Self-Assembled Naphthylidene-Containing Schiff Base Anchored Polystyrene Nanocomposites Targeted for Selective Cu(II) Ion Removal from Wastewater

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ABSTRACT: Self-assembled composite adsorbents that combine the controllability of self-assembly with a mild operation process are promising for removal of heavy metal ions in wastewater. The design and preparation of functionalized composite adsorbent materials with multiple-site adsorption ability remain the most attractive in effectively removing heavy metal ions. Inspired by the macroporous structure of charged polystyrene (PS) resin and chelation of Schiff bases with heavy metal ions, smart composite adsorbents are constructed based on the combination and synergistic effect of multiple hydrophobic, π−π stacking, and electrostatic noncovalent interactions between polystyrene resin and naphthylidene-containing Schiff base (NSB). The resulting hybrid nanomaterials (PS-NSB) have uniform porous structures and well-defined and multiple target sites. These properties promote diffusion of the target ion, increase the binding site, and enhance the removal efficacy. This study offers a new strategy to harness a self-assembled Schiff base with integrated flexibility and multifunctions to enhance target metal ion specific binding and removal effects, highlighting opportunities to develop smart composite adsorbents.

1. INTRODUCTION

Among the many water pollutions, heavy metal pollution accounts for a considerable proportion. Heavy metal pollution is easy to be enriched and expanded in the biological chain, and it poses a serious threat to public safety even at trace concentrations. Therefore, the problem of heavy metal pollution in water has seriously jeopardized the ecological environment and human life and health.1,2 At present, the methods for treating heavy metals are adsorption, photocatalytic degradation, chemical precipitation, ion exchange, electrochemistry, membrane separation, and so on.3−7 Adsorption mainly uses adsorption materials with high specific surface area or special functional groups to adsorb heavy metal ions in wastewater. As a traditional heavy metal wastewater treatment method, the adsorption method has the advantages of simple operation, high efficiency, low energy consumption, no secondary pollution, and low investment cost and is considered as the most promising method for removing heavy metals from wastewater.8−11 The research method for the treatment of heavy metal ions by adsorption is to prepare functional materials with high specific surface area or functional groups, which have high adsorption capacity and the ability of rapid adsorption and balance. However, commercial materials as adsorbents not only lead to unspecified forces but also restrict selectivity against target heavy metals and thus the removal performance of the heavy contamination. The development of new organic functional materials is also a hotspot in current water treatment research. By synthesizing functional materials, modifying and grafting existing materials, or giving them new groups and new functions, the resulting materials have the capability of chemical adsorption and specific chelation with heavy metal ions in water, so as to remove heavy metal ions. In light of this, constructing composite adsorbents, which synergize multiple interaction capability and superior selectivity, would be highly imperative for promoting sewage treatment.

Although copper is an essential trace nutrient for living organisms, it can still have adverse public health effects when ingested in large doses.12 Therefore, it still remains a formidable challenge to design and create high efficient adsorbing materials for selective removal of copper. Polystyrene (PS) resin is a promising commercial absorbent candidate that has shown porosity, high specific surface area, and long service life with superior reusability.13,14 Nevertheless, the direct application of polystyrene resin is hindered by its unspecified interaction forces due to the fact that it mainly adsorbs hydrophobic substances from aqueous solution by van der Waals forces and adsorbs heavy metal ions by electrostatic
interaction. Various strategies such as encapsulation of an organic small molecule to resin have been explored to resolve these problems.\textsuperscript{15} For example, immobilization of polyethylene-imine nanoclusters onto a cation exchange resin through self-cross-linking has been explored to improve the adsorption ability of Cu(II).\textsuperscript{16} A Schiff base is a kind of compound with an imine (–C=\(\text{N}\)) structure formed by the reaction of active carbonyl and amino compounds in the molecule and can form stable complexes with transition metal elements.\textsuperscript{17,18} Schiff base compounds and their metal complex compounds have wide applications in medicine, catalysis, and analytical chemistry.\textsuperscript{19–21} Schiff bases, especially some aromatic Schiff bases, tend to form stable complexes with copper due to the presence of –C=\(\text{N}\) double bonds and –OH group of the aromatic ring.\textsuperscript{22} Currently, increasing composite base on Schiff base molecules has been obtained for selective removal of trace heavy ion pollutants.\textsuperscript{23,24}

Herein, we report a novel noncovalent self-assembly strategy based on the combination of sulfonate group charged polystyrene resin and naphthylidene-containing Schiff base (NSB) to design and engineer composite nanoadsorbents for selective removal of Cu(II) (Figure 1). In the resulting complex absorbents, the naphthylidene-containing Schiff base is inserted into the polystyrene both through \(\pi–\pi\) stacking between aromatic ring and naphthalene ring and electrostatic force between sulfonate groups and the protonated amino group. Moreover, Schiff bases have shown flexibility and versatility in designing self-assembled nanomaterials for Cu(II) adsorption due to double coordination interactions between –C=\(\text{N}\) groups and –OH groups with copper ions. Therefore, the PS-NSB composite demonstrates high absorption efficiency along with excellent selectivity for the copper ion. Additionally, the absorption efficiency of the nanoagents was readily manipulated by modulating the solution pH values, ionic strength, and temperature. Meanwhile, the experimental results of the adsorption equilibrium from Cu(II) solution correlated well with the kinetic equation. Taken together, the combined multiple noncovalent interactions simultaneously increase selectivity for copper, leading to enhanced absorption efficiency.

![Figure 1. Illustration of the preparation of PS-NSB nanocomposite based on the strategy of noncovalent assembly by using Schiff base and sulfonate group charged polystyrene resin as building blocks for preferential adsorption of Cu(II).](image)

2. RESULTS AND DISCUSSION

2.1. Characterization of PS-NSB and Metal Composites. The polystyrene resin (PS) is an excellent commercial absorption material due to its macroporous structure, high specific surface area, good mechanical strength, low fluid resistance, fast exchange speed, and strong pollution resistance.\textsuperscript{3,14} Because of these unique advantages, polystyrene resin shows potential in environmental protection such as removal of heavy metals from sewage. It has adsorption capacity due to van der Waals force, and it has screening performance because of its network structure and high specific surface area. The initial PS bead was present as a spherical bead with diameters of 400–600 \(\mu\)m and well characterized in our previous reports.\textsuperscript{25–27} On the other hand, Schiff base molecules have good complexation for most transition metal ions since the lone pair electrons contained in nitrogen atoms and carbon–nitrogen double bonds can be used as electron donors to coordinate with most metal ions to form stable complexes.\textsuperscript{17,18} The introduction of a naphthalene ring with a planar structure, large volume, and strong rigidity increases the \(\pi\) conjugate of Schiff base molecules, thereby facilitating assembly with the host resin material. When chelated with a metal ion, the phenolic hydroxyl oxygen atom on the naphthalene ring of the Schiff base is also involved in coordination and can be complexed with a plurality of transition metal ions to form a more stable coordinated chelate.\textsuperscript{22}

Figure 2a–c,g–i shows the SEM photographs of the modified PS-NSB resin before and after chelation with metal ions. It can be seen that the surface of the PS-NSB resin is rough and shows a macroporous morphology, indicating that the functionalization of NSB does not affect its surface morphology, which may be due to the planar rigid structure of the naphthalene ring in the Schiff base molecule. This macroporous morphology facilitates the mass transfer and diffusion of the adsorption process. Furthermore, the elemental Cu and Ca cross section distribution of PS-NSB shown in Figure 2d–f,j–l detected by SEM-EDS clearly demonstrated that Cu and Ca were embedded into PS-NSB resin and were homogeneously distributed within the composite resin. It can be interpreted that the electrostatic attraction of charged sulfonate groups of PS resin will facilitate the divalent metal cation to further diffuse into the internal region of PS. This mentioned that the Schiff base can chelate with metal ions through coordination interaction to form a stable metal complex. The uniform coverage of copper indicates that the distribution of Schiff base compounds is homogeneous, which again confirmed the assembly between Schiff base molecules and host materials. Atomic force microscopy (AFM) images presented in Figure 3 also reveal that these composite materials are macroporous structures, almost consistent with the SEM result. As shown in Figure 4, transmission electron microscopy (TEM) analysis disclosed that abundant nanoclusters within tens of nanometer size could be found in PS-NSB composites, which originated in random dispersion of the –C=\(\text{N}\)– group and –OH group on the NSB chain.

Figure 5 shows the FTIR spectra of NSB molecules and the resulting PS-NSB composite materials. The characteristic absorption peak at around 3400 cm\(^{-1}\) in PS-NSB significantly enhanced, which could be assigned to the stretching vibration of –OH groups that likely combined the phenol –OH with water. Peaks appearing at 2927 and 2848 cm\(^{-1}\) in PS-NSB were
assigned to the stretching vibration of flexible alkyl chains with −NH groups in the introduced ligands. In addition, it could be seen from the infrared spectrum that characteristic peaks of −C=N, C=O, and C=C appeared at 1634, 1280, and 1540 cm$^{-1}$ after the modification process. The above changes in the infrared absorption peaks indicate that the Schiff base groups have been successfully introduced into the inner space in resin beads. TG was performed to investigate the thermal properties...
of PS and PS-NSB from room temperature to 700 °C in a nitrogen atmosphere given in Figure 6. We can observe that all samples show apparent weight loss at nearly 100 °C, which can be attributed to the evaporation of water molecules inserted into the resin. With respect to PS resin, a sharp drop in weight appears at an elevated temperature (400−470 °C), indicating thermal degradation of the network structure of PS. Moreover, the introduction of Schiff base molecules slightly reduced the thermal stability of the composite resin, mainly because the presence of the strong hydrophobic naphthalene ring of the Schiff base ensured high thermal stability.28,29 Therefore, self-assembled naphthylidene-containing Schiff base anchored polystyrene nanocomposites could be applied for developing the absorbent of high thermal stability. However, after adsorption of bivalent copper ions, major losses in weight of the PS-NSB-Cu are found at 300 and 450 °C, which seems that the coordination bond of the copper coordinate chelate breaks at lower temperature.

2.2. Adsorption Performances of PS and PS-NSB Nanocomposites. It can be clearly seen from Figure 7 that a pH value increase does not significantly enhance the adsorption effect and the adsorption efficiency is poor (<30%) for the PS resin alone. However, the adsorption of Cu(II) by PS-NSB resin is greatly affected by the pH value of the solution. Some basic reactions involved in the solution are as follows:

\[
\begin{align*}
\text{R-SO}_3\text{Na} + \text{H}^+ & \rightarrow \text{R-SO}_3\text{H} + \text{Na}^+ \\
2\text{R-SO}_3\text{H} + \text{Cu}^{2+} & \rightarrow (\text{R-SO}_3\text{Cu})_2 + 2\text{H}^+ \\
\text{Ar-C=N} + \text{Cu}^{2+} & \rightarrow \text{Ar-C=N-Cu} \\
\text{Ar-C=N} + 2\text{H}^+ & \rightarrow \text{Ar-C=N-H} + \text{H}_2
\end{align*}
\]

Under strong acidic conditions (pH < 3), H+ and Cu(II) will compete for the site of the absorbent surface, and at the same time, the protonation of the sulfonate of PS and −C=N...
group in Schiff base will also be unfavorable for the adsorption of Cu(II) (reactions 2 and 3), so the adsorption amount is lower. When the pH value is increased to 3–4, the deprotonation of the sulfonate group and $\text{C}=\text{N}$ group is enhanced and conducive to binding and chelating with copper ions, thus promoting adsorption of copper ions. When the pH value continues to increase to around 6, the addition of hydroxyl oxygen can enable formation of a more stable coordinate chelate with the $\text{C}=\text{N}$ group (reactions 3 and 4). Notably, the Cu(II) absorption performance by the Schiff base with longer ethylenediamine spacers was remarkable, indicating the self-assembly effect on the fabrication of the composite adsorbent, which was due to the electrostatic driving force of negatively charged sulfonate of PS and deprotonated ethylenediamine of the Schiff base. In more alkaline conditions, precipitation of copper hydroxide occurs simultaneously with adsorption of divalent copper ions. Therefore, the optimum pH value obtained from the above is 5.5–6.5 and adjusted to this range in subsequent adsorption experiments.

In actual production, the types of heavy metal ions in wastewater are often various, so the influence of the competitive ions especially alkaline earth ions of the solution on the adsorption performance must also be investigated. Hence, it is crucial to assess the capture tendency of PS-NSB toward the target ion in the presence of other competitive ions. The influences of divalent competitive ions on divalent copper ion removal performance of the obtained PS-NSB hybrid adsorbent were also measured, with the original PS as control. Experimental data from Figure 8a,b shows that the removal rate of Cu(II) by PS-NSB decreases with the increase of the proportion of competitive ions; when the molar ratio is increased to 1:64, the removal rate only decreases from 100 to 60%, which indicates that PS-NSB still has a good Cu(II) cleaning effect in the presence of high concentrations of competing ions than PS resin. The effect of ionic strength on the adsorption effect of specific metal ions mainly includes the influence of the existence of heavy metal ions and the adsorption sites on the adsorbent surface. In order to eliminate the interference of ionic strength, we also measured the influences of the monovalent sodium ion on copper ion removal performance of the obtained PS-NSB hybrid adsorbent. Figure 8c reveals that adsorption of PS-NSB materials is insensitive to lower ionic strength, probably due to the formation of inner surface complexes of divalent heavy metal cations with carbon–nitrogen double bonds and the phenolic hydroxyl oxygen atom on the Schiff base molecule, thus confirming the self-assembly of PS and Schiff base. However, at high ionic strength, the adsorption capacity of heavy metal ions slightly decreases with increasing ionic strength. According to the electrostatic double layer theory, when the ionic strength of the solution increases, the double-layer static electricity of the adsorbent is compressed and the repulsion is weakened, which may cause the adsorbent ions to aggregate and change the total adsorption sites of the adsorbent, thereby changing its adsorption effect of heavy metal ions. This is because sulfonate groups of PS resin can sequestrate divalent copper ions via nonspecific electrostatic forces and other competitive ions would compete for the active sorption sites, while carbon–nitrogen double bonds and the phenolic hydroxyl oxygen atom of the Schiff base are considered to fix Cu(II) by specific coordination complexion. Therefore, when the concentration of divalent competing ions in the water is high, PS-NSB can still meet the demand for Cu(II) removal.

Moreover, temperature is one of the important environmental factors affecting adsorption. It has different effects on a series of chemical and physical processes such as adsorption–desorption, precipitation–dissolution, and oxidation–reduction of heavy metals. Therefore, changes in temperature may also result in changes in the amount of adsorption. We also tested the adsorption curve of PS-NSB versus the absorption temperature. As depicted in the curves of Figure 8d, the adsorption rate of the PS-NpN2 nanocomposite increased with the increment of the solution temperature, mainly because the increase of temperature increases the number of active sites of the adsorbent and increases the diffusion rate of heavy metal ions from solution into the interior of PS-NSB. It also shows that the adsorption of Cu(II) on PS-NSB is an endothermic
process and high temperature is more favorable for the adsorption reaction.

2.3. Adsorption Kinetics of PS and PS-NSB Nanocomposites. The adsorption is an important factor affecting the adsorption of heavy metal ions by the adsorbent. As the adsorption time is prolonged, the treatment cycle is prolonged and the economic benefits are affected. The macroporous structure of the resin material and the large specific surface area will help to increase the rate of adsorption of heavy metal ions, greatly reducing the time required to reach equilibrium. It was found from Figure 9a that the adsorption of Cu(II) by PS resin reached dynamic equilibrium for more than 250 min. In the initial adsorption stage (0–20 min), the adsorption of Cu(II) by PS-NSB increased significantly. After reaching a certain period of time (about 60 min), the adsorption rate of composites gradually slowed down and finally reached equilibrium. This is mainly due to the fact that, in the early stage of adsorption, a large number of adsorption sites on the surface of PS-NSB composite materials have not been occupied and Cu(II) is rapidly adsorbed; as the adsorption process progresses, the surface of PS-NSB materials is occupied by more and more Cu(II). Due to the repulsive force between the Cu(II) and the reduction of the adsorption site, the remaining Cu(II) is not easily adsorbed, and therefore, the adsorption rate is slowed down until the adsorption equilibrium is reached. In contrast, the adsorption rate of composites is much faster than that of PS resin, indicating that PS-NSB materials have good application prospects. In addition, in order to further study the adsorption mechanism of PS resin and PS-NSB resin, the kinetic adsorption process of Cu(II) was simulated by the pseudo-second-order model, the adsorption process conforms to the pseudo-second-order kinetic adsorption model, indicating that the adsorption of Cu(II) on the resin is controlled by the internal diffusion process (physical adsorption) and the surface reaction process (chemical adsorption). This is because the resin is a sphere filled with pores on the surface and the Schiff base group inside the PS has a good chelation effect on Cu(II), so the adsorption process has both chemical adsorption and physical adsorption.

Adsorption capacity and desorption capacity are two optimal parameters for evaluating the adsorption effect of the adsorbent. The ideal adsorbent should not only have high adsorption performance but should also be recyclable, both of which can be important criteria to measure the practical application of the adsorbent. We used HCl–NaCl solution to desorb the PS-NSB composite after Cu(II) adsorption. The results in Figure 10 show that the removal rate of Cu(II) by PS-NSB decreases with the increase of elution readsorption times, but after five adsorption–desorption cycles, the removal rate is still as high as 90%, compared with the first adsorption. This shows that the PS-NSB composite showed excellent reusability after five cycles. Therefore, it has broad application prospects and expands new ideas for the research of similar self-assembled nanocomposites in the future.

Table 1. Kinetic Parameters of PS, PS-NpN1, and PS-NpN2 Nanocomposites for Cu(II) Removal at 298 K

| Model                     | $R^2$ | $q_e$ (mg/g) | $K_1$ (min$^{-1}$) |
|---------------------------|-------|--------------|--------------------|
| pseudo-first-order model  |       |              |                    |
| PS                        | 0.98539 | 19.62       | 4.32 x 10$^{-3}$   |
| PS-NpN1                   | 0.97137 | 24.18       | 2.05 x 10$^{-2}$   |
| PS-NpN2                   | 0.97284 | 24.02       | 3.14 x 10$^{-2}$   |
| pseudo-second-order model |       |              |                    |
| PS                        | 0.99757 | 19.79       | 1.2 x 10$^{-4}$    |
| PS-NpN1                   | 0.99846 | 24.87       | 4.06 x 10$^{-3}$   |
| PS-NpN2                   | 0.99951 | 24.57       | 9.01 x 10$^{-3}$   |

*Experimental data from Figure 9.

3. CONCLUSIONS

In summary, we developed new composite materials through self-assembled naphthylidene-containing Schiff base anchored polystyrene nanocomposites driven by electrostatic and π–π stacking interactions as adsorbents for Cu(II) removal. These composite adsorbents possess large surface area, developed internal microporous structures, excellent stability against high temperature, and efficient selectivity, thus enabling diffusion of...
the target ion and enhancing the removal efficacy. Meanwhile, PS-NSB composites demonstrate excellent cyclic adsorption properties and can maintain good adsorption capacity after repeated use. Present interesting research work offers versatility in the preparation of effective adsorbent materials for heavy ion removal in wastewater treatment.

4. EXPERIMENTAL SECTION

4.1. Materials and Instruments. Sulfonate group charged polystyrene resin (cross-linking degree of ~8%) was obtained from Jiangsu Nanda Environmental Technology Ltd. Before being employed, the bead particles were sieved (0.4–0.6 mm) and subjected to extraction with ethanol in a Soxhlet apparatus to remove the residue impurities. Finally, the resulting PS beads were dried under vacuum at 358 K for 24 h. In addition, we have previously synthesized two different lengths of ethylenediamine spacer naphthylidene-containing Schiff base (NSB) units (Figure 1), abbreviated as N₄N₁ and N₄N₂. The metal ion used was the nitric acid solution of metal and obtained from Beijing Chemical Co. Ltd. (Beijing, China). The solvents used were purchased from Beijing Chemical Co. Ltd. (Beijing, China) without further purification.

4.2. Preparation of the PS-NSB Nanocomposites. The PS was purified to remove impurities: First, hydrochloric acid solution with a pH of 2 was prepared. A certain amount of PS was immersed in hydrochloric solution and stirred at room temperature for 10 h. After standing, the solution was washed to the neutral state with distilled water. Then the resulting PS was treated with sodium hydroxide (mass fraction 5%) by the same treatment process and dried at 40 °C under vacuum to a constant weight before further use. Two different lengths of the ethylenediamine spacer naphthylidene-containing Schiff base (NSB) molecule (Figure 1), abbreviated as N₄N₁ and N₄N₂, were reported in our previous work. In a typical self-assembly method, 2 g of the prepared Schiff base containing the naphthylene group was dissolved in 100 mL of ethanol solution overnight until completely dissolved into a yellow solution. Then 10.0 g of swelled PS resin was added into the obtained ethanol solution containing Schiff base molecules. Under stirring at a constant temperature overnight, the PS resin and the naphthylidene-containing Schiff base molecule self-assembled driven by electrostatic force and π–π stacking force. After incubation, the PS showed a yellow color, indicating the formation of nanocomposites. After the reaction was complete, the product was separated by suction filtration, repeatedly washed with absolute ethanol and deionized water to remove the residual reactants and inorganic salts, making the pH of washing solution neutral, and dried at 60 °C under vacuum to a constant weight to obtain microspheres before further use.

4.3. Adsorption Performance Tests. Static adsorption kinetic experiment: PS-NSB (0.50 g) and PS (0.50 g) were placed in 500 mL of copper nitrate solution (concentration of Cu²⁺ is 15 mg/L) and then oscillated at a rate of 600 rpm in a constant temperature shaker at 298 K. Removing 1 mL of the solution at regular intervals, the concentration of copper ions in the sample was determined, and the adsorption removal efficiency was calculated. Finally, the kinetic curves of adsorption time and removal rate were obtained.

Effect of pH on adsorption: 10 portions of PS-NSB (0.05 g) and PS (0.05 g) were accurately weighed and placed separately in a 150 mL conical flask. 50 mL of copper nitrate solution (concentration of Cu²⁺ is 15 mg/L) was added to each conical flask, and the pH value of the solution was adjusted to 1–7 (equal spacing) by HNO₃ and NaOH. Then the sample was placed in a constant temperature oscillator with a rotational speed of 600 rpm. After 24 h of constant temperature oscillation, the sample was taken out and the equilibrium Cu²⁺ concentration and the corresponding pH value were determined.

Competitive adsorption experiment: 50 mL Ca²⁺/Cu²⁺ solutions with molar ratios of 0, 8, 16, 32, and 64 (Cu²⁺: 15 mg/L) were put separately in 150 mL conical flasks. Then PS-NSB (0.05 g) and PS (0.05 g) were added in the corresponding conical flask. The sample was placed in a constant temperature (298 K) water bath shaker with a rotating speed of 600 rpm, and the concentration of Cu²⁺ in the solution at equilibrium was determined after being shaken for 24 h. In the same way, the competitive ions were changed into Mg²⁺ or Na⁺, and the concentration of Cu²⁺ in the solution was determined after the experiment.

Effect of temperature on adsorption: PS-NSB (0.05 g) and PS (0.05 g) were placed separately in 150 mL conical flasks. 50 mL of copper nitrate solution (concentration of Cu²⁺ is 15 mg/L) was added to each conical flask and then oscillated at a rate of 600 rpm for a certain period of time in a constant temperature shaker at different temperatures (25, 45, 65 °C). After the adsorption was complete, a certain amount of solution was taken, and the concentration of Cu(II) was measured by a spectrophotometer.

4.4. Characterization. Infrared spectroscopy (FTIR) was determined by an FTIR Fourier infrared spectrometer (Thermo Nicolet Corporation, Madison, WI, USA) by the KBr tablet method in the wavenumber range of 3600–500 cm⁻¹. Scanning electron microscope images were obtained by a Field Emission Gun FEI QUANTA FEG 250 (FEI Corporation, Hillsboro, OR, USA) with energy dispersive spectroscopy (EDS) for qualitative chemical analysis. Morphology characterizations of the materials were also obtained on air-dried carbon-coated copper grids by using a transmission electron microscope (TEM) Hitachi HT7700 (Ibaraki, Japan) and a Nanoscope model Multimode 8 Scanning Probe Microscope (Veeco Instruments, USA). The pH of the solution was measured by a HANNA pH meter. The metal ion concentration was determined by a Shimadzu AA-6800 atomic absorption/emission spectrometer. Thermogravimetry-differential scanning calorimetry (TG-DSC) data were recorded with a NETZSCH STA 409 PC Luxx Simultaneous thermal analyzer (Netzsch Instruments Manufacturing Co., Ltd., Germany) under a nitrogen atmosphere. The experiment was carried out in a G-25 model incubator shaker with a thermostat.

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Notes
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