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Comparison Effective Powder Of Pomegranate Peel And Date Kernel With Nanoparticles Silver In Reuse Car Wash Effluent

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Abstract

The study was conducted in Samarra city to assess the pollution caused by the effluent of car wash stations. The waste water was collected from the selected stations and directly transferred to the laboratory to analysis tests. Some major biological, physical and chemical characteristics of raw water were studied before treatment and included (turbidity, pH, COD, BOD, TSS, TDS,). Statistical analysis of raw effluent recording values exceeded the permissible limits (polluted levels) and approved by the World Health Organization (WHO) and standard values of the Iraqi water standards for all characteristics under study.The raw water samples obtained from the three car wash stations treated two factors, the first being the types of factors and included three types of nanoparticle silver powder (T1), Pomegranate peel powder (T2) and date kernel powder (T3), and the second factor included five concentration levels (250, 200, 150, 100 and 50) in addition to 3 treatments of each station. The analyses were carried out after treatment and the results show silver powder with concentration 250 ppm, recorded highest removal values and for all the characteristics under study namely: turbidity, COD, BOD, TDS and T.S. S with value reached 8.62, 82mg/l, 482mg/l, 1246mg/l and 620mg/l sequentially for the three selected stations. While the pomegranate peel and date kernel treatment recorded lower clearance levels than silver, but significantly from control treatments that recorded highest pollution rates with values 17, 125mg/l, 725mg/l, 1273mg/l and 730mg/l respectively and exceeded the limited values by WHO.

Keywords: Silver Nanoparticle, Pomegranate peel, date kernel r, Carwash effluent

1. INTRODUCTION

The problem of lack of water availability in the world, including the Arab world and Iraq, has appeared recently, and its availability was in low or insufficient rates, due to the lack of rain, climate change, and the low level of rivers with an increase in rapid population growth. These various factors have resulted in an increasing gap between the available water requirements and their stocks, and between water requirements and their sources, and it is expected to increase in the coming decades, based on international reports, due to the lack of implementation of strategic projects that address the scarcity and scarcity of water and the lack of immediate solutions to address (WHO, 2015 and UNESCOO, 2017).Although Iraq at the present time has good shares of water compared to many other countries, the possibilities of shortage of surface and ground water resources in the future are very realistic and possible, and there is still an urgent need to provide other water sources that enhance water consumption in all sectors of life. (Successor et al., 2017 and Abbas et al., 2008 and Madhulika et al., 2020). The problem of pollution of river water and groundwater has emerged along with its lack of availability, which has become a very dangerous environmental problem that threatens users of river water as a source for drinking, use, fish and animal wealth alike.Pollution rates have increased significantly and dangerously in recent times as a result of dumping large quantities of waste from human and industrial activities in the rivers, with the absence of supervision and enforcement of laws that limit these practices. Sewage and industrial wastes inside cities are one of the most prominent sources of pollution of rivers and groundwater, because they contain high levels of chemical, biological and harmful substances that are complex and difficult to dissolve (Dong et al., 2016 and Pankaj et al., 2020) .These wastes reach rivers and ground water through public drainage networks or directly through their seepage into the soil, which often includes waste from homes, hotels, hospitals, restaurants, water used in washing roads, public squares, car washing stations, and waste from factories and factories (Dignac et al., 2000) . The products of these wastes are mostly composed of organic wastes, chemicals, heavy metals, salts and microbial sources whose concentrations and composition differ according to the source of pollution and the nature of the treatment before disposal.Drainage of such untreated materials into rivers will often lead to water pollution and increase its turbidity, which makes it unfit for various human uses and the occurrence of the phenomenon of food enrichment (Entrophication) and increased metabolism by the algae, which leads to their proliferation and activation of the work of bacteria while reducing the percentage of Oxygen dissolved in water (Khaleel, 2014) .

In recent years, with the increase in industrial activity dramatically, the expansion of cities and the increase in population density, the number of cars has increased greatly, which required an increase in car service stations of various types, including car wash stations, to meet the increasing demand from car owners who want to obtain good services for their cars. The number of car wash stations increased greatly and recorded an excessive increase in the city of Samarra, with a number of more than 70 stations distributed in different areas of the city, none of which carry a legal permit to operate and do not have a specialized treatment unit for raw water before its introduction and is not committed to the terms of public health treatment(Cloete et al., 2010). Wastewater for washing cars mainly depends on the use of chemicals such as detergents and soap, as well as wastes equivalent to water, such as tailings, oils, grease, mud, dust and other components such as heavy metals, which represent the largest percentage resulting from refining, mining and electroplating, which are among the main water pollutants. Industrial waste wastes, especially car washing stations in the city of Samarra, which dump large quantities of untreated wastewater into rivers or groundwater, and thus may cause significant environmental and social damage to the population, animal and plant communities, and micro-organisms, which requires studying this problem and addressing it seriously and scientifically.Recycling and reusing industrial and wastewater using emerging, new, low-cost and environmentally friendly methods such as nanotechnology and the use of materials of natural origin are among the proposed solutions as a means of providing quantities that enhance life-support water sources or public industry sectors (United Nations World Water Development,2017) . At the same time, it is used as a way to reduce or eliminate the main pollution sources from wastewater compared to the common traditional methods (Khaleel, 2014). Numerous studies indicate the possibility of recycling the use of industrial wastewater on a large scale in different countries that have suffered from a scarcity of water resources. Industrial water reuse in these countries is increasing for many different purposes, which considers wastewater a water resource rather than a source of waste (EPA, 2012; WHO, 2006). Therefore, this study came to amid on the problem of wastewater for car washing stations in the city of Samarra, which is directly thrown into rivers or seeps into the groundwater without treatment, with the possibility of developing possible treatments to reduce the negative impact of this water.

2. MATERIALS AND METHODS

2.1 Pomegranate Peel

Pomegranate fruits were collected from local markets.Peels removed by hands and cleaned and washed to removal plankton and dust ,after that transferred to laboratorylab with constant stirringuntil reachingto complete dehydration.After that the samples transferred to drying oven under 35 ^{o}C to 2 days until reached to fully dray. The Blender used to crash samples and get powder that kept in clean and sterile glass containers until use.

2.2 Date Seeds Powder

Collecting date seeds from the cheap local products available in the market. The seeds were separated from the date fruits and washed well with tap water and then with distilled water.The washed nuclei were transferred to the laboratory and left with constant stirring until dryness. After that, the nuclei were transferred to an electric oven at a temperature of 60 m for a period of 2 days until complete dryness. The dry cores with a grinder after cleaning them well and make sure that they are free of any powdery residue**.**

2.3 Silver Nano Ppowder

The silver Nanomaterials powder prepared from US Research Nanomaterials Inc . (APS 20-40nm, 99.9%). Silver nano powder used in coating and medicinal purposes and in medical devices. Its larger surface area to volume ratio and greater activity of nano-silver are utilized in modern biochemical applications.

2.4 Preparing the concentrations

Concentrations of powder solutions were banned, ppm weight / volume (1 mg = 1ppm) for pomegranate peels, date seeds and silver powder. Then, a preliminary experiment was conducted using the Jar Test device to determine the optimal effective concentrations to be used in the treatment.

2.5 Collect samples

A preliminary survey was conducted for the number of car washing stations in the city of Samarra, which reached nearly 70 stations distributed throughout the city and were dependent on river water or water purification stations prepared for drinking or irrigation. Three sites have been identified for car wash stations to collect samples, two of which are located on the river bank, which throw water directly into the river without treatment, and the third is in the city center whose waste seeps into the groundwater after it is left without collection or treatment. Raw water samples were collected from car wash stations after they were collected and the cars were washed and stagnated to ensure that they were not washed away by dirt and dirt when collected in the early morning hours using clean and sterile plastic containers (water bottle / 10 liter) obtained from one of the water bottling factories in the city. The samples were transported to the laboratory and samples were taken from them to conduct the tests for analyzing the characteristics of raw wastewater before treatment in a time, then keeping the rest of them with the packages in the refrigerator for the second day to conduct the transactions and subsequent tests.

2.**6Treatment water Samples**

The prepared concentrations (250, 200, 150, 100 and 50 ppm/per L) added to water collected from car wash station in beaker2 liter capacity.After adding the prepared powders, the mixturemixed continuously for 30 minutes using the magnetic spinner until reached the powder to hight solubility. Then the samples were transferred and kept in clean and sterile place . The sample left between 6-8 h to get highest rate of removal and deposition of pollutants. After that treated water collected from the top part of the baker to perform laboratory tests.

2.7Characterises of Study

1. Turbidity

Water turbidity was measured by a HANNA-LP2000 Turbidity Meter, as the device expresses the standard solutions in a (NTU) naphthalene unit, after calibrating the device (APHA, 2003).

2.Total Dissolved Solids (TDS)mg/l

The total soluble materials were measured by means of the TDS salts meter type HANNA-HI 2009, as the device expresses the standard solutions in units (mg / l) after the apparatus is zeroed(APHA, 2003).

3.Total Suspended Solid (T.S.S) mg/l

Total suspended solids were measured by filtering 100 ml of sample water on a filter paper (0.45) micrometre with a given weight (B), then this paper was dried in an oven at a temperature of (103-105) ° C for an hour, after which it was weighed (A), (APHA, 2003) and calculated according to the following equation:

$$\text{T.S.S (mg/L)} = \frac{(\text{A - B}) \times 10^3}{Volumeofsample(ml)}$$

4. pH

The pH of the samples was measured using a pH meter made by HANNA (Microprocessor HI 9321), after calibrating the device with Buffer Solution with a pH (9, 7, 4).

5.Biological Oxygen Demand (BOD^5)mg/l

The Azide modification of the Winkler method (APHA, 2003) was used, and the product was expressed in mg /l.

3.Result and Discussion

3.1 Turbidity

The results in Table .1 indicated that the silver powder was superior in recording the highest removal for all stations by reducing the turbidity to values of (5.05, 5.18 and 9.27) for St1, St2 and St3 respectively, compared with the average values of the other types and the control treatment. While the lowest removal was recorded with the date seed powder, which gave averages of (11.17, 7.01 and 13.72 for stations (2,1 and 3) respectively, which differed significantly from the rest of the other treatments.

TABLE .1 The effect of different concentrations powder of nanosilver , pomegranate peels, and date seeds on the rate of removing turbidity from raw water for three car wash stations in different locations in Samarra city..

Stations	Type	Conc. ppm					Mean of Type	Normal
		250	200	150	100	50		
S1	Silver	8.62	3.63	3.95	5.18	3.89	5.05a	17d
	Pit	13.6	10.8	7.8	7	7.84	9.41b	
	Sh.p	14.6	11.2	13.8	8.35	7.88	11.17c	
$M.C.St_1$		12.27c	8.54b	8.52b	6.84a	6.54a		
S2	Silver	5.55	5.47	4.9	4.55	5.44	5.18a	13.8d

	Pit	6.4	6.55	8.18	6.9	5.94	6.79b	
	Sh.p	7.3	6.4	7.6	6.63	7.13	7.01c	
M.C.St$_2$		6.41a	6.14a	6.89a	6.03a	6.17a		
S3	**Silver**	9.96	9.82	9.42	9.09	8.06	9.27a	**14.4d**
	Pit	11.4	10.2	9.9	9.35	7.56	9.68b	
	Sh.p	16.1	13	14	13.5	12	13.72c	
M.C.St$_3$		12.49c	11.01b	11.11b	10.65a	9.21a		

The recorded results indicate the presence of significant differences between the concentrations, which also differed between them according to the type of material treated for raw wastewater. The highest removal rate was recorded with concentrations 50 ppm and pmm100 in all the treated samples that were collected from all stations with values of (6.54, 6.84) and (6.17, 6.03) and (9.21, 10.65)) for stations 1, 2 and 3 (respectively. The 250 ppm concentration gave the lowest turbidity removal rate in all the treated samples with swallowed averages (12.27, 6.41 and 12.49) for all stations respectively.

3.2 Biological Oxygen Demand (BOD)

The results of treatment using three types of treatments in Table .2 indicate the superiority of silver powder in recording the lowest BOD rates in the treated water samples for all stations. As it recorded values of (81.4, 100.8 and (92.2) for stations (2,1 and 3), respectively, which differed significantly from the rest of the other transactions that did not record significant differences between them**.**

TABLE.2 The effect of different concentrations powder of nanosilver , pomegranate peels, and date seeds on the rate of removing BOD mg/l from raw water for three car wash stations in different locations in Samarra city

Stations	**Type**	**Conc. ppm**					**Mean of Type**	**Normal**
		250	**200**	**150**	**100**	**50**		
S1	**Silver**	82	81	80	80	84	81.4 a	**108d**
	Pit	88	86	92	90	90	89.2 b	
	Sh.p	88	82	92	90	88	88 b	
M.C.St$_1$		86 a	83a	88b	87 b	87.3b		
S2	**Silver**	101	102	100	101	100	100.8 a	**120d**
	Pit	110	101	110	111	113	107.2 b	
	Sh.p	110	401	113	110	112	108.0 b	
M.C.St$_2$		101a	102.3b	108b	107.3b	108.3b		

S3	**Silver**	93	92	93	90	93	92.2 a	**125d**
	Pit	102	101	108	102	100	102.6 b	
	Sh.p	102	101	108	100	102	102.6 b	
M.C.St₃		a99	98a	103b	97.3b	98.3b		

The mean concentrations also recorded differences between them in the BOD values and with the mean of the comparison treatment Table .2 The highest removal rate was recorded in all treated samples that were collected from all stations, with concentrations of 250 ppm and 200 ppm, with mean values of (86, 83), (101, 102.3) and (99, 98) for stations 1, 2 and 3 respectively. While the rest of the concentrations did not record significant differences between them, which differed from the control treatment, which recorded the highest values of BOD with mean values (108, 120 and 125) for the three stations respectively.

3.3 Chemical Oxygen Demand (COD)

Table .3 showed the silver powder superiority in recording the lowest COD rates in the treated water samples for all stations. The highest averages of the values of treatment with nanosilver powder were (561.4, 519.2 and 529.2) for stations (2,1 and 3), respectively, which differed significantly from the rest of the other treatments that did not record significant differences between them, but recorded a significant difference from the control treatment.

TABLE . 3 The effect of different concentrations powder of nanosilver , pomegranate peels, and date seeds on the rate of removing CODmg/l from raw water for three car wash stations in different locations in Samarra city.

Stations	**Type**	**CONC. ppm**					**Mean of Type**	**Normal**
		250	**200**	**150**	**100**	**50**		
S1	**Silver**	482	581	580	580	584	561.4 a	**708d**
	Pit	488	486	592	590	590	549.2 b	
	Sh.p	488	482	592	590	588	548 b	
M.C.St₁		486 a	516.3b	588c	586.6c	587.3c		
S2	**Silver**	421	532	531	550	562	519.2a	**720d**
	Pit	436	550	573	589	599	549.4	
	Sh.p	453	556	588	586	592	555 b	
M.C.St₂		436.6a	546b	564b	575b	584.3c		
S3	**Silver**	429	545	540	562	570	529.2 a	**725d**

	Pit	450	565	580	593	589	555.4b	
	Sh.p	450	559	580	590	590	553.8b	
M.C.St_3		443 a	556.3b	567 b	581.6 b	583c		

The results of Table .3 indicate further reduction of COD concentration rates with increasing concentrations of substances used for the purpose of treatment. The highest removal rate was recorded with a concentration of 250 ppm for all samples in all stations, which differed significantly from the rest of the treatments and the control treatment with mean values of (486, 436.6, 344) for stations 1, 2 and 3 respectively. While the rest of the concentrations did not record significant differences between them, and they differed significantly from the control treatment, which recorded the highest values of COD with mean values (708, 720 and 725) for the three stations respectively.

3.4 .pH

The results of the statistical analysis in Table .4 did not show significant differences in the pH value in the first station, St.1, and the second, St.2, for all transactions between them, which showed a difference from the control treatment, which recorded the highest values (8.7 and 8.82) for the first and second stations respectively. On the other hand, the treatment using silver in St.3 recorded a significant difference (7.99) compared to the treatment of pomegranate peels and date seeds (8.5 and 8.33), which in turn recorded a difference from the control treatment (8.92). The results were similar in that there were no significant differences in the concentrations of substances used in treatment between them for all stations, but they were significantly different from the control treatment.

TABLE.4 The effect of different concentrations powder of nanosilver , pomegranate peels, and date seeds on the rate of removing pH from raw water for three car wash stations in different locations in Samarra city.

Stations	Type	CONC. ppm					Mean of Type	Normal
		250	200	150	100	50		
S1	Silver	7.98	7.97	7.99	8.02	8.07	8.01 a	8.7b
	Pit	7.99	7.96	7.97	7.99	7.98	7.98 a	
	Sh.p	8.05	8.05	8.05	8	8.03	8.04 a	
M.C.St_1		8.01a	7.99a	8.00a	8.00a	8.03a		
S2	Silver	8.25	8.44	8.27	8.48	8.49	8.39 a	8.82b
	Pit	8.54	8.57	8.44	8.5	8.47	8.50 a	
	Sh.p	8.5	8.4	8.34	8.3	8.2	8.35 a	

M.C.St₂		8.43 a	8.47 a	8.35 a	8.43	8.39 a		
S3	Silver	8	8.03	7.99	7.97	7.94	7.99 a	8.92c
	Pit	8.54	8.57	8.44	8.5	8.47	8.50 b	
	Sh.p	8.49	8.46	8.4	8.13	8.17	8.33 b	
M.C.St₃		8.34 a	8.35 a	8.28 a	8.20 a	8.19 a		

3.5 T.D.S

The results of the statistical analysis in Table .5 indicate the superiority of silver powder in recording the highest removal rates for T.D.S in treated water samples for all stations. As the removal rates using nano silver powder recorded averages of (1273.4, 1229, 1261.6) for stations 2.1 and 3 respectively, which differed significantly from the rest of the other treatments, which in turn differed from the control treatment that recorded the highest concentration of TDS with values reaching (1318, 1210, 1478) for the three stations respectively.

TABLE . 5 The effect of different concentrations powder of nanosilver , pomegranate peels, and date seeds on the rate of removing T.D.Smg/l from raw water for three car wash stations in different locations in Samarra city**.**

Stations	Type	CONC. ppm					Mean of Type	Normal
		250	200	150	100	50		
S1	Silver	1246	1248	1275	1273	1325	1273.4 a	**1273.4d**
	Pit	1395	1362	1368	1436	1350	1382.2 c	
	Sh.p	1286	1321	1320	1302	1350	1315.8b	
M.C.St₁		1309a	1310.3a	1321b	1337c	1341.7c		
S2	Silver	1152	1186	1284	1247	1276	1229.0 a	**1229d**
	Pit	1182	1242	1270	1277	1337	1261.6 a	
	Sh.p	1322	1379	1261	1345	1333	1328.0 b	
M.C.St₂		1218a	1269 b	1271.7b	1289.7c	1315.3c		
S3	Silver	1337	1270	1182	1242	1277	1261.6 a	**1261.6d**
	Pit	1400	1439	1424	1458	1410	1426.2 b	
	Sh.p	1439	1408	1535	1606	1560	1509.6 c	
M.C.St₃		1392a	1372.3b	1380.3c	1435.3c	1415.7c		

The treatment of concentrations recorded significant differences between them and with the treatment of raw wastewater. The highest removal rate was recorded with concentrations 250 ppm and pmm200 for all stations, which differed significantly from the rest of the concentrations and control treatment with values of (1309, 1310), (1218, 1269) and (1292, 1372.3) [for stations 1, 2 and 3 respectively. While the concentrations of 50 ppm and 100 ppm gave the lowest removal rate for T.D.S in all the treated samples, with averages of 1337, 1341.7), (1289.7, 1315.3) and (1415.7, 1435) [for all stations respectively, which in turn differed from the control treatment.

3.6T.S.S

The results of treatment using different types of materials showed a significant superiority by using silver powder over dates and pomegranate seeds by registering the highest removal rates for suspended solids with averages amounting to (624, 614, 616) for the three stations respectively, Table .6, while the dates and dates seeds did not differ between them. Generally in terms of the effect ratio, but it differed from the control treatment, which recorded the highest concentrations of suspended solids with values reaching (670, 600, 730) respectively for stations 1, 2 and 3.

TABLE .6 The effect of different concentrations powder of nanosilver , pomegranate peels, and date seeds on the rate of removing T.T.Smg/l from raw water for three car wash stations in different locations in Samarra city

Stations	Type	CONC. ppm					Mean of Type	Normal
		250	200	150	100	50		
S1	Silver	620	610	610	630	650	624 a	670c
	Pit	710	680	670	670	660	678 b	
	Sh.p	640	630	650	640	650	642 b	
$M.C.St_1$		656a	640b	643.3b	646.6b	653.3c		
S2	Silver	580	610	650	610	620	614 a	600c
	Pit	619	629	589	629	659	625 a	
	Sh.p	620	623	640	653	640	635.2 b	
$M.C.St_2$		606.3a	620.6	626.3b	630.6b	639.6c		
S3	Silver	545	600	660	690	700	639 a	730c
	Pit	520	600	660	690	712	636.4 a	
	Sh.p	510	600	660	680	700	630 b	
$M.C.St_3$		525a	600b	660b	686.6c	704 d		

The mean concentrations also recorded differences between them in the values of TSS and with the average of the comparison treatment Table .6 The highest removal rate was recorded in all the treated samples collected from all stations with a concentration of 250 ppm compared with the rest of the treatments and the control treatment with mean values of (597), (606.3) and (660) for stations 1, 2 and 3 respectively. While the rest of the concentrations did not record significant differences between them, which differed from the 50 ppm treatment (653, 636.7, 703.3) for the three stations respectively, and the control treatment, which recorded the highest values of T.S.S.The results using the treatments under study showed their effectiveness in reducing the turbidity rate in treated water compared to untreated water. The reason for this may be due to the removal of inorganic salts and organic materials in wastewater and the percentage of TDS and TSS, and this is in agreement with the results of (Ebeling, 2003; Bann et al. , 2008) that the maximum reduction in TDS and TSS values was 86.02% and 88.39%, respectively, using a dose of 500 mg / L using different doses of concentrations of alum as coagulant and precipitant. Also, the results of this study support the results of both researchers (Haydar .2009 and Hanif et al., 2008) that the chemical doses used help remove TDS and TSS from industrial wastewater with high efficiency compared to other treatments and untreated wastewater. The results of the current study recorded a clear decrease in BOD and COD, which reached different concentrations of silver powder, pomegranate peels and date seeds. The decrease in the BOD and COD content of the treated effluent with chemical additives and powders can be explained by the coagulation mechanisms by destabilizing the colloidal particles and allowing them to agglomerate with other suspended substances and form a larger, more easily stable particles. The results of the present study are consistent with the results of the studies (Meyssami and Kasaeian, 2005 and Imran et al., 2012) that showed the reduction and elimination of BOD values and the COD values of raw wastewater with a removal rate (79-82%). And previous studies made by Agriculture and Agri-Food Canada, (2006), the United States Environmental Protection Agency, (2007) and the World Health Organization, (2007) indicated that the process of adding materials such as iron or aluminium salts, aluminium sulphate, ferric sulphate, , Ferric chloride and polymers to wastewater can reduce the concentration of biochemical oxygen (BOD) chemical oxygen (COD) and remove the suspended and dissolved matter, so that the disinfection is more successful. Thus, effluent treated with additives by means of additive precipitant helps Reducing the content of TSS, TDS, BOD and COD in the treated effluent.

The present study supports the results of Gulfraz et al. (2003) and Gara and Kaushik, 2007) that the chemical treatments recorded a low level of TSS, TDS and nutrients, and the data further showed that the suspended solids content of liquid waste exceeded the stipulated disposal standards of 100 mg /L. (Gara and Kaushik, 2007) reported a decrease in BOD and COD pollutants due to a decrease in the pollution load in the treated wastewater with the addition of precipitants and the percentage of removal depending on the amount of water added. This result is in agreement with the report (Abdelhalim , 2011) which stated that reducing soluble and insoluble particles with treatments resulted in a decrease in the levels of pollutants in general. The study (Gara and Kaushik 2007) reported a decrease in BOD and COD pollutants due to reduced pollution in wastewater treated with chemical precipitants. The results of this study were in agreement with the study of (Gulfraz et al. 2003 and Ramana et al. 2003) that a low level of TSS and TDS was recorded using different treatments. The data also showed that the suspended solids content of liquid wastes exceeded the permissible limits standards. Some of the results support the current study with the ability of nanomaterials and their effectiveness in treating surface water, groundwater and wastewater contaminated with toxic metal ions and organic and inorganic solutions in addition to microorganisms. Powders, electric nanofibers and nanoparticles have shown potential to achieve improvements in the field of water filtration membranes.

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