non-radioactive solutions are given in Tables 1 and 2 for Isparta pumice and zeolite 4A adsorbents, respectively.

Based on the data reported within experimental designs (Tables 1 and 2), the following statistical models have been constructed with coded and actual variables:

- adsorption of cobalt ions from non-radioactive solutions onto Isparta pumice;
- regression model with coded variables:

(7)
$$\hat{Y} = 76.996 - 17.333x_2 - 7.659x_2^2 - 9.5x_1x_2$$

subjected to: $-1 \le x_i \le +1, \forall I = 1,2$

- regression model with actual variables:

(8)
$$Y = 50.99 + 95.33 \text{ SD} + 0.681 C_0 - 3.782 \times 10^{-3}$$

 $- C_0^2 - 1.733 \text{ SD} C_0$

subjected to: $0.25 \le SD \le 0.5 (\% \text{ w/v}); 10 \le C_0 \le 100 \text{ (mg/L)}$

- adsorption of cobalt ions from non-radioactive solutions onto zeolite 4A;
- regression model with coded variables:

(9) $\hat{Y} = 77.157 + 17x_1 - 18.1x_2 + 11x_1x_2$ subjected to: $-1 \le x_i \le +1$, $\forall I = 1,2$

	Ι	Response			
Run number $-$	Sorbent dosage		Initial cobalt concentration		Removal efficiency
(11)	SD (% w/v)	level ^a x_1	$C_0 (\mathrm{mg/L})$	level ^a x_2	Y(%)
1	0.5	1	100	1	33.0
2	0.25	-1	100	1	62.0
3	0.5	1	10	-1	90.0
4	0.25	-1	10	-1	80.0
5	0.5	1	55	0	85.5
6	0.25	-1	55	0	87.3
7	0.375	0	100	1	61.0
8	0.375	0	10	-1	90.0
9	0.375	0	55	0	58.2
10	0.375	0	55	0	56.4

Table 1. Experimental design for non-active cobalt ions removal using Isparta pumice adsorbent

^a -1 - low value; 0 - center value; +1 - high value.

Table 2. Experimental design for non-active model solutions of cobalt ions adsorption on zeolite 4A

	F	Response			
Run number (N)	Sorbent dosage		Initial cobalt concentration		Removal efficiency
(1)	SD (% w/v)	level x_1	$C_0 (\mathrm{mg/L})$	level x_2	Y(%)
1	0.050	1	150	1	82.7
2	0.015	-1	150	1	34.7
3	0.05	1	50	-1	96.0
4	0.015	-1	50	-1	92.0
5	0.050	1	100	0	99.0
6	0.015	-1	100	0	49.0
7	0.0325	0	150	1	60.0
8	0.0325	0	50	-1	98.0
9	0.0325	0	100	0	83.0
10	0.0325	0	100	0	82.0

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- regression model with actual variables:

(10)
$$\hat{Y} = 122.646 - 285.714 \text{ SD} - 0.771 C_0 + 12.571 \text{ SD} C_0$$

subjected to: $0.015 \le SD \le 0.05$ (% w/v), $50 \le C_0 \le 150$ (mg/L).

The significance of the coefficients was tested with the Student's t-test, on condition that the value of each coefficient should be greater than the significance level. Thus, in the regression equations mentioned above only the meaningful coefficients were retained.

In order to test the estimated regression equations for the goodness of fit, use is made of the Fisher F-test for the significance level of p = 0.05. In this respect one should compute the following statistical estimators. The error mean square (S_0^2) that has been found by using the repeated observations [15]:

(11)
$$S_0^2 = \frac{1}{n_0 - 1} \sum_{i=1}^{n_0} (Y_{0_i} - \overline{Y}_0)^2$$

where n_0 is the number of experiments in the center point (reproducibility), Y_{0_i} denotes the values of response recorded in the center point and Y_0^- is the average value of Y_{0i} . The residual mean square (S_{res}^2) has been computed as [15]:

12)
$$S_{\text{res}}^2 = \frac{1}{N-L} \sum_{j=1}^{N} (Y_j - \widehat{Y}_j)^2$$

where N is the number of observations (experimental runs), L is the number of significant coefficients in the regression equation, Y_i is the response (experimental value) and \hat{Y}_i denotes the predictor of response according to regression equation. Note that, the regression model is an adequate fit to the experiment if the F-ratio is smaller than the tabulated value of $F_{tab(p,f1,f2)}$ [15]:

(13)
$$F = \frac{S_{res}^2}{S_0^2} < F_{tab(p,f_1,f_2)}$$

The outcomes of F-ratio test are focused in Table 3 for both regression models. According to the results from Table 3, the F-ratio is lower than the tabulated value in both cases revealing the adequacy of the regression models.

Table 3. Statistical analysis for regression equations (response: removal efficiencies)

Model	Degree of freedom	F-ratio (computed value)	F-ratio ($p = 0.05$) (tabulated value)	Model adequacy
Isparta pumice	$f_1 = N - L = 7 f_2 = n_0 - 1 = 1$	150.8	236.8	150.8 < 236.8 adequate
Zeolite 4A	$f_1 = N - L = 7 f_2 = n_0 - 1 = 1$	73.7	236.8	73.7 < 236.8 adequate



Fig. 1. Response surface plot and contour-line map for removal efficiency depending on sorbent dosage and initial cobalt concentration. Sorbent: Isparta pumice.

After testing the adequacy according statistical analysis, the models have been applied for the prediction using the simulation techniques. In this respect the dependence between the removal efficiency (response) and factors have been ascertained by drawing the response surface plot and contour line map. Such dependencies are shown in Figs. 1 and 2 for Isparta pumice sorbent and zeolite 4A, respectively.

In the case of cobalt removal from non-radioactive solution using Isparta pumice sorbent, the response surface plot indicates with increasing initial concentration of cobalt ions in solution, while the removal efficiency (response) is decreasing for the same amount of sorbent. This outcome is more pronounced at higher value of sorbent dosage (Fig. 1). The influence of initial concentration of cobalt upon response appears as main, quadratic and interaction effects. The influence of sorbent dosage is dictated only by interaction effect. Thus, according to Fig. 1, with increment of sorbent dosage for the initial cobalt concentration lower than 55 mg/L the removal efficiency is growing. For the higher initial concentration of cobalt in solution (i.e. $C_0 >$ 55 mg/L), the interaction effect leads to the diminishing of response with the increasing of sorbent dosage. By simulation techniques, the optimal condition of adsorption using Isparta pumice was found to be $C_0 = 10 \text{ mg/L}$ and

SD = 0.5% w/v. In these conditions a maximum removal efficiency of 96.4% was computed (predicted value). The experimental value of response in such conditions corresponds to 90%.

Figure 2 shows the response surface plot for cobalt ions removal by adsorption using zeolite 4A. For this system, the main effect of both factors is evident. Thus, the increasing sorbent dosage leads to improvement of response, while the increasing of initial solute concentration conducts to the diminishing of removal efficiency. Due to the interaction effect between factors, the influence of sorbent dosage is more intense for higher values of initial solute concentration while the influence of cobalt initial concentration is more obviously at lower values of sorbent amount. The optimal experimental condition of adsorption using zeolite 4A was found by experimental design (Table 2) to be $C_0 = 100 \text{ mg/L}$ and SD = 0.05% w/v. In this situation a maximum removal efficiency of 99% was obtained.

It is worth of making a comparison between both investigated sorbent materials. Thus, by applying Isparta pumice, a removal efficiency of 90% is obtained experimentally using a sorbent dosage of 0.5% w/v that is necessary to treat a synthetic wastewater with a 10 mg/L initial solute concentration. In the case of application of zeolite 4A, the removal performance



Fig. 2. Response surface plot and contour-line map for removal efficiency depending on sorbent dosage and initial cobalt concentration. Sorbent: zeolite 4A.

Run number – (N) –]	Response			
	Sorbent dosage		Initial activity of solution		Removal efficiency
	SD (% w/v)	level x_1	A_0 (Bq/L)	level x_2	DF
1	0.15	1	15,200	1	7.5
2	0.05	-1	15,200	1	3.8
3	0.15	1	7600	-1	15.4
4	0.05	-1	7600	-1	3.8
5	0.15	1	11,400	0	6.1
6	0.05	-1	11,400	0	4.2
7	0.1	0	15,200	1	7.5
8	0.1	0	7600	-1	12.0
9	0.1	0	11,400	0	13.2
10	0.1	0	11,400	0	12.7
9 10	0.1 0.1	0 0	11,400 11,400	0 0	13.2 12.7

Table 4. Experimental design for radioactive cobalt adsorption on zeolite 4A

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Model	Degree of freedom	F-ratio (computed value)	F-ratio ($p = 0.05$) (tabulated value)	Model adequacy
Zeolite 4A	$f_1 = N - L = 6 f_2 = n_0 - 1 = 1$	49.0	233.9	49.0 < 233.9 adequate

of 99% can be obtained using a sorbent dosage of 10-fold lower than for Isparta pumice. Thus, by using the sorbent amount of 0.05% w/v (zeolite 4A) a synthetic waste water of higher solute concentration (100 mg/L) was efficiently treated. All these facts indicate that the commercial molecular sieve (zeolite 4A) is the most efficient adsorbent and very few amounts of such sorbent are required to treat high cobalt concentration waste water. The moderate efficiency of Isparta pumice and its property to be available in nature in a huge amount indicates that such material belongs to low-cost sorbent category.

Adsorption studies dealing with radioactive solutions

The utmost efficient investigated sorbent material, i.e. zeolite 4A, was used for adsorption experiments dealing with removal of ⁶⁰Co from radioactive model solutions. In this case the central composite design of experiment, resulting in 10 experimental runs was used. The experimental design is reported in Table 4.

Based on the data obtained according to experimental design, the response surface models that describe the dependence between decontamination factor and design variables were developed using the regression analysis. The equations in terms of coded and actual variables may be written as follows, after testing the significance of regression coefficients by means of Student's t-test. – regression model with coded variables:

(14) $DF = 10.895 + 2.855x_1 - 2.08x_2 - 4.094x_1^2$ - 1.963 x_1x_2 subjected to: $-1 \le x_i \le +1, \forall I = 1,2$

regression model with actual variables:

(15) $\hat{DF} = -16.724 + 502.4 \text{ SD} + 4.858 \times 10^{-4}$ $A_0 - 1.638 \times 10^3 \text{ SD}^2 - 0.01 \text{ SD} A_0$ subjected to: $0.05 \le \text{SD} \le 0.15$ (% w/v); $7600 \le A_0 \le 15,200$ (Bq/L). The statistical analysis of regression equation concerning F-ratio test is shown in Table 5. According to Fischer's test for a confidence level p = 0.05, the regression model is adequate and can be used for the prediction.

Figure 3 illustrates the dependence between the decontamination factor (DF) and the design variables (factors of the adsorption process). Thus, the sorbent dosage has a positive main effect upon decontamination factor (response). This means that by increasing sorbent dosage the decontamination factor also increases. Due to the interaction effect this influence is more intense at lower values of initial activity of solution. The increment of initial activity of solution leads to declining of decontamination factor. Owing to the interaction effect such influence became more evidently at higher values of sorbent dosage.

The optimal conditions of ⁶⁰Co removal from aqueous solutions given by the experimental design approach was found to be of SD = 0.15% w/v and $A_0 = 7600$ Bq/L. In such conditions a maximal decontamination factor of 15.4 was found experimentally.

All calculations and graphical illustration in this work were performed by means of Mathcad and Matlab software.

Conclusions

In this work, the removal of cobalt ions from aqueous solutions by adsorption using thermally activated materials such as Isparta pumice and zeolite 4A sorbents was investigated via design of experiments and response surface methodology. According to experimental design approach, the optimal conditions that ensure the maximal removal efficiencies of 90% and 99% have been obtained experimentally for Isparta pumice and zeolite 4A, respectively.

The commercial zeolite material 4A is the most efficiently investigated sorbent for the removal of cobalt ions. To treat effectively the effluent by adsorption,



Fig. 3. Response surface plot and contour-line map for decontamination factor depending on sorbent dosage and initial activity. Sorbent: zeolite 4A.

zeolite 4A requires a sorbent dosage of 10-fold lower than for the case of Isparta pumice use. For the initial concentration of cobalt higher than 55 mg/L the Isparta pumice sorbent has a decrease in adsorption efficiency that is typical of low-cost sorbent materials. By contrast, the commercial zeolite 4A is very efficient adsorbent for the same condition of $C_0 > 55$ mg/L.

In addition, the experiments with 60 Co radionuclide were carried out to test the ability of zeolite 4A to remove radioactive compounds. The maximum decontamination factor (DF) given by experimental design was about 15.4 corresponding to the optimal conditions of sorbent dosage 0.15% w/v and initial solution activity of 7600 Bq/L.

In response to surface modeling the empirical models were constructed to predict the removal efficiency of cobalt and radiocobalt ions by adsorption onto zeolite 4A and Isparta pumice. The response surface plots and contour line maps were also drawn for assessing the effects of process variables, i.e. sorbent dosage and initial solute concentration/activity. All these studies obviously showed that the experimental design and response surface methodology is the efficient approach for modeling and optimization of adsorption processes. Introducing the third factor, namely pH as an input variable to the experimental design, one can extend the applicability of the models allowing better understanding of the mutual interactions of these factors in adsorption of metal ions, as well as radionuclides, from water solutions.

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