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# SURFACTANT ASSISTED REMOVAL OF Cu(II), Cd(II) AND Pb(II) FROM CONTAMINATED SOILS

The study deals with the removal of residual contaminants Cu(II), Cd(II) and Pb(II) from soil using surfactants sodium dodecyl sulfate (SDS), sodium dioctyl sulfosuccinate, and Triton x-100. Surfactants were used with and without chelating agent ethylenediaminetetraacetic acid (EDTA). SDS (10 mM) was the most effective surfactant for removing metals. Replacing distilled water with SDS enhanced metal removal by the factor of 5.5, 28.8, and 29.1 for Cu(II), Cd(II), and Pb(II), respectively. SDS with EDTA was efficient in removing metals. Interaction of metal ions with respect to adsorption and desorption were also studied.

# 1. INTRODUCTION

Heavy metals generally denote the group of metals with densities greater than 5 g/cm<sup>3</sup>. At concentrations above a threshold, they are of apprehension due to their mobility and toxicity in field soils. Cadmium, copper, lead, mercury, nickel and zinc cause considerable danger to humans and animals. Several studies reported on the surfactant enhanced remediation of soil contamination. Surfactant molecules contain hydrophilic and lipophilic moieties. They form aggregates which are known as micelles. Surfactants enhance removal of residual (low level) soil contaminants by solubilization and by reduction of interfacial tension that promotes contaminant mobilization in soils. Copper, cadmium and lead have been chosen for the present study.

Heavy metals are widely used in industry and agriculture. Metal contaminants in soil can be found dissolved in soil moisture, adsorbed on soil surface or remain fixed as a compound. Cation exchange capacity (CEC), pH and complexation with organic matter control metal adsorption on soil particles [1].

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#### 1.1. COPPER, CADMIUM AND LEAD AS SOIL CONTAMINANTS

Copper has a relatively low mobility in soils, due to its high tendency to form complexes with organic compounds of low molecular weight. Bradl [1] states that soil organic matter as well as oxides of manganese and iron act as sinks for copper in soils. Thus the readily formed metal-chelate complex is stable in a narrow range of pH (6.1 < pH < 7.3). Fe can displace Cu from CuEDTA complex for soil pH below 5.7. Copper is an important micronutrient for plants. It activates many plant and human physiological processes [1].

Cadmium is a toxic heavy metal harmful to humans, animals and plants. High cadmium uptake causes kidney dysfunction. Main sources of soil contamination include fertilizers, pesticides besides industrial and municipal wastes emissions. Plating operations and disposal of cadmium-containing wastes as well are sources of cadmium contamination [5]. Complexation of cadmium with organic legends is weak due to competition of Ca in soils [1]. Cadmium is highly toxic to living organisms. It can accumulate in the kidney and hinders its function. It is highly mobile in soils compared to Pb(II) and Cu(II).

Lead battery manufacturing, pigment and chemical manufacturing, lead-contaminated wastes are the primary industrial sources of lead. Lead mobility in soil is restricted by adsorption, ion exchange, precipitation and complexation with sorbed organic matter. Lead has a long residence time and a low mobility in soils. It binds to Mn oxide in the soil more strongly than other metals such as copper and zinc [1]. It causes diseases in animals and mental impairment in children. There is no vital need for lead and cadmium in the metabolism of plants or animals.

# 1.2. REMEDIATION TECHNIQUES FOR CONTAMINATED SOILS AND SOIL WASHING SOLUTIONS

Immobilization, physical separation and extraction are modes of site remediation for metal contaminated sites. Reusing of extracting agents influences the cost of site remediation. High permeability and homogeneity of soil sites are prerequisites to adopt in-situ soil flushing.

At high concentrations, surfactants enhance the solubilization of many hydrophobic organic compounds by increasing the solubility of contaminants through micellar solubilization [4, 3, 22]. The use of soil washing fluids to remove mixed contaminants (organics and heavy metals) present in soils has been successfully demonstrated [11, 14, 19]. The optimum pHs and surfactant concentrations for the removal of marine diesel fuel from soils, using surfactant SDS and EDTA in the presence and absence of lead in the soil have been determined earlier [22]. An earlier detailed study [16] reported on the impact of hydrocarbons (crude oil and diesel oil) on the natural weathering process, when they are present in sandy soils. Here, evolved CO<sub>2</sub> served as

a measure of oil biodegradation. Also, in a phytoremediation study [11], the amount of CO<sub>2</sub> liberated was used to assess the effectiveness of surfactant enhanced degradation of engine oil present in soil bound mixed contaminants (engine oil and heavy metals). An inclusive site remediation study affirms that a surfactant's ability to remove soil bound metal contaminants is governed by its dosage, initial metal concentration and ability to extract all metal contaminants [21]. Besides many earlier studies, a few recent studies also reported on the use of both chelates and surfactants to remove heavy metals from soils [18, 8, 14]. In phytoremediation, surfactants and chelates are shown to assist the plant uptake of soil bound heavy metals [15, 20]. In an in depth column study [16], EDTA was used as a soil washing solution to extract large portions of toxic heavy metals from a site containing mixed contaminants.

#### 1.3. COMPETITIVE ADSORPTION AND DESORPTION OF HEAVY METALS IN SOILS

Soil pH and organic content strongly influence adsorption. Metal ion adsorption in soil involves cation exchange, specific adsorption, organic complexation and coprecipitation. Most heavy metals are present in the soil in the form of cations. Hence, the negative charge density on the soil particle surface influences metal adsorption. Higher valency ions have more metal replacing power. The greater the degree of hydration, the less effective is the ion in replacing another ion. A study devoted to the competitive adsorption of Cd(II), Cu(II), and Pb(II) on goethite [2] has convincingly demonstrated that sorption on goethite surface increased with metal electronegativity in the order Cu(II) > Pb(II) > Cd(II). This study also traced the discrepancies in metal adsorption results reported in different studies to the speciation of metals adsorbed, soil site density, pH and surface charge. For ions Cu(II), Pb(II) and Cd(II), it was noted that the electronegativity of characterizing metal affinity to soil sites was independent of their respective ionic radii (0.72 Å, 1.20 Å and 0.97 Å) or their hydraulic radii (4.19 Å, 4.01 Å and 4.26 Å). An earlier investigation provides a superb discussion in terms of diffusion kinetics related to the competition of lead, cadmium and chromium to occupy cationic sites of clinoptilolite [10]. Competitive metal sorption tests [17] related to Pb(II) and Cd(II) indicate that sorption of Pb(II) and Cd(II) is reduced in the presence of each other and that Pb(II) sorption is initially faster than Cd(II) sorption. In recent study [14], the competitive adsorption and desorption behavior of Zn (II) and Cu(II) on sandy soils were reported.

The present study evaluates the potential of surfactants to enhance remediation of a sandy soil (98% of sand and 2% of bentonite) contaminated with Cu(II), Cd(II) and Pb(II). The soil with known ingredients was chosen to permit tests under controlled conditions without interference from extraneous factors. The soil clay content was low to promote competition of metals to the limited available soil particle sites. Batch tests were conducted to investigate adsorption and desorption of these metals. Sodium do-

decyl sulfate (SDS), sodium dioctyl sulfosuccinate (AOT), and Triton x-100 (Tx-100) as well as EDTA (ethylenediaminetetraacetic acid) were used as extracting agents. Interference effects in adsorption and desorption of the three metals were also studied.

### 2. MATERIALS AND METHODS

Batch tests were conducted to study the enhanced removal of heavy metals from a contaminated sandy soil. Experimental materials included soil samples, three types of surfactant solutions, target contaminants Cu(II), Pb(II), and Cd(II) in the form of CuCl<sub>2</sub>, PbCl<sub>2</sub> and CdCl<sub>2</sub>. Distilled water was used for making solutions. Nitric acid was used for digestion. Test sandy soil was formed by mixing 98% of sand and 2% of bentonite. The sand was purchased from Unimin Canada Ltd., and the grain size corresponds to mesh 40. Bentonite was obtained from Sial Inc., Canada and the particle size corresponds to mesh 325 (Table 1).

Table 1
Characteristics of sand and bentonite

Material	CEC <sup>a</sup> [meq/100g]	Organic matter <sup>b</sup> [%]	Particle size <sup>3</sup>
Sand	ca. 0	0.07	$mesh 40$ $D_m = 0.42 \text{ mm}$
Bentonite	110.5 pH = 5.9	2.90	$mesh 325$ $D_m = 0.044 \text{ mm}$

<sup>&</sup>lt;sup>a</sup>Li [8].

The measured hydraulic conductivity of the mixed soil was 0.0037±0.00015 cm/s. A nonionic surfactant (Tx-100) and two anionic surfactants (AOT and SDS) were the soil washing fluids. Anionic surfactants were chosen as they have a lower adsorption tendency to soil and can displace metal cations adsorbed to soil particles. All the surfactants except SDS were purchased from Fisher Scientific, Canada. SDS was obtained from Sigma-Aldrich, Canada. Target contaminants were purchased in the anhydrous finely powdered form of CuCl<sub>2</sub> (97%), PbCl<sub>2</sub> (100%), CdCl<sub>2</sub> (99.1%) from Fisher Scientific, Canada. They were mixed with the soil and distilled water to get soil samples with known concentrations of Cu(II), Pb(II), and Cd(II). Detailed properties of soil washing solutions (surfactants and EDTA) and the soil ingredients are provided in Tables 1–3 and also in a related publication [14].

<sup>&</sup>lt;sup>b</sup>Combustion at 550 °C.

US std. sieve size.

 $$\operatorname{\texttt{Table}}$\ 2$$  Properties of Tx-100 and EDTA

Product	Tx-100	EDTA	
Туре	nonionic surfactant	chelating agent	
Molecular formula	$C_8H_{17}C_6(OC_2H_4)_nOH$ , $n = 9-10$	$Na_{2}C_{10}H_{14}O_{8}N_{2}\cdot 2H_{2}O$	
Molecular weight	625	372.24	
CMC	0.22- 0.24 mM [4]		

 $$\operatorname{\texttt{Table}}$\ 3$$  Properties of SDS and AOT

Product	SDS	AOT	
Type	anionic surfactant	anionic surfactant	
Molecular formula	C <sub>12</sub> H <sub>25</sub> OSO <sub>3</sub> Na	$(C_9H_{17}O_2)_2$ CH $_2$ CHSO $_3$ Na	
Molecular weight	288.38	444.57	
CMC, mM	8.20 [12]	1.124 [13]	

Sand was kept in an oven at 550 °C (2 h) to eliminate most of the residual organic matter. It was later washed two times with hot and cold water and was dried in an oven at 105 °C for 24 h. The final organic content of sand was 0.07%. Metal solutions containing 15 mM equal molar concentrations of Cu(II), Cd(II), and Pb(II) were added to bentonite. This corresponds to weight ratios of 190.5, 337.2, and 621.6 mg/kg of soil for the contaminants Cu(II), Cd(II), and Pb(II). Solution to bentonite proportion was 1 dm<sup>3</sup> to 0.1 kg. Bentonite was shaken on a wrist action shaker (Burrell, Burrell scientific, and USA) at 80 rpm for 24 h at the room temperature of  $22 \pm 2$  °C. The mixture was centrifuged at 3500 rpm for 30 min. The supernatant was collected and filtered for analysis using the atomic absorption (AA) spectrophotometer (Perkin Elmer Analyst 100) which was able to determine the metal concentrations down to 0.1 mg/dm<sup>3</sup>. Standard metal salt solutions of known concentrations were used to get calibration curves for data analysis. Bentonite was dried in the oven at 105 °C for 24 h. Following this, the dried contaminated bentonite was stored for 1 month at room temperature. In the next step, the batch test samples were prepared by adding 4.9 g of sand and 0.1 g of bentonite in a plastic sample tube and mixing them well to attain a relatively homogeneous soil pile. A mass balance equation was also used to determine the amount of metal retained in the bentonite and consequently in the sandy soil. In order to verify these data, the soil sample was digested with nitric acid. AA analysis showed less than 5% deviation between results of the two methods. Average contaminant levels of Cu(II), Cd(II) and Pb(II) in units of mg/kg of the soil were 162, 324 and

587, respectively. Standard solutions containing known metal concentrations were used to develop calibration curves for the AA machine. These permitted the data interpretation with respect to metal concentrations in soil samples.

Soil samples were dried initially at 105 °C for 24 h. SDS, AOT and Tx-100 were used at various concentrations and combinations with EDTA to study their effect and ability to remove Cu(II), Pb(II), and Cd(II) from the soil. Distilled water was also used as the control. The batch reactor was a 50 cm³ centrifuge plastic tube. 5.0 g (4.9 g of sand + 0.1 g of bentonite) of contaminated soil was added to the reactor, after it was weighed by a balance that could weigh to the nearest 0.1 mg. Then 0.40 cm³ of the washing solution was added at various concentrations. Samples were equilibrated on a wrist action shaker at 80 rpm for 24 h. Following this, the samples were centrifuged for 20 min at 3000 rpm and the supernatant was taken for AA analysis. Measurements were made to find pH variations. All batch tests were done in triplicate. Average values and standard deviations are reported.

Soil sample 1 was formed using 15 mM of each of the three metals (Cu(II), Cd(II), and Pb(II)). Soil samples 2–4 also contained the same proportions of sand and bentonite as soil sample 1. Bentonite portion was contaminated with either 15 mM Cu(II) alone (sample 2), or 15 mM Cd(II) alone (sample 3) or, 15 mM Pb(II) alone (sample 4). Sample preparation steps were identical. Retention efficiencies denote the ratio of the retained metal concentration to the initial metal concentration.

### 3. RESULTS AND DISCUSSION

# 3.1. EFFECT OF SURFACTANT CONCENTRATION AND SURFACTANT TYPE ON METAL EXTRACTION

Distilled water, one nonionic and two anionic surfactants were used to investigate their removal effect on Cu(II), Cd(II) and Pb(II). The initial pH values correspond to measured pH of the extracting solution before adding it to the soil sample. Final pH corresponds to values after equilibrating for 24 h.

Results shown for Tx-100 in Fig. 1 indicate that desorbed metal concentrations increase with the increase in the surfactant concentration  $C_s$  till the point, where it is 0.25 mM. This concentration is nearly equal to the CMC (critical micelle concentration) values in water reported in an earlier study [4]. Beyond this concentration, metal removal tends to stay relatively constant. Results for SDS and AOT tests indicate that the anionic surfactants too demonstrate a noticeable increase of metal removal at or near CMC concentrations. Above the CMC, the amount of metal removal does not show any significant variations.

A slight decrease in removal rate (Figs. 2 and 3) which is noticed at concentrations well beyond CMC may be a result of metal precipitation at higher surfactant concen-

trations. The precipitated metal does not appear in the supernatant which gets analyzed for metal concentration. Surfactants can enhance the removal of heavy metals by mechanisms such as ion exchange, counter-ion binding, and dissolution precipitation. Depending on the surfactant type and the metal ion involved, one of these procedures is dominant. In the removal of Cu(II), Cd(II), and Pb(II) using SDS and AOT, counter ion binding and precipitation can play an important role. With increasing concentrations beyond the CMC, the micelles which trapped the metal cations appear to precipitate the metals and allow them to attach to soil particles. In the case of Cu(II), a greenish blue patch was discernible in the sample tubes. Therefore, above the CMC concentrations, increases in metal concentrations should not be expected in the supernatant.

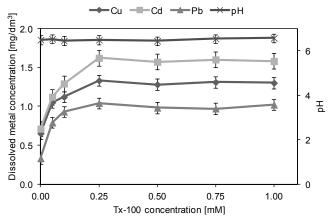


Fig. 1. Metal removal with Tx-100

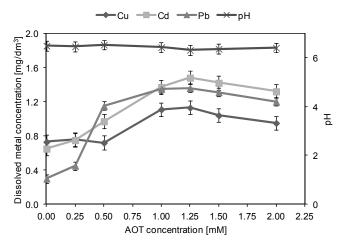


Fig. 2. Extraction of metals with AOT

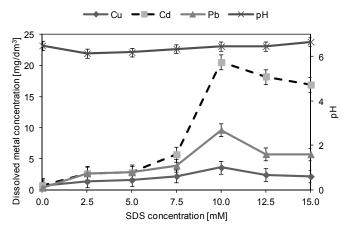


Fig. 3. Extraction of metals with SDS

Distilled water serving as the blank extracting solution removed 0.65 mg/dm<sup>3</sup> of Cu(II), 0.71 mg/dm<sup>3</sup> of Cd(II), and 0.33 mg/dm<sup>3</sup> of Pb(II) by solubilization (Figs. 1–3). The maximum desorbed concentrations of Cu(II) were 1.33 mg/dm<sup>3</sup>, 3.60 mg/dm<sup>3</sup>, and 1.13 mg/dm<sup>3</sup> with Tx-100, SDS, and AOT, respectively. In comparison to distilled water, these amounts (Table 2) correspond to 2.05, 5.54, and 1.74 times greater removal of Cu(II). The highest desorbed concentrations of Cd(II) were 1.62 mg/dm<sup>3</sup>, 20.46 mg/dm<sup>3</sup>, and 1.50 mg/dm<sup>3</sup> with Tx-100, SDS, and AOT amended solutions. These correspond to 2.28, 28.81, and 2.11 times greater removal of Cd(II) in comparison to distilled water. Finally, the maximum desorbed concentrations of Pb(II) were 1.04, 9.63, and 1.40 mg/dm<sup>3</sup> with Tx-100,SDS, and AOT extracting solutions which correspond to 3.16, 29.18, and 4.23 times greater removal of Pb(II) in comparison to distilled water. Surfactant losses occur due to adsorption by the soil. Hence, higher CMCs were noted in the soil during batch experiments. As nonionic surfactants do not carry charges, they cannot participate in the ion-exchange and counter-ion bindings processes and are expected to show less removal capability in comparison with anionic surfactants. However, results indicated that the nonionic surfactant Tx-100 has nearly equal removal efficiency compared to AOT. This may be related to the formation of precipitates of cations from soil solution at high concentrations.

#### 3.2. EFFECT OF ADDING THE CHELATING AGENT TO THE SURFACTANTS

Due to low solubility of EDTA in distilled water, EDTA disodium salt was applied as the commonly used alternative due to its higher solubility. Figure 4 shows removal efficiencies of Cu(II), Cd(II), and Pb(II) with EDTA.

Metal removal efficiency increased with increasing concentrations of EDTA. When the chelate concentration was changed from 1 mM to 10 mM, solution pH decreased from 5.60 to 4.60. Increased acidity of solution influences metal solubility and

its extraction. EDTA exhibited the following order of increased metal extraction: Cd(II) > Cu(II) > Pb(II). Figure 4 also illustrates the removal efficiencies of Cu(II), Cd(II), and Pb(II) with various combinations of surfactants and EDTA (1 mM). The reported pH values relevant to each test denote the final pH during the test. Cu(II) removal efficiency with the combination of EDTA and SDS (10 mM) reached 92% (Fig. 4).

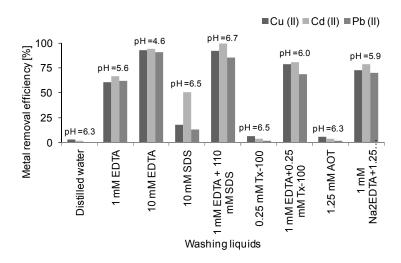


Fig. 4. Extraction of metals with surfactants and EDTA

Compared with metal removal with EDTA alone, it is an increase of 30%. Addition of Tx-100 (0.25 mM) and AOT (1.25 mM) also improved the Cu(II) extraction capability of EDTA (1 mM) by 18% and 12% respectively. The removal of Cd(II) was significantly increased to 99.5% by adding SDS (10 mM) to EDTA (1 mM). However, Tx-100 (0.25) and AOT (1.25) only improved the metal removal marginally by 14% and 12%, respectively. Pb(II) removal (Fig. 4) was also augmented by a combination of EDTA and SDS to 85%. This showed less improvement in comparison with the removal of the other two metals. Addition of Tx-100 and AOT did not display considerable improvement in the removal of Pb(II) by EDTA. Combination of 10 mM SDS and 1 mM EDTA was an effective extraction solution for Cu(II), Cd(II), and Pb(II). More test details are given in a related reference (Schalchian, 2006).

## 3.3. INTERACTION AND COMPETITION IN COMPOSITE SAMPLES

Fig.ure 5a demonstrates that Cd(II) exhibits a higher affinity to the soil adsorption sites, when all the three metals were introduced to the soil sample simultaneously

(sample 1). Cd(II) adsorption in the composite sample (sample 1) remained at the level of adsorption for the individual sample (sample 3).

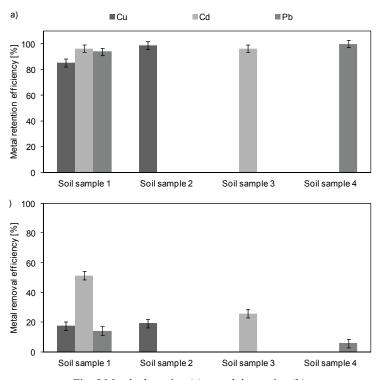


Fig. 5 Metal adsorption (a), metal desorption (b)

Generally, the adsorption order of these three metals (Fig. 5a) in sample 1 (composite case) was as follows: Cd(II) > Pb(II) > Cu(II). Results indicated that adsorption of Cu(II) decreased in the presence of the other two metals from 99% (sample 2) to 85% (sample 1). Pb(II) adsorption also exhibited a slight decrease in the presence of Cu(II) and Cd(II). In samples containing individual metals (samples 2 and sample 4), the absence of competition with other metals for all the available strongly binding soil particle sites permitted a robust adsorption of a single metal (Cu(II) or Pb(II)). Desorption test data (Fig. 5b) using 10 mM SDS indicated that Cu(II) desorption experienced a marginal decrease from 19% to 17.8% when Cd(II) and Pb(II) were also present in the soil (sample 1). This may be due to low mobility of Cu(II) in the soil and its high tendency to make complexes with organic compounds. However, compared to individual metal samples (samples 3 and 4), desorption of Cd(II) increased from 26% to 51% in the composite case (sample 1). Compared to individual metal samples (sample 4), in composite metal samples, desorption of Pb(II) increased from 7% to 13%. In samples 3 and 4, all stronger soil particle adsorption sites were available for a single

metal (Pb(II) or Cd(II)) in the absence of competition among metals. While discussing their results, in an earlier study [2] devoted to soil bound metal interference studies, it has been observed that Cu(II) is likely to adsorb on soil sites not available for Pb(II) and Cd(II) and hence does not follow adsorption and desorption trends of other metals with respect to metal interference in composite samples. Summarized results of batch extraction are given in Table 4.

Table 4
Summarized results of batch extraction

Surfactant type	Tx-100	SDS	AOT
Optimum concentration, mM	0.25	10	1.25
[Proportion to CMC]	[1.08]	[1.22]	[1.11]
Maximum Cu(II) removed, mg/dm <sup>3</sup>	1.33	3.60	1.13
Ratio to Cu(II) removed by water	2.05	5.54	1.74
Maximum Cd(II) removed, mg/dm <sup>3</sup>	1.62	20.46	1.50
Ratio to Cd(II)removed by water	2.28	28.81	2.11
Maximum Pb(II) removed, mg/dm <sup>3</sup>	1.04	9.63	1.40
Ratio to Pb removed by water	3.16	29.18	4.23

Present tests were conducted with soil with well defined characteristics. In field applications, it may be necessary to repeat some tests on samples formed to resemble closely site specific soils. Field soils contain other trace pollutants. Temperature, pH, hardness, and soil additives influence the observed CMC [12]. Surfactants are less toxic compared to the chelating agents. As such, surfactants are preferred to chelates in site remediation.

#### 4. CONCLUSIONS

Compared to extraction with distilled water, SDS could enhance the removal of Cu(II), Cd(II) and Pb(II), by a factor of 5.5, 28.8, and 29.1 times, respectively. The results of the batch tests demonstrated that all three surfactants used can enhance heavy metal removal from sandy soil and that SDS was the most effective soil washing surfactant. The chelating agent EDTA (15 mM) had a high potential for heavy metal removal. However, chelating agents are not very biodegradable and may induce metal mobility that leads to ground water contamination. A combination of 1 mM EDTA and 10 mM SDS used less EDTA and yielded high removal efficiencies of nearly 92%, 99.5%, and 85% for Cu(II), Cd(II), and Pb(II), respectively. This combination used less EDTA and reduces environmental concerns. Both Cu(II) and Pb(II) showed a reduction in their adsorption to soil particles when Cd(II) was present. In terms of desorption, both Cd(II) and Pb(II) experienced an increase in their removal

efficiency in the presence of Cu(II). Cd(II) and Pb(II) had little effect on Cu(II) desorption.

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