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Modification of magnetic nanoparticles for sorption and removal of clodinafop-propargyl herbicide from aqueous solution

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ABSTRACT

In this research, a novel method is reported for the surface modification of magnetic nanoparticles by 4-aminoacetanilide with affinity toward clodinafop-propargyl. The modified nanoparticles were characterized by Fourier transform infrared spectroscopy and also by elemental analysis and thermogravimetric analysis. The surface morphology was studied using scanning electron microscopy. The adsorption behavior was studied by Langmuir, Freundlich and Redlich–Peterson isotherm model. The resulting grafted nanoparticles were utilized for adsorption and removal of clodinafop-propargyl herbicide from real water samples such as seawater, river water and agricultural wastewater samples. The removal percentages for the spiked samples were 28.3%, 98.9% and 63.5% for seawater, river water and agricultural wastewater, respectively. The profile of the clodinafop-propargyl uptaken by the modified magnetic nanoparticles indicated good accessibility of the active sites on the modified nanosorbent.

Keywords: Surface modification; 4-Aminoacetanilide; Clodinafop-propargyl; Herbicide

1. Introduction

Nowadays, herbicides are widely used all over the world [1]. There are very strong herbicides that are easily absorbed by plants, soil and surface water [1]. Clodinafop-propargyl is one of those toxicants, which is related to aryloxyphenoxy-propionic family [2]. This group of toxicants are utilized in variety of crops such as barely, wheat, soybean, cotton, tomato and potato [3], but the herbicide, clodinafop-propargyl, is mostly utilized in wheat fields [4,5]. The molecular structure of clodinafop-propargyl is $C_{17}H_{13}ClFNO_4$. Its chemical name is propynyl(R)-2-[4-[(5-chloro-3-fluoro-2-pyridinyl)oxy]phenoxy]propanoate and was discovered in 1987 by Ciba Geigy [2]. This herbicide can be used to remove weeds, and it works by disrupting acetyl co-enzyme A carboxylase, which plays an important role in the synthesis of plants' fatty acid [3]. According to the Cancer Assessment Review Committee, clodinafop-propargyl has been introduced as a carcinogen for humans [6,7]. This agency reveals documents showing prostate tumor, ovarian tumor and liver tumor in mice [8].

The use of nanotechnology is important for the reduction of environmental pollution. In recent years, nanoparticles have received great attention due to their high surface area to volume ratios and nanoscale sizes [9]. There are various ways to synthesize magnetic nanoparticles such as co-precipitation, sol–gel methods, the reverse micelle technique and hydrothermal synthesis [10].

Our interest in nanomagnetic particles comes from their physical properties, size and magnetic properties, due to their potential applications in many biological and industrial fields. Nanomagnetic particles are easily synthesized by co-precipitation method and separated from a sample solution using magnetic field. In this research among mentioned methods, the co-precipitation technique was applied to synthesize magnetic nanoparticles. A novel method has been reported for the surface modification of magnetic nanoparticle by 4-aminoacetanilide. Modified iron oxide nanoparticles are necessary to increase its effectiveness in environmental applications. The aim of this research is to provide a quick and easy way to sorption and removal of clodinafop-propargyl herbicide from water.

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2. Experimental

2.1. Instruments

Fourier transform infrared (FTIR) spectra in transmittance mode were applied from 400 to 4,000 cm^{-1} on a Jasco FT-IR model 410 (Japan). Elemental analysis was recorded on a Thermo-Finnigan (Milan, Italy) model Flash EA elemental analyzer. Thermogravimetric analysis (TGA) at the rate of 10°C min^{-1} in nitrogen atmosphere was performed using a TGA-50H (Shimadzu Corporation, Kyoto, Japan). To study surface morphology, scanning electron microscopy (SEM) was applied on an EM 208 (Philips, Netherlands). Ultraviolet–visible spectra were carried out by Jasco ultraviolet–visible spectrometer (V-530, Jasco Inc., Ashikaga, Japan) for measurement of clodinafop-propargyl concentration at wavelength of 270 nm.

2.2. Reagents and solutions

4-aminoacetanilide, 1,4-dioxane, xylene, cyanuric chloride, petroleum ether, ethanol, methanol, acetic acid and other inorganic acid and salts (95.0% purity) were purchased from Merck (Darmstadt, Germany). The stock solution (500 mg L^{-1}) of clodinafop-propargyl was provided in methanol. To adjust the pH of the solution, acetate buffer or phosphate buffer was utilized.

2.3. Synthesis of functional organic material modified magnetic nanoparticles

2.3.1. Preparation of magnetic nanoparticles

Co-precipitation method was utilized to synthesize the iron magnetic nanoparticles [11]. Aqueous solutions of $FeCl_2.4H_2O$ (3.97 g) and $FeCl_3.6H_2O$ (2.307 g) were dissolved in 100 mL water. Thereafter, 100 mL of ammonia solution (0.1 M) was added to the solution in a nitrogen atmosphere, for 2 h at 85°C. This led to changes in reactant's color from brown to black. A strong magnet was utilized to separate the iron oxide nanoparticles from liquid, rinsed twice with distilled water and ethanol, and dried in a vacuum desiccator.

2.3.2. Modification of magnetic nanoparticle by cyanuric chloride

The solution obtained from the mixture of 50 mL xylene, 1,4-dioxan (1:1) and 1 g iron oxide particle was sonicated for 1 h. Thereafter, 2 g of cyanuric chloride was added to the solution and shaken for 24 h. The modified nanoparticles were separated by a Tesla magnet and washed by petroleum ether. The precipitation was dried in a vacuum desiccator.

2.3.3. Immobilization of 4-aminoacetanilide onto magnetite nanoparticle (AAI–MNP)

At this step, after dissolving 0.5 g of 4-aminoacetanilide in 50 mL acetate buffer (pH = 5), the modified nanoparticle was added to it. The mixture was stirred for 48 h at 40°C. The precipitation was rinsed with 50 mL of acetate buffer (pH = 5), 50 mL of NaCl (1%) and 100 mL of distilled water. The precipitation was dried in a vacuum desiccator (see Fig. 1).

2.4. Isotherm studies

Isotherm study was continued by adding 0.01 g of AAI–MNP to a series of micro tubes filled with 1 mL of diluted solution of clodinafop-propargyl (1–100 mg L^{-1}) in buffer (pH = 5), and were shaken for 30 min at 25°C. The amount of clodinafop-propargyl on the AAI–MNP was measured by calculating as:

$$Q_e = (C_0 - C_e)V/W \quad (1)$$

where C_0 is the initial concentration (mg L^{-1}); C_e is a equilibrium concentration (mg L^{-1}); $V(L)$ is the volume of the solution and $W(g)$ is the mass of AAI–MNP.

2.5. Procedure

A set of sample solutions were spiked with clodinafop-propargyl and taken in a sealed tube, and the pH was adjusted to the optimum value of 5. Then, 0.02 g of AAI–MNP was added to the solutions and shaken for 15 min, and the magnetic nanoadsorbents were removed using a magnetic field. The clodinafop-propargyl concentration present in supernatant was measured, and the amount of clodinafop-propargyl removal was calculated from the following equation:

$$\text{Removal (\%)} = [(C_0 - C_e)/C_0] \times 100 \quad (2)$$

3. Results and discussion

3.1. Characterization

As shown in Table 1, the FTIR spectrum clearly shows the bond between the nanomagnetic particle and ligand (4-aminoacetanilide) (Fig. 2). The peak areas at 3,404 and 572 are related to stretching bond of OH and Fe–O, respectively, which indicate the formation of Fe_3O_4. According to this table, the existence of C–O, C–Cl and C=N indicates modification of magnetic nanoparticles by cyanuric chloride. Moreover,

Table 1
Fourier transformation infrared and elemental analysis information

Fourier transformation infrared			
Magnetic nanoparticles	3,404.71 cm^{-1} O–H stretching	572.75 cm^{-1} Fe–O stretching	
Modified magnetic nanoparticles	1,638.23 cm^{-1} C=N stretching	1,016.30 cm^{-1} C–O stretching	661.22 cm^{-1} C–Cl stretching
AAI–MNP	1,721.16 cm^{-1} C=O stretching	1,632.03 cm^{-1} N–H stretching	1,398.14 cm^{-1} CH_3
Elemental analysis	C (%)	H (%)	N (%)
AAI–MNP	1	1.5	0.131

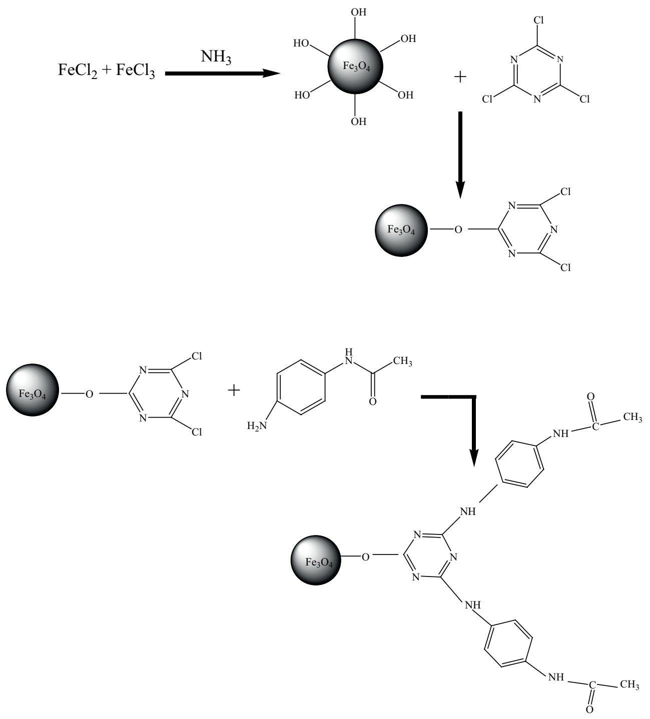

Fig. 1. Synthesis and grafting process of AAI–MNP.

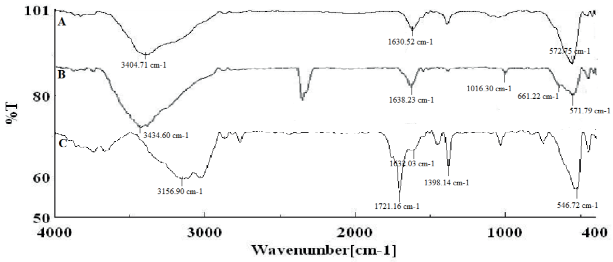

Fig. 2. FTIR spectrum of (A) magnetic nanoparticles, (B) modified magnetic nanoparticles and (C) AAI–MNP.

the existence of NH and C=O in AAI–MNP indicates that the ligand has successfully bonded with nanoparticle. The result of elemental analysis is also presented in Table 1. According to this table, the increasing amount of carbon concluded that 4-aminoacetanilide has been successfully immobilized on magnetic nanoparticles. TGA has been applied to examine the thermal behavior of AAI–MNP (Fig. 3). TGA showed the stability of AAI–MNP up to 500°C. A 0.8% weight loss in 180°C illustrates the amount of adsorbed water. The second weight loss (1.4%) showed decomposition of ligand that has been immobilized to the inorganic part of magnetic nanoparticle. To study surface morphology and particle size, transmission electron microscopy (TEM) and SEM image was applied. The TEM image in Fig. 4 shows that the particles are aspheric and agglomerated. Average diameters of particles are 30–80 nm. The SEM image (Fig. 5) showed a size less than 80 nm and illustrated bumpy and porous surface.

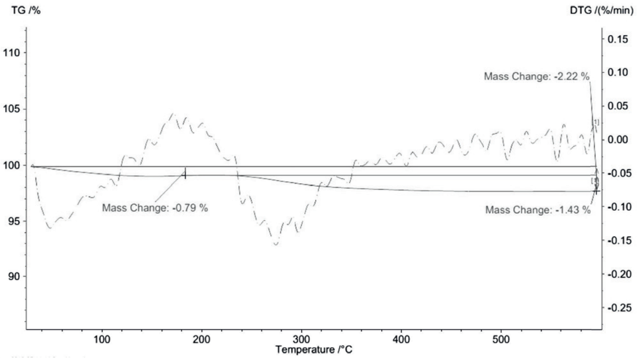

Fig. 3. TGA image of AAI–MNP.

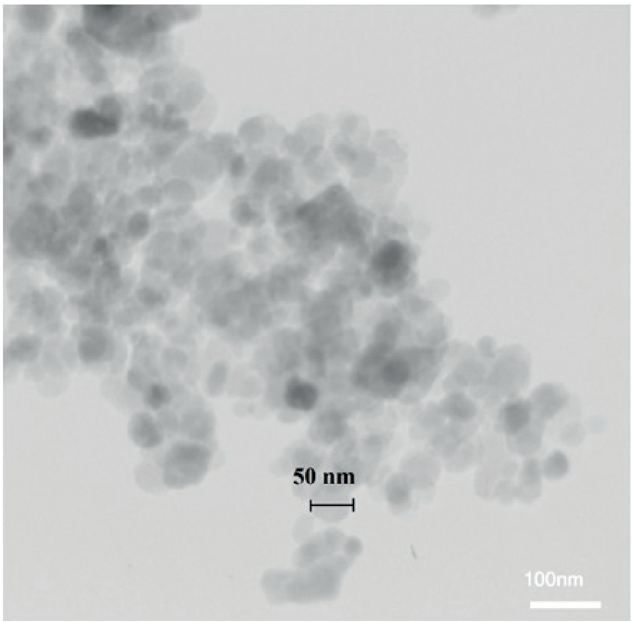

Fig. 4. TEM image of AAI–MNP.

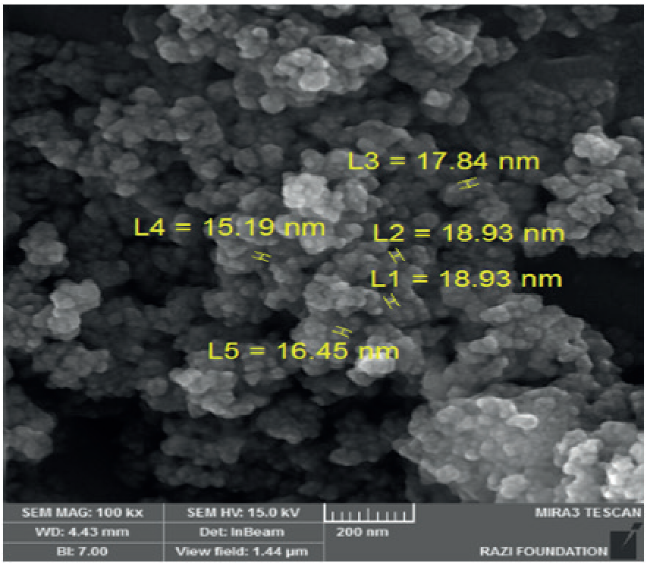

Fig. 5. SEM image of AAI–MNP.

3.2. Optimization of parameters

Batch method was applied to determine the amount of clodinafop-propargyl sorption at different pH level. Fig. 6 shows that the maximum sorption of clodinafop-propargyl occurred at pH 5, due to the fact that most hydrogen bonding occurs at this pH. Magnetic nanoparticles were dissolved in alkaline pH and hydrolyzed in acidic pH (pH lower than 3), such that pH levels higher than 9 and less than 3 were not used in the study.

It was clearly showed in the kinetic study (Fig. 7) that the best time for complete removal of clodinafop-propargyl was 15 min. Clodinafop-propargyl's adsorption halftime was only 8 min. The high adsorption rate of clodinafop-propargyl indicates the availability of 4-aminoacetanilide to trap the toxicant.

It can be concluded from Fig. 8 that temperature does not have any impact on clodinafop-propargyl's adsorption by AAI–MNP within the temperature range studied here, i.e., 20°C–40°C, so it can be used at different temperatures.

3.3. Adsorption isotherms

Surface adsorption studies have been utilized to measure the percentage of clodinafop-propargyl's adsorption per unit of AAI–MNP. Adsorption isotherms are optimized as a function of equilibrium concentration at 25°C to remove clodinafop-propargyl (see Fig. 9). Based on Langmuir isotherms, all active sites of AAI–MNP have a similar tendency to adsorb the clodinafop-propargyl molecules. Langmuir equation is defined as follows [12]:

$$C_e/q_e = (1/q_{\max} K_L) + (C_e/q_{\max}) \tag{3}$$

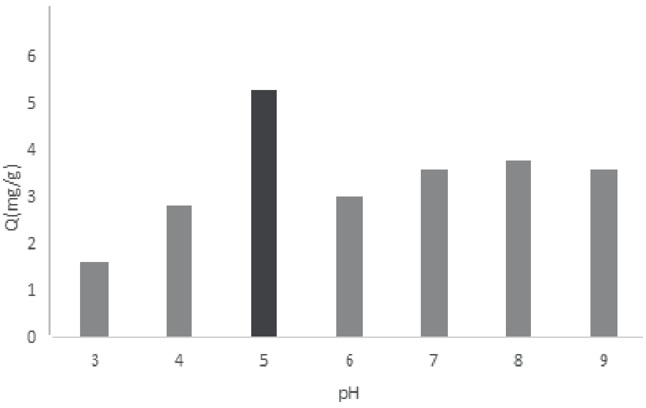

Fig. 6. Sorption of clodinafop-propargyl onto AAI–MNP at different pH.

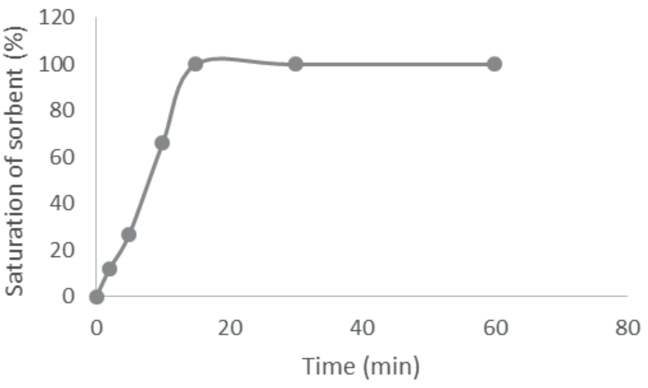

Fig. 7. Kinetics of clodinafop-propargyl onto AAI–MNP.

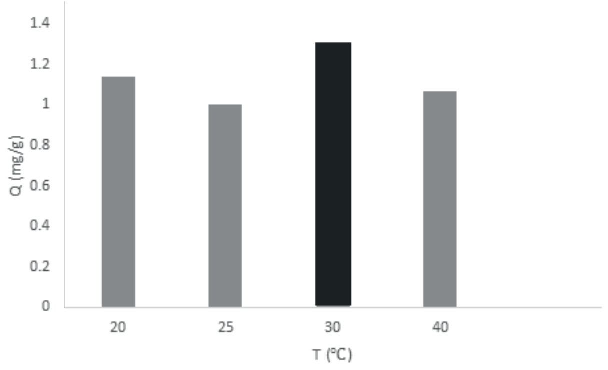

Fig. 8. Sorption of clodinafop-propargyl onto the AAI–MNP at different temperature.

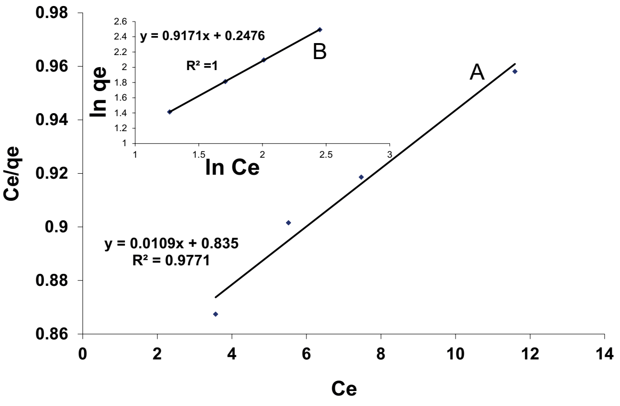

Fig. 9. Langmuir isotherm (A), and Freundlich isotherm (B) for clodinafop-propargyl adsorption onto AAI–MNP at 25°C.

Table 2
Isotherms parameters for adsorption of clodinafop-propargyl by AAI–MNP at 25°C

Langmuir isotherm model			
$q_{\max}$ (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2
91.74	0.01	0.62–0.83	0.9771
Freundlich isotherm model			
K_F (mg g^{-1}) (L mg^{-1})$^{1/n}$	n		R^2
1.28	1.09		1
Redlich–Peterson isotherm model			
g	A (L g^{-1})	B (L mg^{-1})^g	R^2
0.13	3	1.35	0.9978

Table 3
Removal of Clodinafop-propargyl in different water samples

Sample	Clodinafop-propargyl in sample (μg L^{-1})	Added (μg L^{-1})	Remained in the sample after sorption (μg L^{-1})	Removal (%)	RSD (%)
River water	N.D.	2,000	22	98.9	10.1
Agricultural wastewater	N.D.	2,000	730	63.5	28.5
Seawater	N.D.	2,000	1,434	28.3	13.6

Note: RSD – Relative standard deviation; and N.D. – Not detected.

In this equation, C_e indicates the equilibrium of clodinafop-propargyl concentration in solution (mg L^{-1}); q_e the equilibrium sorption capacity of clodinafop-propargyl (mg g^{-1}); $q_{\max}$ (mg g^{-1}) the maximum adsorption capacity of AAI–MNP for clodinafop-propargyl adsorption and K_L is Langmuir constant (L mg^{-1}). The amount of $q_{\max}$ (Table 2) indicates that the sorption of clodinafop-propargyl is significant (91.74 mg g^{-1}). One of the most important parameters of the Langmuir equation is dimensionless separation factor (R_L), which can be obtained via following equation:

$$R_L = \frac{1}{(1+K_L C_0)} \tag{4}$$

The amount of R_L shows one of the following results, favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), irreversible ($R_L = 0$) or linear ($R_L = 1$) [13]. According to Table 2, the amount of R_L is 0.62, which indicates that the sorption of clodinafop-propargyl is favorable.

The Freundlich isotherm (see Fig. 9) is an empirical equation that expresses heterogeneous adsorption of a system [14,15]. This empirical equation is defined as follows:

$$\ln q_e = \ln k_F + 1/n \ln C_e \tag{5}$$

where $1/n$ is the heterogeneity factor, and k_F is the Freundlich constant (mg g^{-1})(L mg^{-1})$^{1/n}$. The experimental results of Freundlich model is related to adsorption of a heterogeneous modified surface. This isotherm can be derived assuming a logarithmic decrease in the enthalpy (H) of adsorption by the sorbent with the increase in the fraction of occupied sites. Freundlich parameters are listed in Table 2. The amount of heterogeneity factor ($1/n = 0.9171$) indicates that the sorption is heterogeneous.

The Redlich–Peterson [16] constants A, B and g ($0 < g < 1$) can be evaluated using the following equation:

$$\ln[(AC_e/Q_e) - 1] = \ln(C_e) + \ln(B) \tag{6}$$

The parameters for the sorption of clodinafop-propargyl onto AAI-MNP by use of linear regression are listed in Table 2. The g values were close to zero, which demonstrates that the isotherms are approaching the Freundlich model.

3.4. Method application

The eligibility of the suggested method was tested to eliminate clodinafop-propargyl from real aqueous samples. The elimination of clodinafop-propargyl from seawater (Caspian Sea, Anzali, Gilan state, Iran), river water (Sepid rod, Gilan state, Iran) and agricultural wastewater (Anzali, Gilan state, Iran) in an optimum condition was implemented. The real samples were spiked with clodinafop-propargyl before being subjected to the suggested method. Table 3 shows an acceptable removal of clodinafop-propargyl in river water and agricultural wastewater, and the results reflect the strength of AAI–MNP to adsorb the toxicant. It can be concluded that the proposed method is a reasonable and appropriate one. The low adsorption of clodinafop-propargyl in seawater is maybe due to the existence of salt, and that could block the active sites of AAI–MNP [17].

4. Conclusion

Simplicity, efficiency and speed are the advantages of co-precipitation method to produce magnetic nanoparticles. This method has been utilized to achieve high-level extraction of clodinafop-propargyl. For more elimination of the clodinafop-propargyl from samples, magnetic nanoparticles were modified. Results indicate that the maximum sorption of the clodinafop-propargyl occurred at pH 5 and in 15 min. This study found that the sorption of clodinafop-propargyl onto AAI–MNP was excellent and temperature had no impact on it within the range 20°C–40°C. This research has corroborated that the sorption rate of clodinafop-propargyl in river water and wastewater is much more than that in seawater.

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