

Removal of lead(II) from aqueous solutions using carbonate hydroxyapatite extracted from eggshell waste

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ABSTRACT

Carbonate hydroxyapatite (CHAP) synthesized from eggshell waste was used for removing lead ion from aqueous solutions. The effects of pH, contact time and initial concentration were studied in batch experiments. The maximum uptake of lead ion was obtained at pH 6.0. Adsorption equilibrium was established by 60 min. The pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models were applied to study the kinetics of the sorption processes. The pseudo-second order kinetic model provided the best correlation ($R^2 > 0.9991$) of the used experimental data compared to the pseudo-first order and intraparticle diffusion kinetic models. The adsorption of lead ion by CHAP increased as the initial concentration of lead ion increased in the medium. The maximum lead ion adsorbed was found to be 101 mg g^{-1} . It was found that the adsorption of Pb(II) on CHAP was correlated well ($R^2 = 0.9995$) with the Langmuir equation as compared to Freundlich isotherm equation under the concentration range studied. This study indicated that CHAP could be used as an efficient adsorbent for removal of lead ion from aqueous solution.

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1. Introduction

Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [1]. Therefore, the removal of hazardous heavy metals cation in wastewater has received much attention in recent years. Many methods have been developed to remove heavy metals from wastewater, namely adsorption, chemical oxidation/reduction, precipitation, ion exchange, electrochemical processes, membrane filtration and reverse osmosis. Among these methods, the metal cation adsorption is quite promising due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness. Synthetic hydroxyapatite (HAP) has been extensively studied for its kinetics and chemical reaction with a wide variety of metals (e.g., Cr, Cu, Cd, Zn, Sb and U) [2–5]. Laboratory-produced hydroxyapatites as well as commercially-available hydroxyapatites have been examined for their dissolution [6], crystallizability, surface activity [7], and thermal stability. Previous works [8,9] also mentioned that the synthetic carbonate hydroxyapatite (CHAP) had higher efficiency in the removal of heavy metals (Pb(II), Cd(II), Cu(II), Hg(II)) than HAP, but, lacks details about its adsorption characteristics to heavy metals cation, which might be due to the high cost of the preparation of CHAP.

The objective of this preliminary study was to investigate the feasibility of Pb(II) removal from aqueous solution by CHAP prepared by eggshell waste. To our knowledge, no CHAP has been used to remove lead ion in aqueous streams. The kinetics of the process was determined, especially in relation to the effects of various factors on the removal. The factors investigated included different Pb(II) concentration, contact time, and initial pH of solution.

2. Materials and methods

2.1. Materials and equipment

Preparation of CHAP was carried out as described by Zheng et al. [10]. The concentration of residual Pb(II) ions in the supernatant was determined by using an atomic absorption spectrophotometer (Perkin-Elmer 700). Scanning electron microscopy (SEM) was conducted with a Hitachi JSM-6700F SEM to observe the surface microstructures of the used CHAP. Fourier transform infrared spectroscopy (FTIR) (Bomem, MB 100) studies were carried out to identify the functional groups. The spectrum was recorded in the range of $400\text{--}4000 \text{ cm}^{-1}$. pH were determined according to a Multi-line 330i pH-meter which was standardized using buffer solutions of different pH values (4.01, 7.00, and 10.00).

The suspensions in all studies were filtered through $0.45\text{-}\mu\text{m}$ nucleopore polycarbonate membrane filters. All the experiments were done in triplicate and the average value was taken for analysis.

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2.2. Preparation of metal solutions

The synthetic solutions were all prepared by diluting Pb(II) standard stock solutions (concentration $1000 \pm 2 \text{ mg L}^{-1}$) obtained by dissolving $\text{Pb}(\text{NO}_3)_2$ in deionized water. Fresh dilutions were used in each experiment.

2.3. Sorption studies

To determine the optimum Pb(II) adsorption conditions, the batch adsorption experiments were conducted with CHAP at room temperature in 250 ml Erlenmeyer flasks. The effect of pH on the adsorption capacity was investigated at pH values in the range of 2.0–9.0 by using known volume of 200 mg L^{-1} Pb(II) solutions. The desired pH of the solutions were maintained by adding HCl or NaOH at the beginning of the experiment and not controlled afterwards. Sorbent was added to medium and the reaction mixture was agitated at room temperature at 225 rpm for 180 min. In the latter experiments the pH of the Pb(II) solutions were adjusted to optimum pH value (6.0 ± 0.1). The effect of contact time was studied in the time range of 5–180 min. Similarly above, metal solutions with the concentration range of $10\text{--}500 \text{ mg L}^{-1}$ were used to assess the effect of initial Pb(II) ion concentrations. At the end of the adsorption process adsorbent was separated from the solution and supernatant was analyzed for residual Pb(II) concentration by AAS (Perkin-Elmer 700). Three replicates were used for each Pb(II) biosorption experiments and the results given were the average values. The adsorption capacity of CHAP was calculated using the general equation [10]:

$$q_e = \frac{(C_0 - C_t)V}{M} \quad (1)$$

where q_e is the amount of Pb(II) adsorbed on the CHAP (mg g^{-1}), C_0 and C_t are the Pb(II) concentration in solution before and after adsorption (mg L^{-1}), V is the volume of the medium (L) and M is the amount of the CHAP used in the reaction mixture (g).

3. Results and discussion

3.1. Characteristics of CHAP

The FTIR spectra of carbonate hydroxyapatite sample which was sintered at 600°C is shown in Fig. 1. The broad $-\text{OH}$ stretching adsorption can be observed at 3446.6 cm^{-1} and the PO_4^{3-} ν_1 and ν_2 vibration adsorption can be observed at 962.4 cm^{-1} and 472.5 cm^{-1} , respectively. The peaks at 603.7 cm^{-1} and 565.1 cm^{-1} are characterized of the PO_4^{3-} ν_4 stretching vibration. The bands at 1458.1 cm^{-1} and 1400.2 cm^{-1} may be assigned to the CO_3^{2-} adsorption. These bands have been mentioned in other literature [11], and are different from the single band of carbonate, which indicates that CO_3^{2-} groups existed in hydroxyapatite.

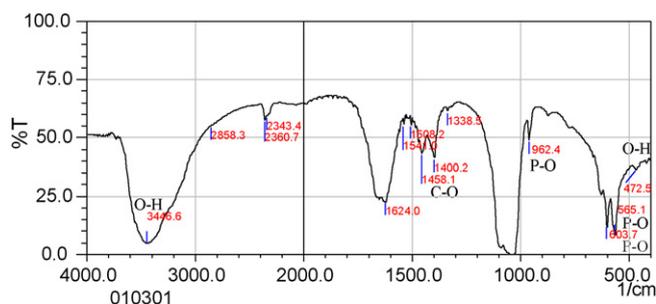


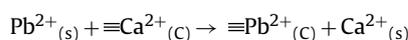
Fig. 1. The FTIR spectra of prepared carbonate hydroxyapatite sintered at 600°C .

Samples of CHAP adsorbent were coated with thin layer of gold under vacuum and examined by scanning electron microscope (Hitachi JSM-6700F). SEM observations show that CHAP appears as platelets. Different pore sizes may be observed on the surface of CHAP as shown in Fig. 2A. Following Pb(II) sorption, the outer surfaces of the original crystals covered with neoformed crystallites (Fig. 2B).

3.2. Effect of pH

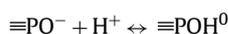
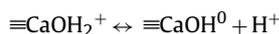
The acidity of solution (pH) is one of the most important parameters controlling uptake of heavy metals from aqueous solutions. In this group of experiments, the concentration of Pb(II) (200 mg L^{-1}), the amount of CHAP (0.2 g) and contact time (180 min) were kept constant. The initial pH of solutions varied from 2.0 to 9.0 with an increment of 1.0 pH units. Fig. 3 describes the effects of pH on CHAP adsorption of Pb(II). The results showed that the adsorption capacities of Pb(II) increased significantly as the pH increased from 2.0 to 6.0 and approaches a plateau at pH range of 6.0–9.0. The adsorption capacities reached $94.5 \text{ mg Pb(II)} (\text{g CHAP})^{-1}$ at pH of 6.0. Since the optimum pH for Pb(II) sorption by CHAP was found to be 6.0, therefore, this pH was used for further study.

There are two possible reactions capable of removing lead ion from the solutions. The first mechanism is the adsorption of Pb^{2+} on the surfaces followed by the ion exchange reaction between Pb^{2+} adsorbed and Ca^{2+} of CHAP. The ion exchange interactions can be presented as follows:



where subscripts (s) and (c) denote solution and CHAP phase, respectively. The metal in the solution ($\text{Pb}^{2+}_{(s)}$) replaces a surface Ca^{2+} of the sorbent ($\equiv\text{Ca}^{2+}_{(c)}$).

The second mechanism is surface complexation by CHAP. Reactions involved in the surface reactions of CHAP that relate to pH variation can be listed as follows:



At lower pH, the existing relatively high concentration of H^+ increases the positively charged $\equiv\text{CaOH}_2^+$ and neutral POH^0 . As a result, the surface of the sorbent is net positively charged. Increased net positive charge is less favorable in complexing Pb^{2+} on the sorbent surface than the net negative charge sites. Thus, increased net positive charge of the CHAP surface in the pH range of 2–3 (Fig. 3) may be the cause of reduced Pb^{2+} removal.

3.3. Effect of contact time

Effect of contact time was studied using solution containing 200 mg L^{-1} concentration of Pb ion using CHAP at optimum pH up to a contact time of 180 min. It seemed that the adsorption consisted of two phases: a primary rapid phase and a second slow phase. The first rapid phase lasted approximately 20 min and accounted for the major part in the total Pb^{2+} adsorption. Adsorption reached a plateau value in approximately 60 min, which showed saturation of the active points (Fig. 4).

In order to investigate the mechanism of sorption, characteristic constants of sorption were determined using a pseudo-first order equation of Lagergren based on solid capacity [12], a pseudo-second order equation (Ho equation) based on solid phase sorption [13] and an intraparticle diffusion model.

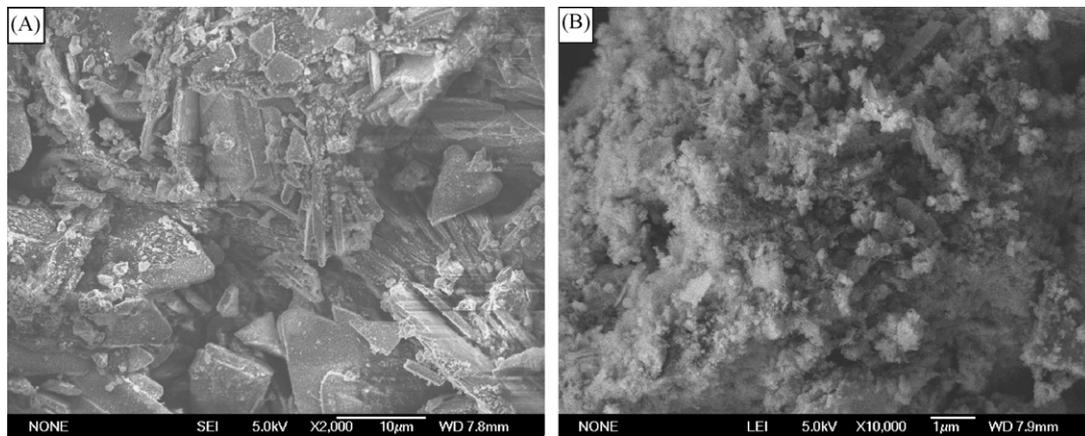


Fig. 2. The SEM characterization of CHAP: (A) starting material (2000 \times) and (B) CHAP following lead adsorption (10,000 \times).

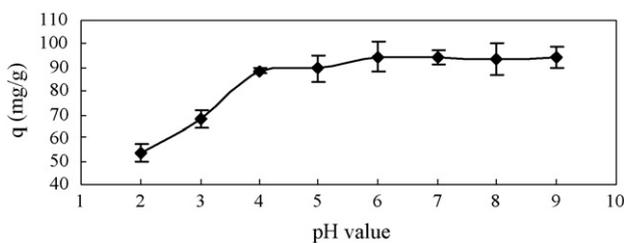


Fig. 3. Effect of pH on the adsorption.

The pseudo-first order equation of Lagergren can be expressed as Eq. (2):

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (2)$$

where q_t is the amount of metal ions adsorbed (mg g^{-1}) at any given time t (min), q_e is the amount of metal ion adsorbed (mg g^{-1}) at equilibrium and K_1 is the pseudo-first order reaction rate constant for adsorption (min^{-1}).

The pseudo-second order reaction rate equation has the form:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (3)$$

where q_t is the amount of metal ions adsorbed (mg g^{-1}) at any given time t (min), q_e is the amount of metal ion adsorbed (mg g^{-1}) at equilibrium and K_2 is the second order reaction rate constant for adsorption (g (mg min)^{-1}). The following expression denotes the initial sorption rate v_0 (mg (g min)^{-1}) [14]:

$$v_0 = K_2 q_e^2 \quad (4)$$

The intraparticle diffusion model [15] was considered in order to determine the participation of this process in the sorption of lead ion by CHAP. According to this model, the plot of uptake (q_t), versus the square root of time ($t^{0.5}$) should be linear if intraparticle

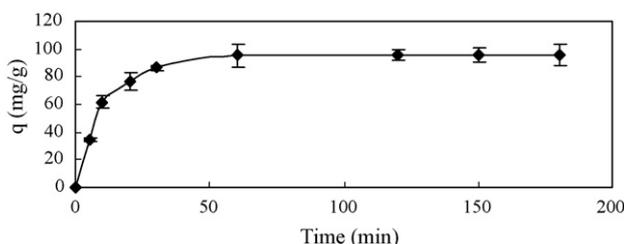


Fig. 4. Effect of time on the adsorption.

diffusion is involved in the overall adsorption mechanism. Furthermore, if this line passes through the origin then the intraparticle diffusion is the rate-controlling step of the process [16]. The initial rate of intraparticle diffusion, K_d , can be calculated in the following way:

$$q_t = K_d t^{0.5} \quad (5)$$

where q_t is the amount of sorbate on the surface of the sorbent at time t (mg g^{-1}), K_d is the intraparticle rate constant ($\text{mg (g min}^{0.5})^{-1}$) and t is the time (min).

Fig. 5A and B shows linear plots of the linearized forms of the pseudo-first order model in Eq. (3) and the pseudo-second order model in Eq. (4) for the adsorption of Pb(II) onto CHAP. K_1 , K_2 and q_e calculated from the slopes and intercepts of the lines obtained by plotting $\log(q_e - q_t)$ against t and t/q_t against t are listed in Table 1. As shown in Table 1, the pseudo-second order model fits better the adsorption kinetics of lead ion on CHAP than the pseudo-first order model. This suggests that the rate-limiting step of this sorption system may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate [17,18]. The q_e calculated from the pseudo-second order rate model of Pb(II) is 100 mg g^{-1} . The initial adsorption rate (v_0) values of Pb(II) is $17 \text{ mg (g min)}^{-1}$.

Fig. 5C shows a plot of the Weber and Morris intraparticle diffusion model for the sorption of Pb(II) onto CHAP. As shown in Fig. 5C, the plot of uptake (q_t), versus the square root of time ($t^{0.5}$) was not linear, which indicated that the intraparticle diffusion was not the rate-controlling step in these adsorption systems.

3.4. Effect of initial metal ion concentration

The experiments were carried out using various concentrations of Pb(II) solution under the determined optimum pH values and contact time. The effect of initial lead ion concentration was investigated in the range of $10\text{--}500 \text{ mg L}^{-1}$. The results are presented in Fig. 6. The Pb(II) adsorption capacity of the CHAP firstly increased with increasing the initial concentration of metal ion and then reached a saturation value at about 300 mg L^{-1} and the maximum equilibrium uptake for Pb(II) was 101 mg g^{-1} . Then the value did not significantly change with the initial metal ion concentration.

Adsorption of Pb(II) by CHAP was studied further for understanding the mechanism by fitting the experimental data to Langmuir and Freundlich adsorption isotherms. The Langmuir isotherm [19] assumes monolayer adsorption onto a surface with a

Table 1
Parameter values calculated using the pseudo-first order and the pseudo-second order models for the adsorption of Pb(II) on CHAP.

Metal ion	Pseudo-first order model			Pseudo-second order model			
	q_e	K_1	R^2	v_0	q_e	K_2	R^2
Pb(II)	46.75	0.0564	0.8731	17	100	0.0017	0.9991

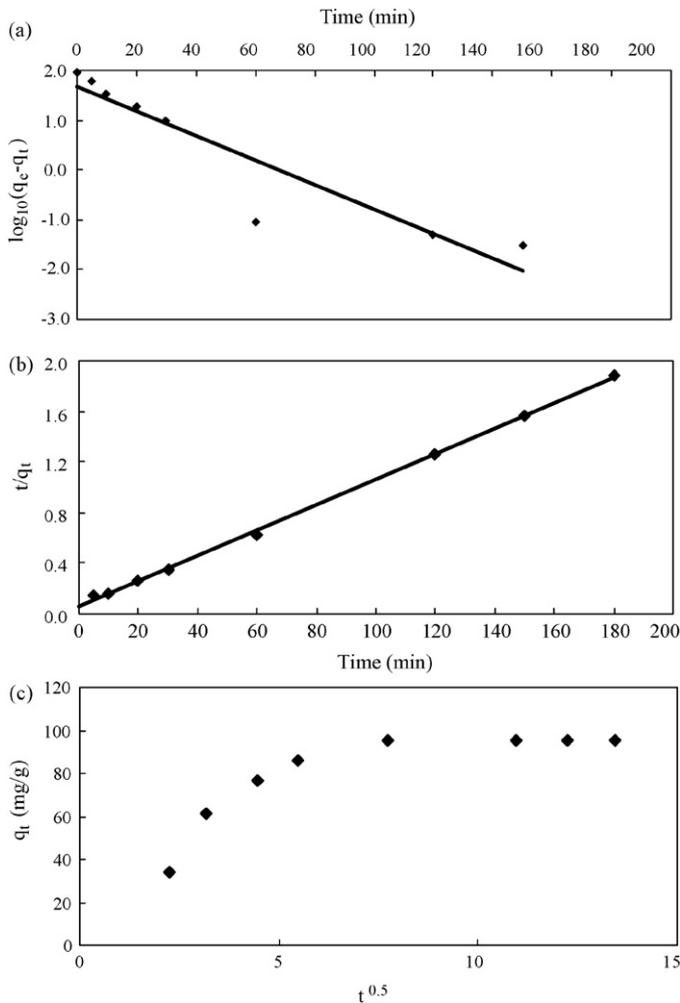


Fig. 5. Linear fit of experimental data obtained using (A) pseudo-first order model and (B) pseudo-second order model, and (C) the amount of single metal ion sorbed versus square root of time.

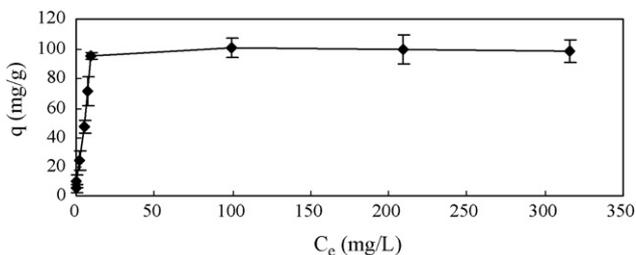


Fig. 6. Effect of initial concentration on the adsorption.

Table 2
Langmuir and Freundlich constants and correlation coefficients for adsorption of Pb(II) on CHAP.

Metal ions	Langmuir			Freundlich		
	q_{max}	b	R^2	K_f	n	R^2
Pb(II)	94.3	0.54	0.9995	18.8	2.72	0.8002

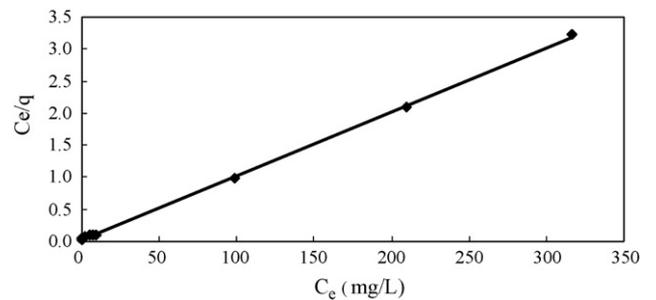


Fig. 7. Langmuir isotherm for the adsorption of lead ion on CHAP.

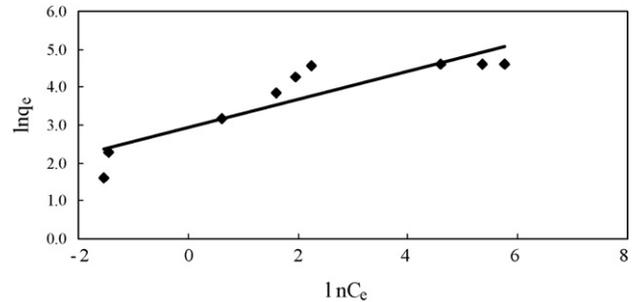


Fig. 8. Freundlich isotherm for the adsorption of lead ion on CHAP.

finite number of identical sites, and its linear form can be expressed as Eq. (7):

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \quad (6)$$

where q_e and q_{max} are the observed and maximum uptake capacities ($mg\ g^{-1}$), C_e is the equilibrium concentration ($mg\ L^{-1}$), and b is the equilibrium constant ($L\ mg^{-1}$).

The Freundlich equation [20] proposes an empirical model that is based on sorption on heterogeneous surface and has the form:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (7)$$

where K_f ($L\ g^{-1}$) and n are Freundlich isotherm constants, q_e is the observed uptake capacities ($mg\ g^{-1}$) and C_e is the equilibrium concentration ($mg\ L^{-1}$).

The linear plots of Langmuir and Freundlich equation representing Pb(II) adsorption by the CHAP are illustrated in Figs. 7 and 8. The adsorption constants of Langmuir and Freundlich equation and their correlation coefficients (R^2) are calculated and represented in Table 2. The correlation regression coefficients show that the adsorption process is better defined by Langmuir than by the Freundlich equation. The Langmuir fit is consistent with strong

Table 3
Adsorption capacities of Pb²⁺ ions by various adsorbents.

Adsorbent	q_{\max} (mg g ⁻¹)	Source
Hydroxyapatite/polyurethane composite foams	150	Jang et al. [1]
Calcium hydroxyapatite	85	Yasukawa et al. [21]
Activated carbon	31.2	Machida et al. [22]
Wheat bran	87	Bulut and Baysal [23]
Crop milling waste	49.97	Saeed et al. [24]
CHAP	94.3	This work

monolayer sorption onto specific sites. According to Langmuir isotherm, the monolayer saturation capacity of CHAP is 94.3 mg g⁻¹ for Pb(II).

Table 3 gives comparative equilibrium capacities (q_{\max}) of lead ion on various adsorbents. The result reveals that CHAP was effective in attenuating lead in aqueous solutions.

4. Conclusions

Sorption of Pb(II) on CHAP, prepared by eggshell waste, was investigated as a function of pH, equilibration time and initial lead ion concentration. The experiments have shown that:

1. CHAP was effective in attenuating lead ion in aqueous solutions and the highest Pb(II) adsorption onto CHAP was obtained at pH 6.0.
2. The pseudo-first order, pseudo-second order kinetic and intraparticle diffusion kinetic models were used to describe the kinetic data for initial Pb(II) concentrations and the rate constants were evaluated. The used experimental data were fitted by the second-order kinetic model, which indicated that chemical sorption was the rate-limiting step, inside of mass transfer. The contact time of approximately 60 min was required to reach the equilibrium.
3. The adsorption isotherm could be well defined by Langmuir equation. Under defined experimental conditions (initial pH 6.0 and initial metal concentration range 10–500 mg L⁻¹), the calculated capacity obtained by Langmuir equation was 94.3 mg g⁻¹ for Pb(II).

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