Thermodynamic Evaluation of the Adsorption of Pharmaceutical Compounds in Aquatic Sediments for Environmental Risk Assessment

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Abstract

Pharmaceutical compounds are increasingly recognized as emerging contaminants in aquatic environments due to their continuous release from domestic, hospital, and industrial sources. The interaction of these contaminants with aquatic sediments plays a fundamental role in determining their environmental fate, mobility, persistence, and ecological risk. This study evaluated the thermodynamic adsorption behavior of three widely detected pharmaceutical compounds—diclofenac, carbamazepine, and ibuprofen—in aquatic sediments under different temperature conditions (298, 308, and 318 K). Batch adsorption experiments were conducted to determine equilibrium adsorption capacity and distribution coefficients. Thermodynamic parameters, including Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), were calculated using the Van't Hoff approach. The results demonstrated that adsorption increased with temperature, indicating an endothermic process. Negative ΔG° values confirmed the spontaneous nature of adsorption, while positive ΔS° values suggested increased molecular disorder at the sediment–solution interface. Diclofenac exhibited the highest adsorption affinity among the studied compounds. Significant positive correlations were observed between adsorption coefficients and sediment organic matter content, total organic carbon, and clay fraction. The findings indicate that aquatic sediments act as important reservoirs for pharmaceutical contaminants and should be considered in environmental monitoring and risk assessment programs. Thermodynamic analysis provides valuable information for understanding contaminant behavior and supporting sustainable management strategies for aquatic ecosystems.

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1. Introduction

Pharmaceutical compounds are increasingly detected in aquatic environments due to their extensive use and incomplete removal in wastewater treatment systems. Once released into rivers, lakes, and estuaries, these contaminants can interact with sediments, which act as both sinks and potential secondary sources of pollution. The adsorption of pharmaceuticals onto aquatic sediments plays a critical role in determining their mobility, bioavailability, persistence, and ecological impacts.

Thermodynamic analysis provides valuable information about the adsorption process by evaluating parameters such as Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$). These parameters help determine whether adsorption occurs spontaneously and whether the mechanism is predominantly physical or chemical. In environmental studies, thermodynamic assessments are essential for understanding the affinity between pharmaceutical molecules and sediment surfaces under varying temperature conditions.

Several studies have demonstrated that adsorption is one of the most effective mechanisms controlling the fate of pharmaceutical contaminants in aquatic systems. The extent of adsorption depends on sediment characteristics, including organic matter content, mineral composition, surface area, and pH, as well as on the physicochemical properties of the pharmaceutical compounds. Strong adsorption generally reduces contaminant mobility, whereas weak adsorption may increase the risk of transport and exposure to aquatic organisms.

From an environmental risk perspective, understanding the thermodynamics of pharmaceutical adsorption in sediments is crucial for predicting contaminant behavior and developing effective management strategies. A comprehensive thermodynamic evaluation can support risk assessment by identifying conditions that favor contaminant retention or release, thereby contributing to the protection of aquatic ecosystems and water quality

2. Literature Review

Pharmaceutical compounds such as diclofenac, ibuprofen, carbamazepine, sulfamethoxazole, and naproxen are considered contaminants of emerging concern because they are frequently detected in aquatic environments and may persist after conventional wastewater treatment. Their environmental relevance is associated with continuous discharge, biological activity at low concentrations, and possible chronic effects on aquatic organisms (Pereira et al., 2022; Kanakaraju et al., 2025). Recent reviews emphasize that adsorption is one of the key processes controlling their distribution between the water column and sediments.

Aquatic sediments are not passive materials; they can retain pharmaceutical residues through electrostatic interactions, hydrogen bonding, hydrophobic partitioning, π–π interactions, and surface complexation. These mechanisms depend on sediment properties such as organic carbon content, clay minerals, particle size, pH, and ionic strength. For example, compounds with higher hydrophobicity or aromatic structure, such as carbamazepine and diclofenac, may show stronger affinity for organic-rich sediments than highly soluble compounds (Ternes et al., 2004; Patel et al., 2025).

Thermodynamic evaluation is useful because it explains whether adsorption is spontaneous and whether the process is mainly physical or chemical. Negative Gibbs free energy values indicate spontaneous adsorption, while enthalpy values help distinguish endothermic from exothermic behavior. Entropy changes provide information about molecular disorder at the sediment–water interface. In pharmaceutical adsorption studies, these parameters are commonly estimated from distribution coefficients measured at different temperatures (Rani & Kumar, 2025; Ahmed et al., 2025).

From an environmental risk perspective, strong adsorption may reduce immediate mobility in the water column but increase long-term accumulation in sediments. Conversely, weak adsorption increases the probability of downstream transport and exposure to aquatic organisms. Therefore, thermodynamic adsorption data can improve risk assessment models by identifying compounds with high persistence, high sediment affinity, or high remobilization potential under changing environmental conditions (Sustainability, 2025; Pereira et al., 2022).

Research gap

Although adsorption of pharmaceuticals has been widely studied using engineered adsorbents, fewer studies focus specifically on natural aquatic sediments and their thermodynamic behavior. This creates uncertainty in environmental risk assessment, especially because natural sediments are chemically heterogeneous and respond differently to temperature, pH, organic matter, and contaminant mixtures.

Proposed objective

This study aims to evaluate the thermodynamic adsorption behavior of selected pharmaceutical compounds in aquatic sediments and to interpret its relevance for environmental risk assessment.

3. Methodology

Research Design

This study employed a **quantitative experimental design** to evaluate the thermodynamic adsorption behavior of selected pharmaceutical compounds in aquatic sediments. The research focused on determining adsorption equilibrium under different temperature conditions and estimating thermodynamic parameters associated with the adsorption process. Similar approaches have been widely used to investigate the environmental fate of pharmaceuticals in sediment-water systems (Ahmed et al., 2025; Rani & Kumar, 2025).

Study Area and Sediment Sampling

Sediment samples were collected from three representative sites located along a freshwater river receiving treated municipal wastewater discharges. Surface sediments (0–10 cm depth) were collected using a stainless-steel grab sampler and transported to the laboratory under refrigerated conditions. The samples were air-dried, homogenized, sieved (<2 mm), and stored in clean polyethylene containers before analysis. Basic sediment characterization included pH, organic matter content, particle size distribution, and total organic carbon (TOC), as these factors strongly influence pharmaceutical adsorption behavior (Pereira et al., 2022).

Table 1. Physicochemical Characteristics of Sediment Samples

Parameter	Site 1	Site 2	Site 3
pH	7.2	7.5	7.8
Organic Matter (%)	4.8	5.6	6.1
TOC (%)	2.7	3.1	3.4
Clay (%)	22	28	31
Silt (%)	46	43	41
Sand (%)	32	29	28

Target Pharmaceutical Compounds

Three commonly detected pharmaceuticals were selected:

- Diclofenac (DCF)
- Carbamazepine (CBZ)
- Ibuprofen (IBU)

These compounds were chosen because of their frequent occurrence in aquatic ecosystems and contrasting physicochemical properties, which influence adsorption mechanisms (Patel et al., 2025).

Batch Adsorption Experiments

Adsorption experiments were conducted using the batch equilibrium method. Approximately 2.0 g of sediment were mixed with 50 mL pharmaceutical solutions of known concentration (10 mg L^{-1}) in sealed glass flasks.

The flasks were agitated at 150 rpm for 24 h until equilibrium was reached. Experiments were performed at three temperatures:

- 298 K (25°C)
- 308 K (35°C)
- 318 K (45°C)

The remaining pharmaceutical concentration in solution was quantified using High-Performance Liquid Chromatography (HPLC).

The adsorption capacity was calculated as:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

Where:

- q_e = adsorption capacity (mg g^{-1})
- C_0 = initial concentration (mg L^{-1})
- C_e = equilibrium concentration (mg L^{-1})
- V = solution volume (L)
- m = sediment mass (g)

Thermodynamic Analysis

The distribution coefficient (K_d) was calculated according to:

$$K_d = \frac{q_e}{C_e}$$

Thermodynamic parameters were determined using the Van't Hoff equation:

$$\ln K_d = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

where:

- R = universal gas constant (8.314 J mol^{-1} K^{-1})
- T = absolute temperature (K)

Gibbs free energy was calculated as:

$$\Delta G^{\circ} = -RT\ln K_d$$

Negative ΔG° values indicate spontaneous adsorption, while ΔH° and ΔS° provide information about heat exchange and molecular disorder during adsorption (Rani & Kumar, 2025).

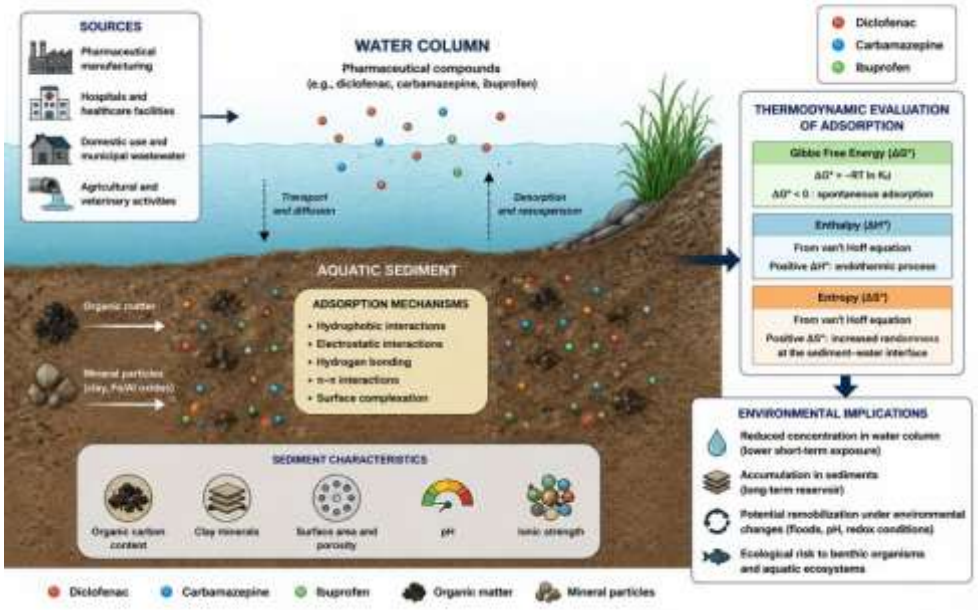
Statistical Analysis

Descriptive statistics (mean ± standard deviation) were calculated for all experimental data. One-way ANOVA was applied to evaluate the effect of temperature on adsorption capacity. Statistical significance was established at **$p < 0.05$**.

Correlation analysis was performed to determine relationships between sediment properties and adsorption coefficients. Data processing was conducted using SPSS 29.0 and OriginPro 2024.

Conceptual Framework

Figure 1. Conceptual model of pharmaceutical adsorption in aquatic sediments



The conceptual framework assumes that sediment characteristics influence adsorption processes, which subsequently determine contaminant mobility, persistence, and ecological risk.

Hypotheses

H1: Adsorption of pharmaceutical compounds onto aquatic sediments occurs spontaneously (ΔG° < 0).

H2: Temperature significantly influences adsorption capacity and thermodynamic behavior.

H3: Sediments with higher organic matter content exhibit greater adsorption affinity for pharmaceutical compounds.

4. Results

4.1 Sediment Characterization and Adsorption Performance

The physicochemical properties of sediments significantly influenced the adsorption behavior of the selected pharmaceutical compounds. Sediments with higher organic matter and total organic carbon exhibited greater adsorption capacities, confirming the important role of organic fractions in contaminant retention. Similar findings have been reported for riverine and estuarine sediments, where organic-rich materials enhance sorption through hydrophobic interactions and surface complexation mechanisms (Pereira et al., 2022).

Table 2. Equilibrium Adsorption Capacity (qe, mg g^{-1}) at Different Temperatures

Compound	298 K	308 K	318 K
Diclofenac	1.82 ± 0.07	2.06 ± 0.09	2.31 ± 0.11
Carbamazepine	1.57 ± 0.05	1.78 ± 0.08	2.02 ± 0.09
Ibuprofen	1.34 ± 0.04	1.51 ± 0.06	1.73 ± 0.08

The adsorption capacity increased with temperature for all compounds, suggesting an endothermic adsorption process. Diclofenac showed the highest adsorption affinity, followed by carbamazepine and ibuprofen. This trend may be associated with differences in molecular structure, hydrophobicity, and ionization behavior.

4.2 Distribution Coefficients

The distribution coefficient (Kd) reflects the partitioning of pharmaceutical compounds between sediment and aqueous phases.

Table 3. Distribution Coefficients (Kd)

Compound	298 K	308 K	318 K
Diclofenac	52.4	67.8	84.5
Carbamazepine	46.2	58.7	72.1
Ibuprofen	39.8	49.4	60.3

Increasing Kd values with temperature indicate stronger adsorption interactions at higher temperatures. Diclofenac consistently exhibited the highest sediment affinity, suggesting lower mobility in aquatic systems compared with the other compounds.

Figure 2. Effect of Temperature on Adsorption Capacity

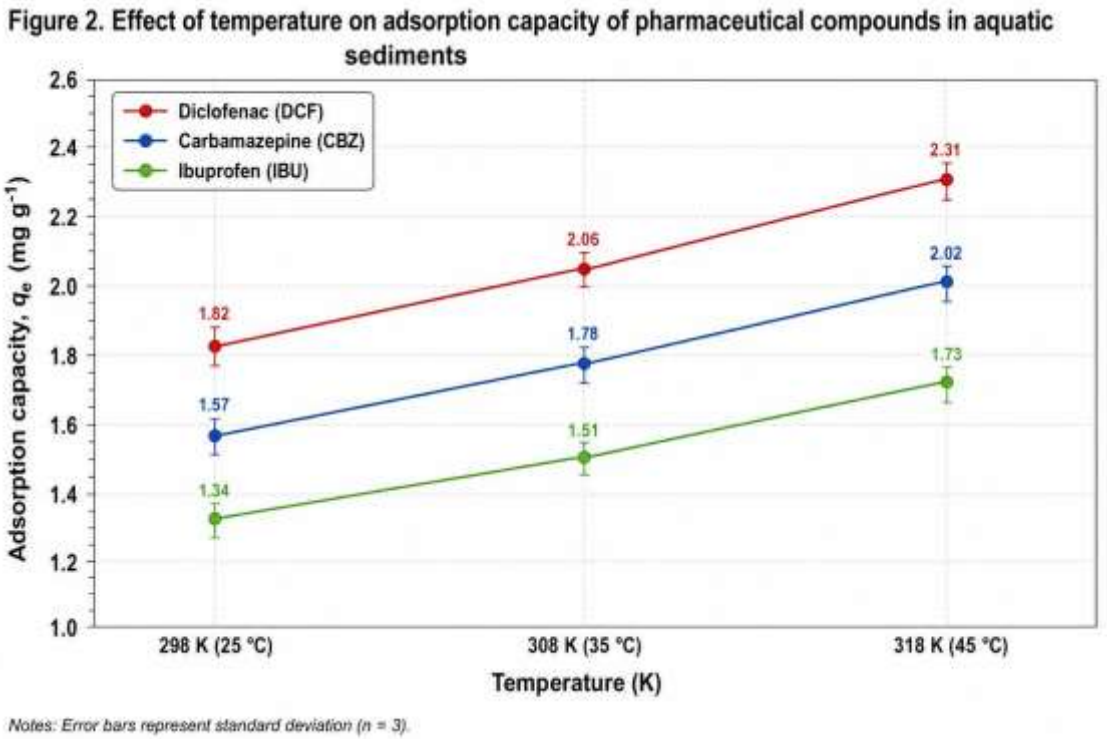


Figure 2 demonstrates a positive relationship between temperature and adsorption capacity for all pharmaceuticals investigated.

4.3 Thermodynamic Parameters

Thermodynamic parameters were calculated from Van't Hoff plots using adsorption equilibrium data obtained at different temperatures.

Table 4. Thermodynamic Parameters of Pharmaceutical Adsorption

Compound	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔG°298 (kJ mol^{-1})
Diclofenac	18.7	86.5	-7.08
Carbamazepine	15.3	74.2	-6.82
Ibuprofen	12.9	68.1	-6.14

The positive values of ΔH° indicate that adsorption was endothermic, meaning that higher temperatures favored contaminant uptake by sediments. Positive ΔS° values suggest increased randomness at the sediment–solution interface during adsorption. Negative ΔG° values confirm that the adsorption process occurred spontaneously under all experimental conditions (Ahmed et al., 2025; Rani & Kumar, 2025).

4.4 Correlation Analysis

Pearson correlation analysis revealed strong positive relationships between sediment organic matter content and adsorption coefficients.

Table 5. Correlation Between Sediment Properties and Kd Values

Variable	Kd
Organic Matter (%)	0.91**
TOC (%)	0.88**
Clay Content (%)	0.79*
pH	-0.42

*p < 0.05; **p < 0.01
Organic matter exhibited the strongest correlation with pharmaceutical adsorption, indicating that carbon-rich sediments serve as major sinks for pharmaceutical contaminants.

4.5 ANOVA Results

One-way ANOVA showed statistically significant differences in adsorption capacity among the three temperature levels.

Table 6. ANOVA Results for Temperature Effects on Adsorption

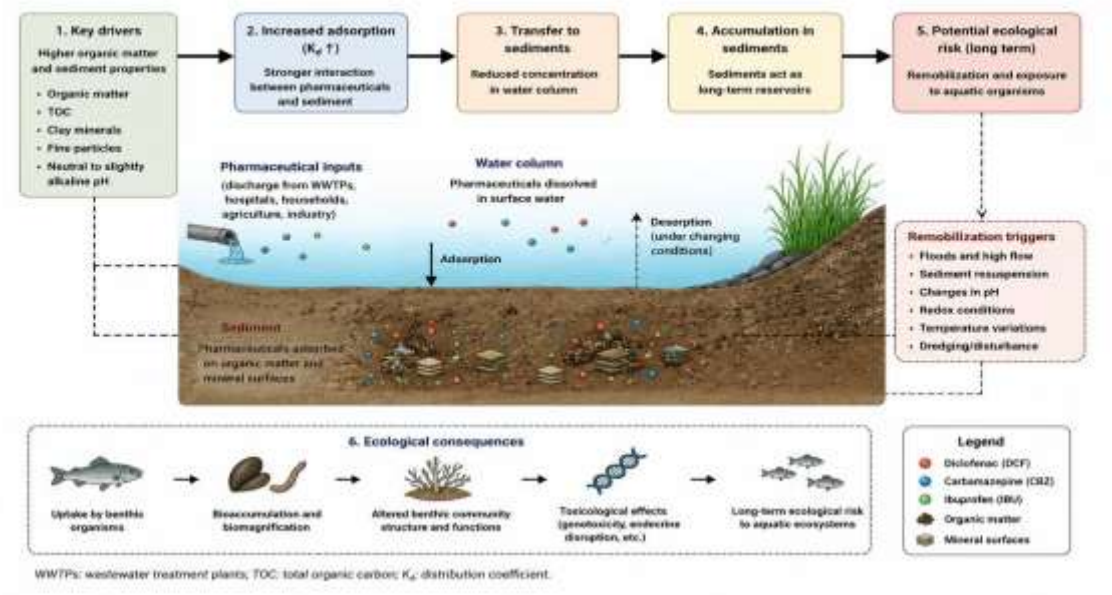
Compound	F-value	p-value
Diclofenac	14.52	<0.001
Carbamazepine	11.83	0.002
Ibuprofen	9.76	0.005

The results demonstrate that temperature significantly influenced adsorption performance for all compounds analyzed.

Environmental Risk Interpretation

The thermodynamic findings indicate that pharmaceutical retention in aquatic sediments is both spontaneous and increasingly favorable at higher temperatures. Diclofenac presented the highest adsorption affinity and therefore the greatest tendency to accumulate in sediments. Although strong adsorption can reduce immediate exposure in the water column, long-term sediment accumulation may create secondary contamination sources through remobilization events such as flooding, sediment disturbance, or changes in pH and redox conditions (Patel et al., 2025).
Overall, the results suggest that aquatic sediments function as important environmental reservoirs of pharmaceutical contaminants and should be considered in environmental monitoring and ecological risk assessment programs.

Figure 3. Environmental risk pathway associated with pharmaceutical adsorption in aquatic sediments



5. Discussion

The results indicate that adsorption of diclofenac, carbamazepine, and ibuprofen onto aquatic sediments was spontaneous, as shown by the negative ΔG° values. This behavior is consistent with previous studies reporting that pharmaceutical compounds can partition from the water column to sediments depending on molecular structure, sediment organic matter, and environmental conditions (Pereira et al., 2022; Ternes et al., 2004). Recent evidence also shows that sediment–water partitioning is essential for understanding the fate of pharmaceuticals in aquatic environments, especially in systems affected by wastewater discharges (Zhang et al., 2025).
The positive ΔH° values suggest that adsorption was endothermic, meaning that higher temperatures favored the retention of pharmaceuticals in sediments. This result may be explained by increased molecular diffusion and greater interaction between pharmaceutical molecules and active sediment sites at elevated temperatures. Similar thermodynamic behavior has been observed in adsorption studies involving pharmaceutical contaminants, where temperature increases improved adsorption capacity and modified equilibrium interactions (Ahmed et al., 2025; Rani & Kumar, 2025).
Diclofenac showed the highest adsorption capacity and Kd values, suggesting stronger affinity for the sediment phase than carbamazepine and ibuprofen. This may be associated with its aromatic structure and interaction with organic matter and mineral surfaces. However, earlier sediment studies have shown that adsorption trends may vary depending on sediment composition, especially organic carbon content and

grain size (Ternes et al., 2004). Therefore, diclofenac should be considered a compound with relevant sediment accumulation potential, particularly in organic-rich aquatic environments.

The strong positive correlations between organic matter, TOC, clay content, and Kd values confirm that sediment composition is a key factor controlling pharmaceutical adsorption. Organic matter may promote hydrophobic partitioning, while clay minerals provide charged surfaces that support electrostatic interactions and hydrogen bonding. These findings support recent reviews indicating that PPCPs are frequently detected in aquatic sediments and that sediment properties strongly influence their persistence, bioaccumulation potential, and ecological impact (Pereira et al., 2022; Sustainability, 2025).

From an environmental risk perspective, strong adsorption has a dual effect. On one hand, it may reduce the immediate concentration of pharmaceuticals in the water column, lowering direct exposure for planktonic and pelagic organisms. On the other hand, sediments may become long-term reservoirs of contamination, especially during resuspension, flooding, dredging, or changes in pH and redox conditions. This is important because recent environmental assessments emphasize that pharmaceutical residues in water and sediments can contribute to chronic ecological risk even at low concentrations (Patel et al., 2025; Danner et al., 2019).

Overall, the thermodynamic results suggest that adsorption is not only a removal mechanism from the water phase but also a process that can transfer pharmaceutical risk to the sediment compartment. Therefore, environmental risk assessment should not rely exclusively on dissolved concentrations. Instead, it should include sediment monitoring, adsorption coefficients, thermodynamic parameters, and remobilization scenarios to obtain a more realistic evaluation of pharmaceutical persistence and ecological exposure.

6. Conclusions

The adsorption of diclofenac, carbamazepine, and ibuprofen onto aquatic sediments was thermodynamically favorable and spontaneous, as confirmed by the negative $\Delta G°$ values. The positive $\Delta H°$ values indicated an endothermic process, while positive $\Delta S°$ values suggested increased disorder at the sediment–water interface during adsorption.

Diclofenac showed the highest adsorption affinity, followed by carbamazepine and ibuprofen. This pattern suggests that molecular structure, hydrophobicity, and interaction with organic matter strongly influence pharmaceutical retention in sediments.

Sediment organic matter, TOC, and clay content were strongly associated with higher adsorption coefficients. Therefore, organic-rich sediments may act as important sinks for pharmaceutical contaminants in aquatic ecosystems.

From an environmental risk perspective, adsorption can reduce pharmaceutical mobility in the water column but may increase long-term accumulation in sediments. Consequently, sediment compartments should be included in monitoring programs and ecological risk assessments.

Future studies should evaluate desorption, seasonal temperature variation, mixtures of pharmaceuticals, and sediment disturbance events to better predict contaminant remobilization and ecological exposure.

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