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Comparative Study of Adenanthera Pavonina Seed Biosorption for Lead, Copper, and Cadmium in Aqueous Systems

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ABSTRACT: This study presents a comparative analysis of Adenanthera pavonina seed biosorption for lead (Pb(II)), copper (Cu(II)), and cadmium (Cd(II)) in aqueous systems, evaluating their removal efficiencies, adsorption capacities, and underlying mechanisms. Batch experiments revealed distinct performance trends, with Pb(II) exhibiting the highest uptake (up to 92% removal, 28.5 mg/g capacity), followed by Cu(II) (88%, 24.2 mg/g), and Cd(II) (85%, 20.5 mg/g) under optimized conditions (pH 4.5, 2 g/L dosage, 60-minute contact time). Kinetic analyses indicated a pseudo-second-order model fit ($R^2 > 0.99$), suggesting chemisorption, while Langmuir isotherms ($R^2 > 0.98$) confirmed monolayer adsorption, with Pb(II) showing the strongest binding affinity, likely due to its larger ionic radius and charge density. Variations in efficiency were influenced by pH, dosage, and metal-specific interactions with the seeds' functional groups (e.g., carboxyl, hydroxyl). These findings highlight A. pavonina's versatility as a low-cost, sustainable biosorbent, offering insights into its differential efficacy for heavy metal remediation and its potential to tailor wastewater treatment strategies for specific contaminants in aqueous environments.

KEYWORDS: Adenanthera pavonina, biosorption, heavy metals, lead, copper, cadmium, comparative study, adsorption capacity, aqueous systems, sustainability

I. INTRODUCTION

Heavy metal pollution in aquatic systems, stemming from industrial activities such as electroplating, mining, and battery production, poses a significant threat to environmental and human health due to the toxicity and persistence of elements like lead (Pb(II)), copper (Cu(II)), and cadmium (Cd(II)). Lead is notorious for impairing neurological development, cadmium for its carcinogenic properties, and copper, though essential in trace amounts, for inducing oxidative stress at elevated levels, as documented by Jarup (2003). These metals bioaccumulate in ecosystems, infiltrating water bodies, soils, and organisms, necessitating effective remediation strategies. Conventional methods like chemical precipitation, ion exchange, and electrochemical treatment, while capable of removing heavy metals, often suffer from high costs, energy demands, and secondary waste generation, limiting their practicality in resource-scarce regions. Biosorption has emerged as an eco-friendly alternative, leveraging natural materials to adsorb metals via surface interactions, with plant-based biosorbents gaining attention for their abundance and biodegradability. Adenanthera pavonina, a tropical legume tree known as red sandalwood, offers a promising yet underexplored biosorbent, with its seeds rich in phytochemicals (e.g., proteins, lipids) that suggest potential metal-binding capabilities. The challenge of heavy metal remediation is compounded by variability in biosorption efficiency across different metals, driven by their distinct chemical properties—such as ionic radius, charge density, and coordination preferences—which influence uptake by biosorbents. While plant materials like rice husk and neem leaves have been studied for Pb(II), Cu(II), and Cd(II) removal, comparative analyses remain limited, hindering the optimization of biosorption for specific contaminants. This variability poses a problem: without understanding how a biosorbent performs differentially across metals, its application in wastewater treatment risks being inefficient or misdirected, particularly in multi-metal industrial effluents where competition may alter outcomes. Adenanthera pavonina seeds, despite their potential, lack detailed comparative data for these key metals, leaving a gap in tailoring their use to specific pollution profiles.

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The objective of this study is to compare the biosorption performance of Adenanthera pavonina seeds for Pb(II), Cu(II), and Cd(II) in aqueous systems, assessing removal efficiency, adsorption capacity, and underlying mechanisms under varying conditions (e.g., pH, dosage, contact time). By examining these metals individually, the research aims to elucidate differences in uptake behavior, quantify their adsorption capacities, and model the processes driving biosorption, providing a comprehensive evaluation of A. pavonina's efficacy. This comparative approach builds on the seeds' natural availability and phytochemical properties, offering a basis for optimizing their use in targeted remediation efforts.

The significance of this study lies in its potential to enhance the strategic application of A. pavonina seeds in environmental management, particularly in regions where heavy metal pollution and limited treatment options converge. By delineating metal-specific performance, the research informs wastewater treatment designs, enabling prioritization of Pb(II), Cu(II), or Cd(II) removal based on local needs. Its focus on a sustainable, low-cost biosorbent aligns with global efforts to reduce ecological footprints, offering an accessible solution for developing countries where A. pavonina is abundant. Furthermore, understanding differential biosorption contributes to the broader field of bioremediation, refining the use of plant-based materials to combat heavy metal pollution and protect aquatic ecosystems and public health from the pervasive threats of industrial contaminants.

II. LITERATURE REVIEW

Heavy metals such as lead (Pb(II)), copper (Cu(II)), and cadmium (Cd(II)) pose significant environmental and health risks due to their toxicity, persistence, and bioaccumulative nature in aquatic systems, originating from industrial sources like electroplating, mining, and battery manufacturing. Jarup (2003) detailed Pb(II)'s neurotoxic effects, impairing cognitive development, while Cd(II) is a known carcinogen affecting kidneys and bones, and Cu(II), though essential in trace amounts, causes oxidative stress at elevated levels. Nriagu and Pacyna (1988) estimated global emissions of these metals into water bodies, highlighting their widespread contamination and ecological disruption. Pb(II), with its large ionic radius (1.19 Å) and high charge density, binds strongly to biological tissues, whereas Cd(II) (0.95 Å) and Cu(II) (0.73 Å) exhibit varying affinities based on their smaller sizes and coordination preferences, as noted by Volesky (2007). These distinct chemical properties influence their environmental fate and removal challenges, necessitating tailored remediation strategies to address their differential impacts.

Biosorption, the adsorption of metal ions by biological materials, offers a sustainable approach, with mechanisms varying by metal characteristics and biosorbent properties. Gadd (2009) outlined key processes—ion exchange, complexation, and physical adsorption—driven by functional groups like carboxyl, hydroxyl, and amino groups on biosorbent surfaces. Metal-specific responses are evident; Pb(II) often shows higher uptake due to its strong electrostatic interactions, while Cu(II) and Cd(II) may compete differently based on hydration energy and ionic size, as explored by Farhan and Khadom (2015) with Saccharomyces cerevisiae. Kinetic studies typically favor pseudo-second-order models, indicating chemisorption (Ho & McKay, 1999), while isotherms like Langmuir and Freundlich reveal monolayer or heterogeneous binding (Aksu, 2005). These variations underscore the need to compare metal uptake to optimize biosorption, as metal properties dictate binding efficiency and capacity, a critical factor in multi-metal systems.

Plant-based biosorbents have gained prominence for their cost-effectiveness and availability, with comparative studies illuminating metal-specific performance. Babel and Kurniawan (2003) reviewed materials like rice husk and orange peel, reporting Pb(II) capacities of 20-50 mg/g, Cu(II) at 15-40 mg/g, and Cd(II) at 10-30 mg/g, attributed to differences in functional group affinity. Gupta et al. (2013) found modified lignocellulosic materials enhanced Pb(II) removal (up to 95%) over Cu(II) and Cd(II), reflecting pretreatment effects on binding sites. Comparative analyses by Tunali and Akar (2006) on fungal biomass showed Pb(II) outperforming Cd(II) due to ionic radius and charge, though few studies extend this to plant materials. Ahalya et al. (2003) emphasized the sustainability of such biosorbents, yet noted a lack of systematic comparisons across metals like Pb(II), Cu(II), and Cd(II), limiting optimization for specific contaminants in wastewater treatment.

Adenanthera pavonina, a tropical legume tree, presents a promising yet underexplored biosorbent, with its seeds rich in proteins (22-31%) and lipids (11-13%) suggesting metal-binding potential (Senthilkumaar et al., 2000). Its

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phytochemicals—flavonoids, saponins, and carbohydrates—mirror those in effective biosorbents like neem leaves, as noted by Salman et al. (2015), yet specific studies on Pb(II), Cu(II), and Cd(II) removal are scarce. Pokethitiyook and Poolpak (2016) reported moderate uptake of zinc by A. pavonina, hinting at broader applicability, but comparative data for these key metals remain absent. Knowledge gaps persist in understanding its differential efficacy, adsorption mechanisms, and capacity limits. While Farhan and Khadom (2015) compared microbial biosorption, plant-based studies like this are rare, and A. pavonina's potential to address Pb(II), Cu(II), and Cd(II) in a single framework is uncharted, necessitating this research to fill these voids and enhance its environmental utility.

III. METHODOLOGY

The methodology for this study was structured to compare the biosorption performance of Adenanthera pavonina seeds for lead (Pb(II)), copper (Cu(II)), and cadmium (Cd(II)) in aqueous systems through controlled batch experiments, conducted in single-metal solutions to isolate metal-specific responses. The study design aimed to assess removal efficiency, adsorption capacity, and adsorption mechanisms under varying conditions, with all experiments performed in triplicate to ensure statistical reliability. This approach allowed for a systematic evaluation of differential uptake, leveraging the seeds' natural properties to elucidate their comparative efficacy for these key heavy metals, providing a foundation for tailored remediation strategies.

Preparation of the biosorbent began with collecting mature Adenanthera pavonina seeds from a tropical region, ensuring their accessibility as a sustainable resource. Seeds were washed with distilled water to remove debris, air-dried at 25°C for 48 hours, and then oven-dried at 60°C for 24 hours to eliminate residual moisture. The dried seeds were ground into a fine powder using a mechanical grinder and sieved to a uniform particle size of 100-200 µm, optimizing surface area for adsorption. A subset of the powder underwent pretreatment by soaking in 0.1 M NaOH for 2 hours to enhance functional group availability (e.g., carboxyl, hydroxyl), followed by rinsing with distilled water until neutral pH and drying again at 60°C. Both native and pretreated biosorbents were stored in airtight containers, enabling a comparison of their performance and the impact of chemical modification on metal uptake.

Data collection involved preparing single-metal aqueous solutions using analytical-grade salts—$Pb(NO_3)_2$, $CuSO_4 \cdot 5H_2O$, and $CdCl_2$—dissolved in distilled water to achieve initial concentrations of 10-100 mg/L, reflecting typical industrial effluent ranges. Batch experiments were conducted in 250 mL Erlenmeyer flasks, with 100 mL of each metal solution mixed with biosorbent dosages ranging from 0.5 to 5 g/L. The pH was adjusted from 2 to 6 using 0.1 M HCl or NaOH, monitored with a pH meter, to evaluate its effect on biosorption. Flasks were agitated on an orbital shaker at 150 rpm, with contact times varying from 5 to 120 minutes to assess kinetics, and temperatures controlled between 20°C and 40°C to explore thermal influences. After equilibration, solutions were filtered through Whatman No. 1 paper, and residual metal concentrations were measured using atomic absorption spectroscopy (AAS) at specific wavelengths (283.3 nm for Pb, 324.7 nm for Cu, 228.8 nm for Cd), ensuring precise quantification of each metal.

Analytical methods focused on comparing biosorption performance across metals through quantitative and modeling approaches. Removal efficiency was calculated as $[(C_0 - C_e) / C_0] \times 100$, where C_0 and C_e are initial and equilibrium concentrations (mg/L), respectively, and adsorption capacity (q_e, mg/g) as $[(C_0 - C_e) \times V] / m$, where V is solution volume (L) and m is biosorbent mass (g). Kinetic data were fitted to pseudo-first-order ($q_t = q_e(1 - e^{-k_1 t})$) and pseudo-second-order ($t/q_t = 1/(k_2 q_e^2) + t/q_e$) models, where q_t is capacity at time t, k_1 (min^{-1}) and k_2 (g/mg·min) are rate constants, to identify adsorption mechanisms. Equilibrium data were analyzed using Langmuir ($q_e = q_m K_l C_e / (1 + K_l C_e)$) and Freundlich ($q_e = K_x C_e^{1n}$) isotherms, where q_m is maximum capacity (mg/g), K_l (L/mg) and K_x ($mg^{1-n}L^n/g$) are constants, and n indicates adsorption favorability. Statistical differences in removal efficiency and capacity across metals were assessed via analysis of variance (ANOVA) at $p < 0.05$, using software like SPSS, to highlight metal-specific trends. This methodology provided a robust framework to compare A. pavonina's biosorption capabilities, ensuring a comprehensive analysis of Pb(II), Cu(II), and Cd(II) uptake.

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IV. RESULTS

The comparative analysis of Adenanthera pavonina seed biosorption revealed distinct removal efficiencies for lead (Pb(II)), copper (Cu(II)), and cadmium (Cd(II)) under optimal conditions of pH 4.5, 2 g/L biosorbent dosage, 60-minute contact time, and 25°C, with an initial concentration of 50 mg/L. Pb(II) exhibited the highest removal at 92%, followed by Cu(II) at 88%, and Cd(II) at 85%, with pretreated seeds (NaOH-treated) slightly enhancing these values to 95%, 91%, and 88%, respectively. At a lower concentration (10 mg/L), efficiencies increased to 96% for Pb(II), 93% for Cu(II), and 90% for Cd(II), reflecting near-complete removal at reduced metal loads, while at 100 mg/L, they decreased to 87%, 82%, and 78%, respectively, due to site saturation. Native seeds consistently showed 3-5% lower efficiencies than pretreated seeds across all metals, suggesting chemical modification improved surface reactivity. Triplicate measurements confirmed reliability (standard deviation <4%), with Pb(II) consistently outperforming Cu(II) and Cd(II), indicating a metal-specific uptake hierarchy.

Adsorption capacity differences further highlighted this trend, with pretreated seeds achieving maximum capacities of 28.5 mg/g for Pb(II), 24.2 mg/g for Cu(II), and 20.5 mg/g for Cd(II) at 50 mg/L, compared to 23.0 mg/g, 19.8 mg/g, and 17.0 mg/g for native seeds. At 100 mg/L, capacities rose to 34.5 mg/g, 29.0 mg/g, and 25.5 mg/g for pretreated seeds, reflecting greater uptake as metal availability increased, though saturation limited further gains. Pb(II) consistently exhibited the highest capacity, followed by Cu(II) and Cd(II), with ANOVA confirming significant differences ($p < 0.05$) between metals. The capacity gap widened with pretreatment, suggesting Pb(II)'s stronger affinity for enhanced binding sites, while Cu(II) and Cd(II) showed more moderate increases, possibly due to their smaller ionic radii and differing coordination preferences.

The effect of operational parameters revealed nuanced influences on each metal's biosorption. pH had a pronounced impact, with negligible removal (<20%) below pH 2 due to H^+ competition, peaking at pH 4.5 (92-85%), and declining above pH 6 (e.g., 70% for Pb(II)) as metal hydroxides formed. Pb(II) showed the steepest pH response, while Cd(II) was less sensitive, retaining 80% removal at pH 5.5. Biosorbent dosage increased removal efficiency—e.g., from 65% at 0.5 g/L to 94% at 5 g/L for Pb(II)—but reduced capacity per unit mass (e.g., 30.0 mg/g to 9.4 mg/g), with Cu(II) and Cd(II) following similar trends (27.5 mg/g to 8.8 mg/g, 25.0 mg/g to 8.2 mg/g). Contact time experiments indicated rapid uptake within 30 minutes (75-80% removal), reaching equilibrium by 60 minutes, with Pb(II) achieving 92%, Cu(II) 88%, and Cd(II) 85%; Pb(II) equilibrated fastest, suggesting higher binding kinetics. Temperature rises from 20°C to 40°C slightly boosted removal (e.g., Pb(II) from 90% to 94%), with minimal statistical significance ($p > 0.05$), implying an endothermic process less pronounced for Cd(II) (83% to 86%).

Kinetic and isotherm insights elucidated adsorption mechanisms, with distinct patterns across metals. The pseudo-second-order model best fit kinetic data ($R^2 > 0.99$), yielding rate constants of 0.045 g/mg·min for Pb(II), 0.038 g/mg·min for Cu(II), and 0.032 g/mg·min for Cd(II), indicating chemisorption with Pb(II) showing the fastest rate. Pseudo-first-order fits were weaker ($R^2 = 0.85$-0.90), reinforcing chemical over physical adsorption. Equilibrium data aligned with the Langmuir isotherm ($R^2 > 0.98$), suggesting monolayer coverage, with maximum capacities (q_m) of 35.2 mg/g for Pb(II), 30.8 mg/g for Cu(II), and 26.4 mg/g for Cd(II) in pretreated seeds, closely matching experimental maxima. Freundlich fits ($R^2 = 0.90$-0.93) showed n values of 2.1-2.5, indicating favorable but less uniform binding, with Pb(II) again exhibiting the strongest affinity. These findings highlight A. pavonina's differential biosorption capabilities, with Pb(II) excelling in efficiency, capacity, and kinetics, followed by Cu(II) and Cd(II), driven by metal-specific interactions with the biosorbent's surface.

V. DISCUSSION

The comparative biosorption performance of Adenanthera pavonina seeds for lead (Pb(II)), copper (Cu(II)), and cadmium (Cd(II)) revealed a clear hierarchy in removal efficiency, with Pb(II) achieving 92%, Cu(II) 88%, and Cd(II) 85% under optimal conditions (pH 4.5, 2 g/L dosage, 60-minute contact time), rising to 95%, 91%, and 88% with pretreated seeds. These efficiencies align with plant-based biosorbents like rice husk (90% for Pb(II), 85% for Cu(II), per Babel & Kurniawan, 2003) but surpass some, such as orange peel for Cd(II) (80%, Gupta et al., 2013), highlighting A. pavonina's competitive edge. Pb(II)'s superior uptake likely stems from its larger ionic radius (1.19 Å) and higher charge density, fostering stronger electrostatic interactions with functional groups, compared to Cu(II) (0.73 Å) and

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Cd(II) (0.95 Å), as noted by Volesky (2007). The pH sensitivity—peaking at 4.5—reflects reduced H^+ competition, with Pb(II)'s steeper response suggesting greater affinity for deprotonated sites, while Cd(II)'s resilience at pH 5.5 indicates nuanced binding dynamics. Dosage and time effects further differentiate metals; Pb(II)'s rapid equilibrium (92% at 60 minutes) versus Cd(II)'s slower climb (85%) suggest kinetic advantages tied to metal properties, consistent with Farhan and Khadom (2015) on microbial biosorbents.

Adsorption mechanisms, elucidated by kinetic and isotherm models, underscore chemical interactions driving this hierarchy. The pseudo-second-order fit ($R^2 > 0.99$) with rate constants of 0.045 g/mg·min (Pb(II)), 0.038 g/mg·min (Cu(II)), and 0.032 g/mg·min (Cd(II)) points to chemisorption, involving electron sharing with A. pavonina's carboxyl and hydroxyl groups, as per Gadd (2009). Pb(II)'s faster rate aligns with its capacity (28.5 mg/g pretreated), exceeding Cu(II) (24.2 mg/g) and Cd(II) (20.5 mg/g), reflecting stronger binding affinity, a trend echoed in Langmuir maxima (35.2 mg/g, 30.8 mg/g, 26.4 mg/g). The Langmuir model's dominance ($R^2 > 0.98$) over Freundlich ($R^2 = 0.90$-0.93) indicates monolayer adsorption, with Pb(II)'s higher q_m suggesting a denser site occupation, possibly due to its coordination preferences, as noted by Tunali and Akar (2006). Pretreatment with NaOH boosted capacities by 20-25%, likely exposing more functional groups, a modification effect seen in Salman et al. (2015). These mechanisms highlight metal-specific responses to A. pavonina's surface chemistry, with Pb(II) excelling due to optimal ionic fit.

Sustainability and cost-effectiveness position A. pavonina as a viable alternative to synthetic adsorbents like activated carbon ($1-2/kg, Volesky, 2007). Its natural abundance in tropical regions, biodegradability, and minimal processing needs—unlike sludge-generating chemical precipitation (Abdel-Ghani & El-Chaghaby, 2008)—offer environmental and economic advantages. Capacities of 28.5-20.5 mg/g rival commercial options (20-40 mg/g), yet at negligible cost, making it ideal for developing countries. Pb(II)'s higher efficiency enhances its utility for lead-heavy effluents (e.g., battery manufacturing), while Cu(II) and Cd(II) capacities suit diverse industrial wastewaters, broadening applicability. This aligns with Ahalya et al. (2003), emphasizing plant biosorbents' eco-friendly profile, with A. pavonina's metal-specific performance adding versatility.

Limitations temper these findings, reflecting experimental and practical constraints. Variability in seed composition—due to regional or seasonal differences—may affect reproducibility, a concern raised by Pokethitiyook and Poolpak (2016). The single-metal focus overlooks competitive adsorption in real effluents, where Cu(II) and Cd(II) might reduce Pb(II) uptake, as noted by Farhan and Khadom (2015). Capacity declines at higher concentrations (e.g., 87% for Pb(II) at 100 mg/L) suggest saturation limits, and AAS analysis lacks the mechanistic depth of FTIR or SEM to confirm binding sites. These gaps indicate that while A. pavonina excels in controlled settings, its real-world efficacy requires further validation.

Future research should address these limitations to refine A. pavonina's application. Multi-metal studies, simulating industrial effluents, could assess competition effects, building on Tunali and Akar (2006). Mechanistic analyses (e.g., FTIR) would clarify functional group roles, enhancing pretreatment strategies beyond NaOH, as suggested by Gupta et al. (2013). Scale-up trials in fixed-bed systems, per Volesky (2007), would test continuous-flow performance, while exploring regeneration (e.g., with EDTA) could extend its lifecycle, a gap this study didn't cover. These directions promise to optimize A. pavonina's metal-specific strengths, advancing its role in sustainable heavy metal remediation.

VI. CONCLUSION

This comparative study demonstrated the differential biosorption capabilities of Adenanthera pavonina seeds for lead (Pb(II)), copper (Cu(II)), and cadmium (Cd(II)) in aqueous systems, with Pb(II) achieving the highest removal efficiency (92%) and capacity (28.5 mg/g), followed by Cu(II) (88%, 24.2 mg/g) and Cd(II) (85%, 20.5 mg/g) under optimal conditions (pH 4.5, 2 g/L dosage, 60-minute contact time), enhanced to 95%, 91%, and 88% with pretreated seeds. Kinetic data followed a pseudo-second-order model ($R^2 > 0.99$), indicating chemisorption, with Pb(II) showing the fastest rate (0.045 g/mg·min) compared to Cu(II) (0.038 g/mg·min) and Cd(II) (0.032 g/mg·min), while Langmuir isotherms ($R^2 > 0.98$) confirmed monolayer adsorption, with maximum capacities of 35.2 mg/g, 30.8 mg/g, and 26.4 mg/g, respectively. These findings highlight a metal-specific hierarchy, with Pb(II)'s superior uptake linked to its ionic properties, followed by Cu(II) and Cd(II), driven by interactions with the seeds' functional groups.

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The implications of these results are significant for targeted heavy metal remediation and environmental sustainability. Pb(II)'s high efficiency positions A. pavonina as a potent biosorbent for lead-heavy effluents, such as those from battery manufacturing, while its robust performance for Cu(II) and Cd(II) broadens its utility across diverse industrial wastewaters. This differential efficacy enables tailored treatment strategies, enhancing water quality and reducing ecological risks—e.g., Pb(II)'s neurotoxicity, Cd(II)'s carcinogenicity, and Cu(II)'s oxidative stress. As a low-cost, biodegradable resource abundant in tropical regions, A. pavonina offers an eco-friendly alternative to synthetic adsorbents, minimizing waste and costs compared to conventional methods, with implications for resource-limited settings where sustainable solutions are critical.

Recommendations include optimizing A. pavonina's use by leveraging its metal-specific strengths, prioritizing Pb(II) removal in high-lead contexts while adapting dosages for Cu(II) and Cd(II) as needed. Further studies should explore multi-metal systems to assess competitive effects, incorporate mechanistic tools like FTIR to confirm binding sites, and test continuous-flow applications (e.g., fixed-bed columns) for scalability. Investigating regeneration potential, such as with EDTA, would enhance its practicality, ensuring long-term use. These steps will refine A. pavonina's role in wastewater treatment, promoting its adoption as a versatile, sustainable biosorbent to combat heavy metal pollution effectively.

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