Simultaneous removal of Ni²⁺, Cd²⁺ and Cr⁶⁺ from an aqueous solution by using native algal biomass loaded in Ca-alginate beads

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ABSTRACT

In this research, biosorption process is used for the simultaneous removal of Ni²⁺, Cd²⁺ and Cr⁶⁺ from an aqueous solution by using algae (*Cladophora* sp.) as adsorbent. Ca-alginate loaded algal beads were prepared by mixing algal biomass powder in sodium alginate solution and then adding drop wise into CaCl, solution. Column was prepared by placing glass wool at the bottom followed by a layer of Ca-alginate loaded algal beads (weighing 2.4 g). To make column packing uniform distilled water was passed through the column before passing metal ions solution. Scanning electron microscopy confirms the rough and porous surface of blank and metal loaded Ca-alginate algal beads. Simultaneous biosorption of metal ions was supported by Fourier-transform infrared spectroscopy which indicates the presence of various functional groups like –COOH, –OH, NH₂ and NO₂ on algal biomass which are responsible for adsorption. These results indicated 83.3%, 97.3% and 98.3% removal of Ni²⁺, Cd²⁺ and Cr⁶⁺, respectively in 60 min at pH 3.0 for 150 µg/mL concentration of metal ions mixtures and 0.4 g of adsorbent dose. Metal uptake capacity was 14.71, 14.53 and 69.53 mg/g for Ni²⁺, Cd²⁺ and Cr⁶⁺, respectively.

Keywords: Ca-alginate beads; Ni²⁺; Cd²⁺; Cr⁶⁺; Adsorption

1. Introduction

With each passing day development in science and technology is increasing which lead to the expansion of industrialization, globalization, and urbanization. This increased development has direct relation with the increase in water pollution [1]. Various harmful substances or pollutants are dumped into the water bodies including heavy metals [2]. Heavy metal pollution in wastewater has always been a serious environmental problem because heavy metals are non-biodegradable and can be accumulated in living tissues. Ni²⁺, Cd²⁺ and Cr⁶⁺ are typical examples of toxic heavy metals discharged into the environment through natural sources such as weathering and erosion of rocks, and anthropogenic sources such as chemical manufacturing plants, electroplating, battery, pesticide and fertilizer industries [3]. According to World Health Organization, the maximum permissible limit of nickel, cadmium and chromium in drinking water are 6, 5 and 50 µg/L, respectively [4].

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Nickel is toxic heavy metal and inhaling nickel dust causes diarrhoea, renal oedema, nausea, chest pain, pulmonary fibrosis and gastrointestinal ache [5]. Cadmium is also toxic heavy metals that have been classified by the World Health Organization to be of serious health concern [6]. Apart from the "itai-itai" disease which is a manifestation of cadmium toxicity in humans, kidney dysfunction, hepatic damage and hypertension are also other health implications of cadmium. It also causes cancer and genetic changes and its chronic exposure may even lead to death [7]. Chromium is another toxic heavy metal whose common oxidation states are 2+ to 6+; however, only two oxidation states, 3+ and 6+, are of environmental significance and the hexavalent form is 500 times more toxic than the trivalent. Human toxicity of chromium includes skin irritation to lung cancer, as well as kidney, liver, and gastric damage [8,9].

Due to the toxic effect of these heavy metals, there is need for their removal from industrial wastewaters. Many conventional methods used for the removal of heavy metals include chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation, floatation, and complexation etc. But these methods have disadvantage of secondary waste production [10–13]. Biosorption process used in this research is cheap, cost effective, eco-friendly and no toxic waste products are produced in this process. This process can be used to remove heavy metals from very dilute solutions and has the advantage of biomass regeneration at the end of process [14].

Various kinds of bio sorbents are used for the removal of heavy metals. These bio sorbents include bacteria, seaweeds, algae, fungi, activated sludge, wool, straw and waste tea etc. [15]. Priyadarshanee and Das [16] carried process of biosorption for uptake of toxic metals by using bacterial biomass. Their work was to investigate metal uptake by bacterial biomass in single and multimetal environment. Hemambika et al. [17] worked on the biosorption of copper, cadmium and lead from industrial wastewater by using immobilized and dead fungal cells as adsorbent. Their results depicted that immobilized fungal cell are good adsorbent than dead fungal cells. AjayKumar et al. [18] used activated sludge for the biosorptive removal of Cd²⁺, Cu²⁺, Ni²⁺ and Zn²⁺ from dilute aqueous solutions. Findings of their work indicated maximum uptake by activated sludge in the following order $Cd^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+}$. However, among these biosorbents algae is the most important which is employed for the uptake of heavy metals and other organic compounds. Reason for its extensive use is its high sorption capacity and at the same times its ease of availability [19]. Algal cell wall is composed of alginate, comprising of mannuronic acid and guluronic acid units which in turn possess -COOH group which plays an important role in metal binding capacity. Chains of guluronic acid exhibit phenomenon of dimerization which lead to the stabilization of internal structure of alginate, this particularly happens when -COOH group binds with divalent cations. This binding also enhances alginate gel formation which ultimately leads to increased sorption capacity of biomass [20].

This research work is undertaken to contribute to the search for low cost and locally available materials as adsorbents. Therefore, the dead biomass of *Cladophora* sp. algae was used for the first time, as adsorbent that is cheap, native and abundantly available in Nalla Baan River of Kotli, Azad Kashmir, Pakistan. For this purpose, the dead mass of algae was impregnated in Ca-alginate beads and characterized by using scanning electron microscopy (SEM) and Fouriertransform infrared spectroscopy (FTIR). The beads were then packed in simple analytical grade pyrex glass column having glass wool at the end and used for the simultaneous removal of Ni²⁺, Cd²⁺ and Cr⁶⁺. The metals were then determined spectrophotometrically using chromogenic reagents. Various factors that affect the adsorption process like pH, contact time, adsorbent dose and metal ions concentration were also optimized. The method used in this work for biosorption of metal ions was very simple and easy to operate as compared to methods reported earlier [10-14] that was an additional advantage. There is no involvement of biosorbent incubation, modification by agitation, constant shaking and separation by centrifugation which is being utilized in already reported methods [14,18–23].

2. Experimental set-up

2.1. Materials

For the preparation of different solutions analytical grade reagents were used. These chemicals include Na-alginate (Sigma-Aldrich, United States of America, USA), dimethylglyoxime (DMG) (Merck, Darmstadt, Germany), HCl (Riedel-de Haën, Seelze, Germany), CH₃COCH₃ (Sigma-Aldrich, United States of America, USA), NiSO₄ (Merck, Darmstadt, Germany), $K_2Cr_2O_7$ and Cd(acac)₂ (Peking Chemical Works, China), CaCl₂ (Merck, Darmstadt, Germany), sodium dihydrogen phosphate and sodium hydroxide of Merck, diphenylcarbazide (DPC) and dithizone (DT) of Panreac Quimica (USA), C₂H₅OH of Analar Grade and Glacial CH₃COOH (Sigma-Aldrich, United Stated of America, USA).

2.2. Instruments

UV-visible spectrophotometer of Shimadzu UV-1800 (United States of America, USA) was used to measure absorbance of Ni²⁺, Cd²⁺ and Cr⁶⁺ ions. The pH meter of Model inoLab/pH 7110 (Germany) was used to measure pH of the solutions. Weighing balance of model AEFA200, sonicator of Elmasonic P 60 H (Singen, Germany), FTIR of Shimadzu/ IRAffinity-1S (California, USA), microscope of Nikon Type 104C, microwave oven of Memmert Schutzrat/UN30 (Southern Germany), hot plate of VELP Scientifica (Usmate, Italy) were used during research work.

2.3. Methodology

The stock solution of metal ions mixture (1,000 μ g/mL) was prepared by dissolving 0.66 g of NiSO₄, 0.51 g of Cd(acac)₂ and 0.70 g of K₂Cr₂O₇ in 250 mL distilled water. Then dilutions of stock solution (ranging from 25–150 μ g/mL) were made. Chromogenic reagents solution of 0.1% dimethylglyoxime (DMG) (0.1 g in 10 mL acetone then diluted with distilled water (DW) up to 100 mL), 0.1% DPC (0.1 g in 10 mL glacial acetic acid, diluted to 100 mL by distilled water) and 0.0256% DT (0.0256 in 96 mL ethanol, diluted to 100 mL by using distilled water) were prepared. Buffer solution of pH 6.9 was prepared by adding 10.10 g Na₂HPO₄·7H₂O and 1.69 g NaH₂PO₄·2H₂O in 500 mL volumetric flask. 3% CaCl₂ and 0.5 mol/dm³ HCl solutions were prepared. 50 mmol/dm³ CaCl₂ was also prepared for beads storage.

2.3.1. Preparation of algal beads

Fresh algal biomass was collected from Nalla Baan River of Kotli, Azad Kashmir Pakistan, washed with distilled water and treated with acid (0.5 mol/dm³ HCl solution). The sample was identified as *Cladophora* algae by using gram staining technique. The sample was dried at 80°C then finely ground to powder and used for bead formation. Calcium alginate loaded algal beads were prepared by dissolving 2.0 g of Na-alginate in 20 mL of distilled water (DW) with constant stirring for 20–25 min until clear viscous gel like solution was formed. In the next step, 0.4 g powdered algal biomass was added and stirred until homogenous mixture was formed. Transferred the mixture into a syringe and added drop wise into 3% CaCl₂ solution to prepare calcium alginate loaded algal beads. The beads were stirred for 5–10 min, filtered, washed with DW and stored for further use.

2.3.2. Biosorption procedure

Process of biosorption was carried out in a Pyrex glass chromatographic column. A stand was used to set the chromatographic column. At the bottom of column glass wool was placed to prevent the flow of algal beads and DW was passed through it to make it uniform. Then, the layer of calcium alginate loaded algal beads (weight 2.4 g) were placed and DW was passed through it to settle down. Then metal ions solutions mixture was passed though the column. In first step, 15 mL of 150 µg/mL of metal ions mixture was placed through the column at pH 3.0 and allowed to stand for 1 h. After 1 h filtrate was removed from the column and used to measure absorbance spectrophotometrically. For this purpose, 1 mL of filtrate was taken in three separate test tubes, 2.8 mL DW and 1 mL of chromogenic reagent was added in each test tube. Chromogenic reagents used were 0.1% solution of DMG, DPC and DT for Ni²⁺, Cr⁶⁺ and Cd²⁺, respectively. The absorbance was measured spectrophotometrically at 440, 600 and 540 nm for Ni²⁺, Cd²⁺ and Cr⁶⁺, respectively.

To evaluate removal efficiency of algal biomass, the following formula is used:

$$%removal = C_i - \frac{C_f}{C_i} \times 100$$
⁽¹⁾

And metal uptake capacity is determined by the following formula:

$$Q_e = \frac{C_o - C_f}{W} \times V \tag{2}$$

where Q_e is metal ions uptake capacity of biomass (mg/g), C_o or C_i is initial concentration of metal ions (µg/mL), C_f is final concentration of metal ions present in the filtrate or eluent (µg/mL), W is the weight of algal biomass (g) used and V is volume of metal ions solution in mL taken in the column.

2.3.3. Characterization

SEM was used for the investigation of morphology, texture and surface property of Ca-alginate loaded algal

beads and metal loaded algal beads. To analyze functional groups present in Ca-alginate loaded algal beads and metal loaded algal beads, FTIR spectrophotometer of Shimadzu/ IRAffinity-1S was used.

2.3.4. Optimization of adsorption parameters

To check the stability of Ca-alginate loaded algal beads, they were placed in different pH solution ranging from 2-8. Then the stability of beads was observed after 1 and 24 h. Next the effect of pH was studied by passing 25 mL of 150 µg/mL metal solutions mixture in 0.4 g of the adsorbent packed in column for 60 min at 25°C. The pH of metal solutions was adjusted from 2-8 with 0.1 mol/dm³ HCl and NaOH using a pH meter. After 1 h, the filtrate was removed from the column. The initial and final concentration of metals ions that remained in the filtrate was measured spectrophotometrically. The pH that gives maximum removal of metals was determined. After pH optimization, the effect of time on biosorption process was observed. For this purpose, column was loaded with Ca-alginate beads and mixture of metal ions solution of 150 µg/mL was run through the column. Filtrate was removed after intervals of 15, 30, 45, 60 and 75 min, absorbance was measured spectrophotometrically. In this way, time parameter was optimized. To investigate the effect of initial metal concentration on the adsorption, metal ions solutions of different concentrations (25–300 µg/mL) were prepared. For this purpose, 25 mL of mixture of metal solutions with concentrations of 25, 50, 100,150, 200, 250 and 300 μ g/mL were passed through the column. Then, the amount of biosorbent giving maximum % removal was optimized by loading column with Ca-alginate loaded algal beads having weight of 0.2, 0.4, and 0.6 g and biosorption process was carried out.

3. Results and discussion

3.1. Characterization of sample

3.1.1. SEM analysis

To study the morphology of prepared beads, SEM analysis was done. SEM images of powdered form of blank beads, calcium alginate loaded beads and metal ions loaded algal beads at 1, 2, 5 and 10 μ m are shown in Fig. 1a–d, respectively. SEM images of blank beads showed smooth surface while Ca-alginate loaded algal beads showed rough surface and after biosorption again surface is rough and uneven compared to blank beads. However, surface of Ca-alginate loaded algal beads is more porous which provide great surface area for adsorption of metal ions (Cd²⁺, Ni²⁺ and Cr⁶⁺ ions). Metal ions loaded algal beads (after biosorption) showed greater number of protuberances on its surface and uneven texture as compared to calcium alginate loaded algal beads and blank beads [24,25] which indicate biosorption of metal ions.

3.1.2. FTIR analysis

Functional groups involved in the binding of metal ions were investigated by FTIR analysis. To achieve this purpose FTIR of pure algal biomass, calcium alginate loaded algal beads and metal ions loaded algal beads are shown in Fig. 2.



Fig. 1. Scanning electron microscopy images of blank beads, Ca-alginate loaded algal beads and metal ions loaded algal beads at (a) 1, (b) 2, (c) 5 and (d) 10 μ m, respectively.



Fig. 2. Fourier-transform infrared spectroscopy of pure algal biomass, Ca-alginate loaded algal beads and metal ions (Cr⁶⁺, Ni²⁺, Cd²⁺) loaded algal beads.

As shown in Fig. 2, there was a change in the FTIR spectra of Ca-alginate loaded algal beads after binding with metal ions (Ni²⁺, Cd²⁺ and Cr⁶⁺). Bands intensity was changed due to metal ions binding. Stretching frequency of C–N group was shifted from 1,312 to 1,234 cm⁻¹. Bending frequency of N–H and NO₂ group was shifted from 1,593 to 1,650 cm⁻¹. Hydroxyl, carboxylic and C–N bonds were shifted from 960 to 1,020 cm⁻¹ [26]. Results from FTIR spectrums revealed that –OH, –COOH, –NH₂ and NO₂ groups are involved in simultaneous sorption of metal ions (Ni²⁺, Cd²⁺ and Cr⁶⁺).

3.2. Optimization of parameters

3.2.1. Stability of beads

Effect of pH on the removal of metal ions by prepared Ca-alginate loaded algal beads was checked. For this purpose, beads were placed in buffer solutions of different pH ranging from 2.0 to 8.0. Effect of pH on the stability of beads was observed after one and 24 h. It was observed that after 1-h beads were stable from pH 2 to 6 but destroyed at pH 7 and 8. After 24 h, beads were found to be stable and retained their shape at pH 3.0 but they were dispersed and destroyed at pH 6.0–8.0 as biomass came out of beads at these pH values. Therefore, pH 3.0 was selected for rest of experimental work.

3.2.2. Effect of pH on biosorption process

In order to check the effect of pH on the biosorptive removal of metal ions (Ni²⁺, Cd²⁺ and Cr⁶⁺) from an aqueous solution, biosorption process was carried out from pH 2.0 to 8.0, filtrate was collected after 1 h and absorbance was measured spectrophotometrically. Results obtained (Fig. 3) indicate that at pH 2.0, 81% removal of Ni²⁺ ions occurred while at pH 8.0 only 15% removal was observed. However, at pH 3.0 maximum removals (91%) of Ni²⁺ ions was observed because beads were stable at this pH and maintained their shape. From pH 4–8, the percentage removal was decreased because of less stability of beads and inability to maintain their shape at these pH values. Similar observation was found out in case of Cd²⁺ and Cr⁶⁺



Fig. 3. Effect of pH on % removal of $Ni^{2+},\,Cd^{2+}$ and Cr^{6+} ions from an aqueous solution.

ions. As algal cell wall contains functional groups like hydroxyl, carboxyl, sulfhydryl, phosphate, sulfate and imidazole, etc. and these functional groups played a significant role in the binding of metal ions forming complexes. At pH 2.9, all -COOH groups are deprotonated which leads to the greater binding of metal ions with sorbent. However, at pH less than 3.0, concentration of hydrogen ions is much greater and there is a competition between hydrogen ions and metal ions for binding with the surface of biosorbent which leads to less percentage removal of metal ions. Similarly, at higher pH > 4.5, concentration of hydroxide increases which reaches to the maximum at pH 8.0 leading to the precipitation of metal ions and ultimately results in less percentage removal of metal ions [27,28]. Therefore, pH 3.0 was maintained for the rest of experiment.

3.2.3. Effect of time on metal ions removal

Equilibrium time is a critical factor affecting rate of biosorption. Effect of equilibrium time on biosorption process was studied keeping temperature, pH, metal ions concentration and sorbent dose constant. From the results obtained, it was observed that maximum Ni²⁺ ions removal was achieved at 60 min (91%) and at 120 min metal ions removal was decreased to 76%. Similarly, for Cd²⁺ and Cr⁶⁺ 90% and 92% removal after 60 min and 86% and 91% removal after 120 min was achieved, respectively (Fig. 4). Increased rate of biosorption at 60 min is particularly due to the presence of greater number of binding sites available for metal ions but at higher time interval decrease in the percentage removal of metal ions is observed because the vacant binding sites that were available at the start of the process were occupied and resulted in decreased rate of biosorption [18].

3.2.4. Effect of biosorbent amount

Biosorption process is also affected by the amount of biosorbent used (Fig. 5). Keeping temperature, contact time and pH constant, it was observed that for 150 μ g/



Fig. 4. Effect of time on Ni^{2+} , Cd^{2+} and Cr^{6+} ions removal by using Ca-alginate loaded algal beads.



Fig. 5. Effect of biosorbent dose on biosorptive removal of Ni^{2+} , Cd^{2+} and Cr^{6+} ions from an aqueous solution.

mL of metal ions solution mixture maximum removal for Ni²⁺, Cd²⁺ and Cr⁶⁺ ions was 83%, 97% and 98%, respectively, when amount of biosorbent used was 0.4 g while for higher amount, that is, 0.6 g of biosorbent, 66%, 59% and 65% removal was observed for Ni²⁺, Cd²⁺ and Cr⁶⁺, respectively. This increased rate of biosorption from 0.2 to 0.4 g of biosorbent dose is because of the availability of greater number of active sites present for metal ions binding. However, at higher adsorbent dose, excessive presence of adsorption sites and insufficient metal ions caused low metal ions removal [18]. Hence, amount of biosorbent used for rest of the experiment was 0.4 g.

3.2.5. Effect of metal ion concentration

In order to find the effect of metal ion concentration, mixture of metal ions solutions of different concentrations ranging from 25 to 200 μ g/mL were passed through the column, filtrate was collected after 1 h and absorbance was measured spectrophotometrically. Results obtained are presented in Fig. 6 which shows that maximum % removal was found at 150 μ g/mL that decreased at higher concentration, that is, 200 μ g/mL. Increased rate of biosorption from 25 to 150 μ g/mL is due to the availability of greater number of vacant active sites available for binding with metal ions while at higher metal ions concentration, all adsorbent binding sites are occupied by metal ions. Due to the presence of less number of active sites of adsorbent available for complexation, decreased rate of metal ions biosorption is observed [29].



3.3. Metal uptake capacity of algal biomass

Metal uptake capacity of algal biomass for (Ni²⁺, Cd²⁺ and Cr⁶⁺,) is presented in Fig. 7.

These results indicated that when Ni²⁺, Cd²⁺ and Cr⁶⁺ were simultaneously removed using Ca-alginate loaded algal beads, maximum metal uptake was observed in case of Cr⁶⁺ as compared to Ni²⁺ and Cd²⁺ which is due to greater binding capacity of Cr⁶⁺ ions with the impregnated algal biomass.

3.4. Recyclability of Ca-alginate loaded algal beads

To check the recyclability of biosorbent, consecutive six cycles of loading and eluting the metal ions (Ni²⁺, Cd²⁺ and Cr⁶⁺) were carried under the optimized conditions. It was found that up till sixth cycles the quantitative removal



Fig. 6. Effect of metal ions concentration on the % removal of Ni^2+, Cd^2+ and Cr^6+ by Ca-alginate loaded algal beads.

Fig. 7. Simultaneous metal uptake (mg/g) by Cladophora algae.

Table 1

Comparison of adsorption capacity Q_e (mg/g) of algal biomass loaded in Ca-alginate beads for Ni²⁺, Cd²⁺ and Cr⁶⁺ with different reported adsorbents

Adsorbent	Q _e (mg/g)	Contact time (min)	Instrumentation	Metal ions adsorbed	References
Tamarindus indica L.	13.09	90	Atomic absorption spectrophotometer	Ni ²⁺	[30]
Chlorella miniata	3.0	90	Atomic absorption spectrophotometer	Ni ²⁺	[31]
Cladophora sp.	14.71	60	Spectrophotometer	Ni ²⁺	Present study
Scenedesmus obliquus	11.4	70	Inductively coupled plasma emission spectroscopy (ICP-ES)	Cd ²⁺	[32]
Agar extraction algal waste	8.7	60	Atomic absorption spectrophotometer	Cd ²⁺	[33]
Cladophora sp.	14.53	60	Spectrophotometer	Cd ²⁺	Present study
Spirogyra species	14.7	120	Atomic absorption spectrophotometer	Cr ⁶⁺	[34]
Algal-bacterial aerobic gran- ular sludge	51.0	1,440	Spectrophotometer	Cr ⁶⁺	[35]
Sargassum bevanom	35.41	110	Flame atomic absorption spectrophotometer	Cr ⁶⁺	[36]
Chlorella minutissima	57.33	48 h	Photo bioreactor	Cr ⁶⁺	[37]
Dunaliella 1	58.3	72 h	Spectrophotometer	Cr ⁶⁺	[38]
Dunaliella 2	45.5	72 h	Spectrophotometer	Cr ⁶⁺	[38]
Cladophora albida	25.4	60	Spectrophotometer	Cr ⁶⁺	[39]
Cladophora sp.	69.53	60	Spectrophotometer	Cr ⁶⁺	Present study



Fig. 8. Percent removal and regeneration of Ni^{2+} , Cd^{2+} and Cr^{6+} ions from aqueous solutions by using Ca-alginate loaded algal beads.

of these metal ions is possible. After 6th cycle, only 10% of Ni²⁺, 56% of Cd²⁺ and 46.46% for Cr⁶⁺ ions were removed (Fig. 8). This indicates that biosorbent did not degrade under the experimental conditions after its repeated use.

3.5. Comparison with other adsorbents

The comparison of adsorption capacity of Ca-alginate loaded algal beads with different sorbents for Ni²⁺, Cd²⁺ and Cr⁶⁺ is shown in Table 1. As it is clear from Table 1 that Q_e value of present study for Ni²⁺, Cd²⁺ and Cr⁶⁺ is high as compared Q_e value of many reported methods of the literature. Therefore, Ca-alginate loaded algal beads could be used as a good adsorbent for the removal of Ni²⁺, Cd²⁺ and Cr⁶⁺ ions from an aqueous solution at room temperature.

4. Conclusions

The ability of Ca-alginate loaded algal beads for the removal of Ni²⁺, Cd²⁺ and Cr⁶⁺ ions was studied by using biosorption process. This process is easy, cost effective, eco-friendly and no secondary waste products are produced. Surface morphology of beads is evidenced by SEM. The results obtained from FTIR supported simultaneous biosorption of metal ions by *Cladophora* algae. FTIR spectra revealed that metal ions form complexes after binding with functional groups present on algal surface which led to their biosorption. Maximum removal of Ni²⁺, Cd²⁺ and Cr⁶⁺ ions by this method is 83.3%, 98.28% and 97.29% at 150 µg/mL after 1 h contact time, 0.4 g adsorbent dose and at pH 3.0. Hence, it can be utilized as an outstanding adsorbent for these metals at room temperature.

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