

Nanomaterials for Enhancing Bioconversion and Bioremediation of Wastes

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Anaerobic digestion (AD), microalgae cultivation, and microbial fuel cells (MFCs) are the major biological processes to convert organic solid wastes and wastewater in the agricultural industry into biofuels, biopower, various biochemical and fertilizer products, and meanwhile, recycle water. Various nanomaterials including nano zero valent irons (nZVIs), metal oxide nanoparticles (NPs), carbon-based and multicomponent nanomaterials have been studied to improve the economics and environmental sustainability of those biological processes by increasing their conversion efficiency and the quality of products, and minimizing the negative impacts of hazardous materials in the wastes.

Keywords: agricultural wastes ; circular economy ; anaerobic digestion ; microalgae ; microbial fuel cells ; nanomaterials

1. Introduction

Agricultural production generates large amounts of animal manure, crop residues, and food processing wastes [1], and is responsible for 21% of greenhouse gas emissions [2]. Effective implementation of recycling and valorizing fertilizer nutrients, water, and materials in agricultural wastes can help the agricultural industry to develop a circular economy and transit to sustainable agricultural production [3]. Physical, chemical, and biological technologies have been studied to treat agricultural wastes. Among various waste treatment technologies, anaerobic digestion (AD), microalgae cultivation, and microbial fuel cells (MFCs) technologies are three widely studied approaches for simultaneous production of bioenergy products and treatment of wet agricultural wastes and wastewater [4].

AD is an effective technology with four main biological processes: hydrolysis, acidogenesis, acetogenesis, and methanogenesis for converting organic wastes such as manure and crop residues to biogas (a gaseous mixture of CH₄ and CO₂) as an alternative to natural gas, and digestate as organic fertilizers [5]. Cultivation of microalgae on agricultural wastewater has been considered as a promising technology for recycling energy, water, and fertilizer nutrients in wastewater [6][7][8]. MFCs can directly convert chemical energy stored in organic wastes into electricity via redox reactions under mild conditions. Agricultural wastewater is an ideal substrate for MFCs because of its high soluble organic content, high biodegradability, and abundant availability [9][10].

Microbes and microalgae are cell factories for the bioconversion of agricultural wastes. Various nanomaterials have been studied to improve the efficiencies of microbial and microalgae cell factories by providing micronutrients, promoting multiple phase mass transfer, preventing inhibition, immobilizing microbial cells, economically and efficiently harvesting cells, and promoting electron transfer in electrosynthesis.

2. Nanoparticles for the Enhancement of Anaerobic Digestion

2.1. Nanomaterials for Facilitating Direct Interspecies Electron Transfer (DIET) in AD

Various nanomaterials with unique physicochemical properties including nano zero valent metals (nZVMs) (e.g., Fe, Ni, Cu, Co, Ag, Au), metal oxide NPs (e.g., ZnO, CuO, TiO₂, MgO, NiO, Fe₂O₃), carbon-based nanomaterials (e.g., graphene, diamond, nanotube, and nanofibers), and multi-compound NPs have been studied as additives to improve the AD performance [11][12]. However, nanomaterials can have positive and negative effects on the performance of AD through interactions with feedstock and microorganisms, depending on their compositions and concentrations [13]. **Table 1** summarized the effects of some nanoparticles on AD performance.

Table 1. Effects of various nanoparticles (NPs) in the forms of nano zero valent iron (nZVI), metal oxides, carbonaceous, and multi-compound on AD performance.

Substrate	Nanoparticles	Concentration/Average Size	Effects on AD	Refs.
Sewage sludge	nZVI	0.1% sludge/160 nm	- Increasing in methane yield by 25.2% - Removal efficiency of COD by 54.4%	[13]
	Commercial iron powder	1.6% sludge/0.2 mm	- Increasing in methane yield by 40.8% - Removal efficiency of COD by 66.2%	
Raw manure	nZVI	20 mg/L/9 nm	Enhancing the biogas and methane volume by 1.45 and 1.59 times, respectively, compared to those of the control.	[14]
	Fe ₃ O ₄	20 mg/L/7nm	Enhancing the biogas and methane volume by 1.6 and 1.96 times, respectively, compared to those of the control.	
Digested sludge	nZVI	30 mM/55 nm	Decreasing the methane production by 69% due to the increasing soluble COD, volatile fatty acids, and accumulation of hydrogen.	[15]
Raw manure	Co NPs	1 mg/L	Increasing the biogas and methane yield by 1.7 and 2 times respectively, compared to the control sample.	[16]
	Ni NPs	2 mg/L	Increasing the biogas and methane yield by 1.8 and 2.17 times respectively, compared to the control sample.	
	Fe NPs	20 mg/L	Increasing the biogas and methane yield by 1.5 and 1.67 times respectively, compared to the control sample.	
	Fe ₃ O ₄ NPs	20 mg/L	Increasing the biogas and methane yield by 1 and 2.16 times respectively, compared to the control sample.	
Waste-activated sludge	nZVI	10 mg/g TSS/<50 nm	Increasing methane production to 120%, compared to the control.	[17]
	Ag NPs	100 mg/g TSS/<100 nm	Increased methane production to 117%, compared to the control.	
	Fe ₂ O ₃ NPs	500 mg/g TSS/< 30nm	Increasing methane production to 73.52%, compared to the control.	
	MgO NPs	500 mg/g TSS/<50 nm	Increasing methane production to 1.08%, compared to the control.	

Substrate	Nanoparticles	Concentration/Average Size	Effects on AD	Refs.
Waste-activated sludge	nZVI	0.6–1 g/L	Enhancing the hydrolysis and acidification by destroying the microbial cell integrity.	[18]
			Increasing biomethane production.	
			Increasing VFAs and acetic acid production.	
		4 g/L	Enhancing the hydrolysis and acidification by destroying the microbial cell integrity.	
			Maximum VFAs and acetic acid production.	
			Inhibiting methanogens' activity by long-term accumulation of H₂.	
		10 g/L	Decreasing VFAs and acetic acid production.	
			Inhibiting methanogens' activity by long-term accumulation of H₂.	

Iron-based nanoparticles have been extensively studied to enhance the AD performance. nZVI and Fe₃O₄ NPs have been used as additives to enhance the conversion efficiency and methane generation of AD. However, their effects on the performance of microorganisms are different owing to their physical and chemical properties. The addition of nZVI has showed an increase in the methane and hydrogen production in AD of municipal wastewater and industrial wastewater from brewery and sewage plants [18]. It was reported that the addition of Fe₃O₄ NPs at a 7 nm size and 100 ppm concentration increased methane production by 234% due to the presence of non-toxic Fe³⁺ and Fe²⁺ ions [12]. The main effect of iron NPs in an AD system is to change the interspecies electron transfer in the syntrophic process of AD in which butyrate or hydrogen are used to produce methane. The nZVI can serve as a suitable low release electron donor for methanogenesis in an AD process, resulting in the increase of biogas yield. The magnetite Fe₃O₄ NPs in an AD system can act as the electron conduit when the particles are attached to the membrane surface of different cells to accelerate electron transfer among different microorganisms, leading to the improvement of methane generation [19]. Another positive effect is the Fe²⁺/Fe³⁺ which can promote the growth of microorganisms. Other properties including magnetism, absorptivity, and biocompatibility of Fe₃O₄ NPs which can strengthen the digestion efficiency of pollutants in AD. Fe₃O₄ NPs have been applied in the AD treatment of industrial, municipal, and agricultural wastewater, as well as the solid waste produced from agricultural and municipal activities. Aulenta et al. discovered that the kinetics during the AD of trichloroethene (TCE) dichlorination was increased by the addition of a small amount of Fe₃O₄ NPs at 10 mg Fe/L because of the promoted electron transfer in the dechlorinating culture and the enrichment of *Desulforomonas* species in microcosms [20]. The positive effects of Fe₃O₄ NPs on AD were also demonstrated by the increase in the H₂ production and biogas yield [21]. Similar to nZVI, Fe₃O₄ NPs could also remove heavy metal pollutants such as Cr(VI) in the wastewater due to their adsorptive capacity [22][23]. However, the effects of nZVI and Fe₃O₄ NPs on methane production depend on their concentration. The inhibitory impact of nZVI and Fe₃O₄ NPs at high concentrations on methanogenesis can be attributed to the deactivation of bacteria and the damage of bacterial cell membrane [22].

Studies have shown that ZnO, CuO, Mn₂O₃, and Al₂O₃ significantly reduce biogas production rate that may be attributed to the toxicity of these materials. For example, the use of 15 mg/L CuO NPs decreased the biogas production by 30%. However, some metal oxide NPs such as TiO₂ and CeO₂ at proper concentrations can enhance the biogas production. For example, it was reported that the biogas production increased by 10% by using TiO₂ NPs at a 7.5 nm size and 1120 mg/L concentration. However, the effects of metal oxide NPs on the biogas production depend on their concentrations in the reactor and digestion time. These metal oxide NPs have shown greater inhibitory effect on acetoclastic methanogenesis than hydrogenotrophic methanogenesis. The toxicity of metal oxide NPs increases with time due to the increase of the released metal ions [22]. The addition of silver or gold nanoparticles results in either a decrease or no change in biogas production rate, depending on their concentrations in the reactor [22].

The addition of micro/nano fly and bottom ash from the thermochemical conversion of biomass and coal showed a considerable increase in biogas production, but the addition of fullerene (C₆₀) and silica (SiO₂) nanoparticles, and single-walled carbon nanotubes had no effect on biogas production. The ZnFe nanocomposite can significantly improve methane production by up to 185%. Moreover, ZnFe with 10% carbon nanotubes (ZFCNTs), and ZnFe with 10% C₇₆ fullerene (ZFC₇₆) showed a positive effect on retention time and enhanced methane production up to 162% and 146%, respectively [12].

Nanostructured carbonaceous materials such as biochar have also been studied to strengthen the AD performance and improve the treatment efficiency of organic wastes. However, the types of biochar tested so far are very limited and the exact mechanism remains unclear. Zhang et al. investigated the effects of potassium phosphate- and magnesium-modified biochar and the biochar particle size on AD of cattail. They found that the addition of potassium phosphate-modified biochar with a particle size smaller than 1 mm was the most conducive to methane production, increasing the biogas production by 18.3–20.1%. The use of biochar doped with 2 M MgCl₂ and calcined at 800 °C resulted in a 21.1% increase of specific methane productivity compared with AD without biochar. However, the direct use of raw biochar produced by the pyrolysis of pine wood in AD showed an adverse effect on the methane production. The increased buffer capacity, nutrients released by the biochar, enhanced electron transfer and better aggregation function of small particles may contribute to the improved methane production [24].

3. Nanoparticles for the Enhancement of Microalgae Cultivation

The first generations of biofuels derived from edible oil seeds, food crops, and animal fats, and the second generation of biofuels derived from low-value feedstocks such as non-edible oilseeds, used cooking oil, and lignocellulosic biomass have several disadvantages as alternative fuels including the destruction of vital soil resources, deforestation, and the use of large amounts of fresh water and arable land for the supply of those feedstocks. The third and fourth generations of biofuels by taking the advantage of algae and algae/microbes, respectively, offer several advantages over the previous generations of biofuels including high productivity and growth rate, short harvesting cycle (i.e., one to ten days), higher carbon sequestration capacity (10 to 50 times higher than terrestrial plants), less water and land requirements, high oil yield per acre, having the capacity to grow in the waste stream and extreme weather conditions, and no competition with food chain [25][26][27]. In spite of the mentioned advantages, more studies are needed to improve the microalgae cultivation for the large-scale economic production of biofuels by increasing their productivity, lipid content, and usage efficiencies of CO₂ and light [26]. Among various methods, there is an increasing attention to add functional nanomaterials to algal culture to improve CO₂ adsorption and light conversion efficiency for enhancing photosynthesis and algae growth. On the other hand, some destructive impacts of nanomaterials on algae growth were reported which depended on their concentrations and characteristic properties (e.g., size, crystal structure, and oxidation state), culture medium, and algae species.

3.1. Metallic Nanoparticles as Micronutrients for Algal Cultivation

Trace metals play a key role as micronutrients in microalgae growth. Their effectiveness depends on their concentrations in the culture media and their synergy or antagonistic effect with other environmental factors [25]. However, the enhancement of algal growth and lipid production strongly depends on the type and concentration of nanomaterials. Among various nanomaterials, iron has received considerable attentions due to its low toxicity, biocompatibility and high effectiveness. Microalgae require iron as an essential micronutrient in their fundamental cellular functions of photosynthesis and respiration [28]. As shown by Pádrová et al., adding a trace amount of nZVI (1.7 to 5.1 mg L⁻¹) could increase the growth of green algae (*Desmodesmus subspicatus*, *Dunaliella salina*, *Parachlorella kessleri*, and *Raphidocelis subcapitata*) and eustigmatophycean algae (*Nannochloropsis limnetica* and *Trachydiscus minutus*) [25]. Iron is a vital regulatory element in the gene expression and metabolism of algae. The presence of iron in the culture media can prolong the exponential growth phase and enhance the final cell density [25]. Iron plays a critical role in fundamental cellular functions by acting as a cofactor of key enzymes in photosynthesis and respiration. It can promote chlorophyll biosynthesis and biomass growth by activating the *Crd1* enzyme which plays a key role in the Calvin Benson cycle [26].

The increase of the iron content of algal culture leads to the simultaneous enhancement of the growth rate and lipid content in some microalgae species [25]. Pádrová et al. found that the addition of 1.7–5.1 mg L⁻¹ of nZVI in the culture media for green algae *subcapitata* and *eustigmatophycean* algae enhanced the growth of those algae, and 5.1 mg L⁻¹ nZVI could dramatically increase lipid accumulation [29]. Kadar et al. showed the lipid enhancement in *Tetraselims suecica* and *Pavlova lutheri* by the rate of 41.9% and 46.34%, respectively, after exposing to uncoated nZVI and coated nZVI powder [30]. Pádrová et al. in another study reported the addition of 5.1 mg/L nZVI to the *Trachydiscus minutus* and *Desmodesmus subspicatus* cultures increased the lipid content by about 9% and 38%, respectively. They

claimed that nZVI could provide a suitable source of iron to enhance the cell growth and lipid contents and induce changes in lipids' metabolic pathways resulting in the alteration of the lipid composition [29]. Therefore, iron, especially nZVI, may be a suitable source for the increase of microalgae growth and algal lipid production, and alternation of algal lipid profile by increasing polyunsaturated fatty acids contents [29]. Another study further showed that the growth of the algae was even favored by the iron nanoparticles in comparison with their bulk analogues [30].

Although increasing iron concentration below a given threshold can increase the growth rate and lipid content, iron at concentrations above the threshold negatively impacts the algal biomass and lipid production [25]. Abd El Baky et al. found the concentration of FeCl_3 below 20 mg/L increased the total lipid accumulation, total lipid productivity, and biomass production of *Scenedesmus obliquus* by 28.13%, 95.35 mg per day, and 1.25 mg per liter, respectively, in the period of 18 days [31]. Cao et al. found that the optimum concentration of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ for the highest lipid content and growth rate of *Chlorella minutissima* was between 0.05 to 0.1 mM [32]. Most of the studies suggest that the increase of iron concentrations can increase the algal growth rate and lipid content but the concentrations above 0.002 g L^{-1} and 0.001 g L^{-1} have negative impacts on biomass and lipid production, respectively, due to inhibitory effects [25]. Owing to the high activity, iron NPs can produce various reactive oxygen species (ROS) via Fenton-type reactions that cause oxidative injury to cells via lipid peroxidation and oxidation of thiol groups of proteins and DNA [33].

Algal growth and lipid production are also affected by the environmental stress. The typical response of algae to environmental stress, especially nutrient shortage, is to accumulate a tremendous amount of carbon in the forms of carbohydrates and lipids for self-protection against damage. In the case of lipid accumulation under an environmental stress, the contents of most saturated and monounsaturated fatty acids increase and the content of polyunsaturated fatty acids associated with polar membrane decreases, which leads to the decrease in cellular growth [26]. Several studies showed the additives of nanomaterials could improve algal lipid production via induced stress [29][31][34]. The addition of SiC NPs under xenon illumination can improve lipid biosynthesis through inducing oxidative stress and enhancing the activity of acetyl-CoA carboxylase which is a key enzyme for catalyzing the lipid biosynthesis. Although the SiC NPs at an optimal concentration of 150 mg/L could increase lipid content by 40.26%, the TiO_2 and TiC NPs showed the inhibitory effect on the same algae [34].

3.2. Nanoparticles for CO_2 Supply

Microalgae can fix and convert atmospheric CO_2 to oxygen and biomass through photosynthesis. By considering the role of CO_2 as a carbon source in green algae cultivation, the improvement of CO_2 biofixation can increase the algal productivity and atmospheric CO_2 mitigation [35].

pH is an important factor that affects the CO_2 fixation. Alkaline pH can activate rubisco enzyme which is responsible for CO_2 fixation through the Calvin cycle. Therefore, alkaline pH can enhance algal biomass yield and subsequent photosynthesis efficiency. In fact, photosynthesis and microalgae growth lead to alkalize the culture medium. The generated OH^- ions in reaction with CO_2 can form bicarbonate ($\text{CO}_2 + \text{OH}^- \leftrightarrow \text{HCO}_3^-$) which can further be used as carbon sources for microalgae growth. However, an excessive amount of CO_2 entering the culture would acidify the culture medium through the formation of carbonic acid ($\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3$). Acidic pH decreases the activity of rubisco enzymes which will decrease the CO_2 biofixation efficiency and result in CO_2 loss. Nanostructured adsorbents can be used to adsorb CO_2 at an acidic pH value to retain the CO_2 gas in the culture and consequently enhance algal growth by controlling the availability of CO_2 in the culture medium through an adsorption/desorption cycle [35].

CO_2 adsorption can be achieved through physical and chemical processes. The physical adsorption of CO_2 on nanostructured adsorbents is affected by the surface area, and pore size and volume. The pore size of adsorbents is responsible for the selectivity of an adsorption process. By considering the size of CO_2 molecules ($\sim 0.33 \text{ nm}$), the smaller pore size enhances the CO_2 adsorption rather than oxygen ($\sim 0.36 \text{ nm}$) and nitrogen ($\sim 0.35 \text{ nm}$) adsorption. Moreover, the CO_2 adsorption capacity and selectivity of adsorbents can be enhanced by adding some heteroatoms such as nitrogen, oxygen, and sulfur to the nanostructured surface to offer basic sites [36]. The presence of ammonium groups and OH ions on the aerogel consisting of quaternized chitosan and polyvinyl alcohol increases its CO_2 sorption capacity up to 0.18 mmol/g . It was also reported that the selectivity of the aerogel towards CO_2 was better than the commercial membranes [37]. Another study showed the impregnation of amine on zeolite improved CO_2 adsorption up to 4.44 mmol/g [38]. Therefore, besides the surface area and porosity of nanostructured adsorbents, their surface chemistry and the existence of specific functional groups can significantly influence their adsorption capacity for CO_2 [35][39].

Recent studies showed that nanostructured adsorbents had higher CO_2 capturing capacity and reusability over several adsorption/desorption cycles than other popular adsorbents. This might be attributed to their high specific surface area and functionality that can provide more accessible adsorption sites for CO_2 [35][39]. Carbonization of pine cone shells at

650 °C and subsequent activation by KOH enhanced the CO₂ adsorption capacity up to 7.63 mmol g⁻¹ and 2.35 mmol g⁻¹ at 0 °C under 1 and 0.15 bar pressure, respectively, due to increasing specific surface area and porosity [40]. Several studies reported the promising performance of polyacrylonitrile (PAN) nanofiber in adsorbing and supplying CO₂ for microalgae cultivation [39][41][42]. The addition of PAN nanofiber at 0.1-g·L⁻¹ to the *Chlorella fusca* LEB 111 culture was found to improve biofixation and carbohydrate production by 45% and 2.3%, respectively, compared to the control without the nanofiber [41]. Metal nanoparticles can be added to the nanofiber to further enhance CO₂ biofixation. The addition of iron oxide NPs at 4% w/v to PAN nanofiber significantly enhanced the CO₂ fixation in *Chlorella fusca* LEB 111 to 216.2 mg·L⁻¹·d⁻¹ due to the high CO₂ adsorption capacity of Fe₂O₃ NPs (164.2·mg·g⁻¹), increasing the contact time between gas and microorganisms by enhancing the porosity and providing higher surface area [42] and creating the microorganism–nanoparticle hybrid [43].

4. Nanomaterials for Microbial Fuel Cells

4.1. Nanostructured Bioelectrodes

An MFC requires anode and cathode electrodes. Biofilms on the anode electrode oxidize biodegradable organic matters in wastes to liberate electrons and protons. Protons and electrons from an anode will be combined with oxygen at the cathode electrode to produce water. The electrodes should have high surface area and excellent abilities in extracellular electron transport and electrical conductivity to achieve high power density.

Colonization of microorganisms requires anodes with a high porosity, proper pore size, biocompatibility, low cytotoxicity, and resistance to decomposition. Metal components have high conductivity, but their bacterial adhesion is poor. Furthermore, they may be susceptible to corrosion and liberate toxic heavy metals. Carbon-based materials such as graphene and carbon nanotubes provide great surface area facilitating the colonization of microbes, biocompatibility and high conductivity [44]. Nanostructured biocatalyst electrode architectures can be designed and optimized as an excellent MFC anode [45].

One economic and effective way to increase power output of an MFC is to depose of metal or metal oxide (e.g., gold and ruthenium oxide) nanoparticles on the surface of electrodes [46][47]. It was found that carbon cloth-based anode electrodes deposited with Au with a thickness of 50 nm and 100 nm on each side achieved power density 1.22–1.88 times higher than that obtained with a plain carbon cloth electrode [47]. Another study showed that the dual chamber MFC with a RuO₂-coated carbon felt anode increased the power density by 17 times as compared to that obtained with the MFC using a bare carbon felt anode [46].

Polyaniline that has high electrical conductivity can facilitate the electron transfer from bacteria to external circuit on an MFC anode. Study showed that an anode formed by coating polyaniline nanofiber and electrochemically reducing graphene oxide on the surface of carbon cloth yielded a maximum power density of 1390 mW/m², which was three times larger than that of the MFC with a carbon cloth anode [48]. It was reported that an anode formed by a hydrogel composite with bacterial cellulose as a continuous phase and polyaniline as a dispersed phase could achieve a maximum power density of 117.6 mW/m² in a current density of 617 mA/m², compared to 1 mW/m² and 10 mA/m² using a graphite plate anode at the same condition [49]. Hydrogel can achieve excellent nutrient transfer from the culture medium to attached microbial biofilm, provide favorable conditions for bacteria colonization, and prevent it from spoilage. Polyaniline with a high electrical conductivity can facilitate the electron transfer from bacteria to external circuit [49].

Various metal and non-metal nano-composites such as carbon nanotubes and graphene have been studied as cathode catalysts [50]. Owing to its availability and the high electrochemical oxygen potential, an air-breathing cathode MFC is considered as the most promising configuration. An air-breathing cathode usually consists of an electrode substrate, oxygen reduction reaction (ORR) catalyst layer, and air-diffusion layer [51]. The air-cathode catalyst is pivotal in the performance of MFCs because of its role in improving the intrinsic overpotential and poor kinetics of ORR. Although exhibiting the best ORR performance, Pt group metals-based electrocatalysts have high cost, low abundance, and easy deactivation in the presence of MFC metabolites, hindering them from broad industrial application. So far, numerous non-noble metal inexpensive electrocatalysts with an excellent catalytic ability such as Fe-N/C catalysts have been studied. Various Fe-N/C catalysts were synthesized to introduce Fe and N as dual-dopants on the carbon so that the catalytic sites, i.e., Fe-N_x and N-C_x, can be generated [52]. The typical synthesis method is to pyrolyze the widely available precursors comprising of iron salts, nitrogen-rich molecules, and carbon precursors under a high temperature in either N₂ or NH₃ environment. The carbon component in the catalysts serves as the conductive support and the host of active moieties.

In general, an ideal electrocatalyst should possess good electrical conductivity, hierarchical pore structure, large specific surface area, and competent active sites. Therefore, the iron-containing precursors are normally introduced in various carbonaceous materials including active carbon, graphene, carbon nanotube (CNT), conducting polymers, and porous carbons. The heteroatoms (Fe and N) can be introduced into the carbon materials by pyrolyzing FePc-coated activated carbon [53]; by co-doping hierarchical porous iron and nitrogen in carbons via coupling polypyrrole with iron cation [54], and by using metal-organic-framework (MOF) of dual metal- and nitrogen-doped carbon as a precursor [55].

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