

The Efficiency of Cactus Leaves and Wood Charcoal as a Potential Low-Cost Adsorbent for Removal of Toxic Heavy Metals from Industrial Effluents

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# ABSTRACT

Presence of toxic heavy metals in the environment is of great concern due to their persistence in nature and chronic adverse effects on human health and the environment. Present paper tries to evaluate the efficiency of cactus leaves (*Opuntia f. indica*) and activated carbon made from *acacia etbiaca* as an adsorbent for the removal of heavy metal pollutants such as cadmium, lead and chromium from water. Adsorption properties such as size, dose, initial concentration and time of contact for cadmium, lead and chromium were studied through batch method. Before removing the toxic heavy metals (Cd, Pb and Cr), the fresh unpeeled cactus leaves (adsorbent) and activated carbon were washed with distilled water to eliminate the turbidity and smell from fresh unpeeled cactus. To describe the equilibrium isotherms, the experimental data were analyzed by the Langmuir and Freundlich isotherm models. Thus, the Freundlich model gave the best correlation with the experimental data. Therefore, the findings indicated that the cactus and activated carbon made locally from *acacia etbiaca* were found to be effective and low-cost alternative adsorbents for the removal of toxic heavy metals from industrial effluents. The preparation method allowed the use of these materials by local industries for effective remediation of pollution by removing heavy metals from their effluents.

Keywords: Cactus leaves; *Acacia etbiaca*; Heavy metals; Adsorption, Industrial effluents; Water purification.

# **1. INTRODUCTION**

The toxic heavy metals are commonly present in many environments and as pollutants in many water bodies. The potential harmful effects associated with the accumulation of heavy metals in the environment are well known. The toxic effects of heavy metals on human populations and potential health hazards have been extensively studied by many workers (Jarup, 2003; Jaishankar et al., 2014). Among these, chromium(Cr), cadmium (Cd), lead (Pb) and others are frequently used in industrial processes such as tannery, textile, pharmaceuticals, metallurgy, mining, painting, smelting, batteries, and alloys industries (He et al., 2005; Tchounwou et al., 2012; Ahmed et al., 2017). Most of these heavy metals are often present at high concentration in liquid industrial waste and are often deposited directly in the environment without any pre-treatment. The high toxicity of these metals leads to serious ecological damages, thus, there is an increasing

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necessity to develop processes to eliminate them at least to strongly reduce the concentration in wastewater prior to their release into the environment.

Due to the harmful effects of heavy metals, environmental agencies set permissible limits for their respective levels in drinking water and other types of water. For example, according to World Health Organization (WHO, 2011), the maximal admitted concentration values for chromium (VI), cadmium and lead are 0.05, 0.003 and 0.01mg/L, respectively. These concentration values are considered as thresholds in terms of protection of public health and globally for the maintenance of an ecological equilibrium (Van der Leeden et al., 1990; Loghmanadham, 1997; Zhang et al., 1997; WHO, 2011).

Chromium occurs most frequently as Cr (VI) or Cr (III) in aqueous solutions. The two oxidation states have different chemical, biological and environmental properties (Devi et al., 2012). Cr (III) is relatively insoluble, and is an essential micronutrient (Pechova and Pavlata, 2007), while Cr(VI) is a primary contaminant because of its toxicity to humans, animals, plants and microorganisms (ATSDR, 2002; Mishra and Bharagava, 2016). Chromium has widespread industrial applications; hence, large quantities of chromium are discharged into the environment. The major industries that contribute to water pollution by chromium are mining, leather tanning, textile dyeing, electroplating, aluminum conversion coating operations, plants producing industrial inorganic chemicals and pigments, and wood preservatives (Dakiky et al., 2002).

Lead is distributed in different parts of the environment in the form of metallic, inorganic salts and organic compounds (Tangahu et al., 2011). It is a heavy metal that is both poisonous and a ubiquitous environmental toxicant. The major sources of lead exposure are leaded gasoline, lead-based paints, batteries and industrial effluents (Ahamed and Siddiqui, 2007). Currently, the exposure of lead has been considered as an extreme concern to the public, government and industry. However, environmental lead exposure such as that in domestic tap water, food-borne contamination and industrial effluents continue to pollute the environment (Spivey, 2007), which has toxic effects on the neuronal system and on the function of brain cells (Lidsky and Schneider, 2003; Hsiang and Díaz, 2011;Floraet al., 2012). This underlines the need for developing methods for effective removal of lead from water at least below the regulatory level. Now-a-days, cadmium is also considered as a treat to the human health and environment. Cadmium exists in different isotopic forms and the most common are <sup>112</sup>Cd and <sup>114</sup>Cd (Adriano, 2001). It forms a variety of complex compounds such as organic amines, sulfur complex, chloro-

complexes and chelates. Besides, Cd ions also form soluble salts of carbonates, arsenates, phosphates, and ferrocyanide compounds. Currently, Cd is widely used as alloys in electroplating, as a pigment in paint production (cadmium sulfate and cadmium selenide), in nickel-cadmium battery and as stabilizers for polyvinyl plastic (Cobb, 2008). Furthermore, cadmium is present in most foodstuffs and fertilizers. Thus, Cd considerably exists in environment as a result of human activities such as the use of fossil fuels, metal ore combustion, fertilizers and waste burning. The usage of industrial effluents to agricultural activities may cause the transfer of cadmium compounds adsorbed by plants that may play a significant role in food chain, and accumulate in various human organs. Exposure to Cd affects cell proliferation, differentiation, apoptosis, human fertility and the proper functioning of DNA (Patrick, 2003; Rani et al., 2014). Cadmium causes mutations and chromosomal deletions potentially (Joseph, 2009; Pizent, 2012). Therefore, this indicated that there is a need to remove the toxicity of Cd released to the environment.

The level of such toxic contaminants of Cr, Pb and Cd in discharged wastewater should be reduced, or recycled if possible. Thus, several methods are utilized to remove toxic heavy metals from industrial waste water including chemical precipitation (Brboot et al., 2011); ion exchange (Gaikwad et al., 2010); reduction (Seaman et al., 1999); electrochemical precipitation (Tran et al., 2017); solvent extraction (Silva et al., 2005); membrane separation (Mikulasek and Cuhorka, 2016); reverse osmosis (Pires da Silva et al., 2015); biosorption (Wang and Chen, 2009; Mudhoo et al., 2012) and adsorption (Javaid et al., 2011). Among the methods commonly used for this purpose, adsorption was shown to be economically favorable and technically easy for the removal of the toxic heavy metals. Therefore, adsorption is considered as an effective and versatile method for removing toxic heavy metals like Pb, Cd, Cr, and others, particularly when combined with appropriate regeneration steps. This solves the problems of sludge disposal and renders the system more economically viable, especially if low-cost adsorbents are used (Lakherwal, 2014; Tripathi and Ranjan, 2015). Several publications utilized different inexpensive and locally abundantly available adsorbents like activated carbon (Hung et al., 2005), agricultural by-products (Sulyman et al., 2017; Mohan et al., 2005), waste materials (Kyzas, 2012) and charge minerals (Singh et al., 1992).

In order to reduce the levels of the toxic heavy metals, adsorption is rather simple, cheap and easy to extrapolate at larger scale for practical applications, which showed a good efficiency for

the treatment of polluted liquid media. Thus, the adsorbents materials (plant) selected for this study, cactus (*Opuntia f. indica*) and *acacia etbaica*, grow in the semi-arid regions of Tigray, Ethiopia. It is known cactus to be nontoxic as some of them are used in feeding animals and its fruits are used by residents of the local people, which make it good candidate for the development of processes aimed to be used in agriculture or domestic applications. *Acacia etbaica* is also used as energy sources in majority and medicinal purposes. Therefore, the purpose of this study were to evaluate the efficiency of cactus leaves and locally prepared wood charcoal, which are all locally available, abundant and low-cost adsorbents) in removing Cr, Cd and Pb toxic heavy metals from synthetic and contaminated water samples.

#### 2. METHODOLOGY

#### **2.1.Adsorbent Preparation**

Cactus (*Opuntiaf. indica*) was collected and the spines of the cactus leaves were removed with a knife and pads were rinsed with tap water followed by deionized water. Dissections of fresh cactus pads were performed manually using knife. The fresh *Opuntia f. indica* was cut into two size classes: small (1 cm) and medium (2 cm).

Dry wood logs of *Acacia etbaica* (*A. etbaica*) was cut into pieces, 50-100 cm size, and buried in earth-covered traditional kilns for weeks, where wood is cut and stacked before being covered in earth and carbonized. The charcoal was ground in a high-speed rotary cutting mill and sieved into different mm sizes: < 0.1, 0.1 - 0.25, 0.25 - 0.5 and 0.5 - 1.0 mm. Before the application of the charcoal to our research it was washed several times with distilled water to remove dust and some other residuals. The washed samples were dried at room temperature.

# 2.2.Chemicals

Analytical grade chemicals were used to prepare standards solutions and were used during the analysis.

## **2.3.Sample Preparation**

Standard solutions of heavy metals (Cr, Cd and Pb) were prepared from their stock solutions by serial dilution of stock Cr, Cd and Pb solution (1000 mg/L) (Industrial Analytical (pty) Ltd, South Africa)using deionized water. In order to simulate the actual concentrations of heavy metals in industrial effluents, synthetic water of heavy metals were made by spiking of heavy metals from the stock solution.

# 2.4.Instruments

Varian AA240 FS Fast Sequential Atomic Absorption Photometry(FED 53, USA), which is fully automated PC-controlled true double-beam Atomic Absorption spectrometer with fast sequential operation for fast multi-element flame AA determinations, features 4 lamp positions and automatic lamp selection, operated with SpectrAA Base and PRO software versions were used during the experiment.

The pH of the solutions was measured with a Hatch Lange pH meter (HANNAHI99)using a combined glass electrode calibrated with buffers of pH 2, 4, and 7. The solutions were shaken with B\_HlerHorizintal Shaker (Fisher Scientific), which is thermostatic electronic shaker.

# 2.5.Method

Batch adsorption experiments were carried out at a laboratory room temperature for cactus and wood charcoal adsorbents at the desired initial toxic metal concentration and different pH. The required amount of the adsorbent material was then added and the flask contents were shaken at different time contacts in B\_HlerHorizintal Shaker at 150 rpm (constant speed). The adsorbents filtered, centrifuged and the supernatant was analyzed for final pH and toxic metal concentration using AAS. Throughout the study, adsorption parameters of contact time, pH, dose effect, and initial concentration and adsorption isotherms were studied in batch experiment. A comparison between true wastewater samples from industrial effluents and laboratory simulated synthetic samples were also analyzed.

#### 2.6 Adsorption Isotherm

The average amount adsorbed by the adsorbent at time t,  $q_t$  (mg/g) was calculated for each experiment using the following equation:

Where,  $C_i$  is the initial concentration in the solution (mg/L),  $C_t$  is the concentration in the solution at time t (mg/L, i.e., after filtration), V is the volume of solution (L), and W is the amount of adsorbent (g).

The percentage of adsorption is found from the relation:

$$R(\%) = \frac{C_o - C_e}{C_o} x_{100} - \dots - (Eq.2)$$

The results obtained for the adsorption of heavy metals were analyzed by the Freundlich and Langmuir models. The logarithmic form of the Freundlich model is given by the equation:

Where,  $q_e$  is the amount adsorbed (mg/g),  $C_e$  is the equilibrium concentration of the adsorbate (mg/L), and  $K_F$  and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively (Freundlich, 1906).

Langmuir's isotherm linear equation is given by the equation (Langmuir, 1918):

$$\frac{1}{q_{e}} = \frac{1}{q_{\max}} + \frac{1}{C_{e}q_{\max}b} - \dots - (Eq.4)$$

Where, qe represents the amount adsorbed at equilibrium time (mg/g),  $q_{max}$  and b are Langmuir constants that depend on the maximum monolayer adsorption capacity and adsorption equilibrium constant that relates to the energy of adsorption and <sub>Ce</sub> represents the equilibrium concentration (mg/L), respectively.

An isotherm study was performed by mixing adsorbent to the heavy metal spiked solutions at different initial concentrations while keeping all other parameters constant. The sample was withdrawn for analysis at the equilibrium time chosen based on the experiments.

## **3. RESULTS AND DISCUSSION**

#### **3.1.Equilibrium Time**

The adsorption data for the uptake of heavy metals such as Cr, Cd and Pb versus contact time using 1 g acacia etbiaca and 6 g of fresh cactus (*opuntia f. indica*) are shown in figure 1. The adsorption of heavy metals with fresh cactus as a function of contact time is shown in figure 1(FC); 120 min contact time is considered as a reference. The adsorption of activated carbon of *acacia etbiaca* was remained constant after 120 min contact time figure 1(AE)and taken as a reference. This difference in adsorption kinetics is rather remarkable and is probably related to the presence of water in the fresh cactus, which affects taking up of heavy metals from the solution. A contact time of 120 min was further applied to study adsorption on fresh cactus and activated carbon made from wood logs of *acacia etbiaca*.



Figure 1. Effect of contact time on adsorption of chromium (Cr), cadmium (Cd) and lead (Pb) onto fresh *Opuntiaf. Indica* (FC),dose = 6 g, concentration =  $1 \text{ mgL}^{-1}$ , Particle size = 1 mm and at laboratory room temperature; activated carbon (AE)made from *acacia etbiaca*, dose = 1 g, concentration =  $1 \text{ 1mgL}^{-1}$ , Particle size = 0.25 - 0.50 mm and at laboratory room temperature.

## **3.2 Effect of Adsorbent Particle Size**

It was found that heavy metals such as Cr, Cd and Pb adsorption on fresh *Opuntia. f. indica* (FC) and activated carbon made from *acacia etbiaca* (AE) are strongly dependent of the particle size of the adsorbent. This is shown in figure 2 for a 100 mL solution containing 1 mgL<sup>-1</sup> of Cr, Cd and Pb in contact with 6 g FC and 1g AE adsorbents and 120 min contact time. The highest percentage of removal, both when using FC and AE was observed in the treatments with the smallest particle size. The FC adsorbent sizes of 1 and 2 mm size resulted in the removal of 32% and 27%, respectively, for Cr;35 and 33%, respectively, for Cd, and 38 and 33%, respectively for Pb. The AE absorbent sizes of < 0.1, 0.1 – 0.25, 0.25 – 0.50 and 0.5 – 1.0 mm resulted in removal of 99, 97, 95, and 94.5%, respectively, for Cr; 98.7, 96, 95, and 94% respectively, for Cd, and 99.9, 98, 96, and 94%, respectively, for Pb. This is due to the fact that the smaller  $\bigcirc CNCS$ , *Mekelle University* 208 *ISSN: 2220-184X* 

particle sizes yield a larger surface area of adsorbent, thus increasing the number of adsorption sites and enhancing the adsorption capacity (Gupta et al., 2002; Pal et al., 2006). Therefore, because of its efficient adsorption capacities and ease of separation, the size class approximately 1 cm for FC and 0.25 -0.50 mm for AE adsorbent was chosen for the application of further experiments. *Opuntia f. indica* (FC) is characterized by the production of mucilage, which forms molecular networks that are able to retain large amounts of water (Kilic et al., 2011), complex polymeric substances of carbohydrate nature with a highly branched structure (Gupta et al., 2011) and varying proportions of L-arabinose, D-galactose, L-rhamnose, D-xylose, and galacturonic acid in different proportions. This property of the adsorbent used to chelate the toxic heavy metals and thus removing it from the wastewater. The surface morphology of *acacia etbiaca* is also characterizes by the large number different open pores. These are the active components that provide the large adsorption capacity of *Opuntiaf. indica* and *acacia etbiaca*, respectively.



Figure 2. Effect of adsorbent particle size on adsorption of Cr, Cd and Pb onto fresh *Opuntiaf*. *Indica* (FC), dose = 6 g, concentration =  $1 \text{mgL}^{-1}$ , Particle size = 1 mm, Time = 120 min and at laboratory room temperature; activated carbon (AE) made from *acacia etbiaca*, dose = 1 g, concentration =  $1 \text{ 1mgL}^{-1}$ , Particle size = 0.25 - 0.50 mm, Time = 120 min and at laboratory room temperature.

# **3.3.Effect of Initial pH**

The effect of pH on heavy metals such as Cr, Cd and Pb sorption by fresh cactus and activated charcoal made of *acacia etbiaca* was studied in the pH values of 2, 4, 7, 10 and 12 and is shown in figure 3. The adsorption studies were carried out at laboratory room temperature. A typical pH versus percentage removal of heavy metal contaminants such as Cr, Cd and Pb using FC and activated charcoal made of *acacia etbiaca* showed a remarkable increase in percentage removal of heavy metals at higher pH values. The same trend was also observed for Pb removal by Mbugua et al. (2016) using adsorbent materials derived from cactus leaves (*O. Vulgaris* cactus). The increase in the uptake of heavy metals above pH 10.0 and thereafter no change in the adsorbed amount were observed.



Figure 3. Effect of pH on heavy metal such as Cr, Cd and Pb adsorption onto fresh *Opuntiaf*. *indica* (FC) and activated carbon (AE) made from *acacia etbiaca* adsorbent at experimental conditions: Heavy metal concentrations= Cr = Cd = Pb = 1 mgL<sup>-</sup>; Volume of heavy metal solution = 100 mL; Mass of adsorbent = 1 g; Contact time = 120; Laboratory room temperature.

Thus, maximum uptake of the heavy metals of Cr, Cd and Pb at 93.4% and 96.2% were obtained at pH 10 for FC and AE, respectively. Therefore, pH 10.0 was selected as an optimum value for performing subsequent studies. The result obtained clearly indicates a decrease of protonation due to higher pH results in an increase of negative charge at the surface of the adsorbents, which facilitates adsorption by providing more active surface of the adsorbents, resulting thereby greater adsorption at their surfaces. Similarly, the same trend was observed by Ajaelu et al. (2011); and Mbugua et al. (2016). The pH of solution controls the electrostatic interactions between the adsorbent and the adsorbate. A decrease in the percentage removal with decrease in pH may be due to the competition of hydrogen ions with the adsorbate cations, which retards the electrostatic forces between sorbent and sorbate that leads to reduced sorption capacity (Feng et al., 2011). The effect of pH on the adsorption capacity of FC and AE is also in agreement with the previously reported results for adsorption of heavy metals from aqueous solutions by coconut husk (Agobozu and Emoruwa, 2014) and some waste materials (Yasemin and Zeki, 2007).

# 3.4. Effect of Initial Heavy Metal Concentration

The effect of initial heavy metal concentration values of 0.2, 0.5, 0.75, 1.0, 1.25 and 1.5 mg/L Cr, Cd and Pb on adsorption efficiency onto FC and AE was investigated and is shown in figure 4. It is observed from the figure that the percentage heavy metal (Cr, Cd and Pb) removal decreased with the increase in initial concentrations of the corresponding heavy metal contaminants. Though the percent adsorption decreased with increase in initial heavy metal acconcentration, the actual amount of heavy metal adsorbed per unit mass of adsorbent increased with increase in heavy metal concentration in test solution. The initial heavy metal concentrations of Cr, Cd and Pb provides the necessary driving force to overcome the resistance to the mass transfer of the heavy metals between aqueous phase and the solid phase. The increase in initial heavy metal ions and the adsorbent (FC and AE) surface. Therefore, the increase of the initial concentration of Cr, Cd and Pb enhances the adsorption uptake of the heavy metals by the adsorbents.

#### **3.5. Sorption Modeling**

To describe the equilibrium distribution of heavy metals (Cr, Cd and Pb) between the FC and AE adsorbent surface and the aqueous solution phase, two different sorption models, Langmuir and

Freundlich have been used. These models were also used to calculate the loading capacity of the two forms of FC and AE adsorbents examined in this study.



Figure 4. Effect of initial heavy metal (Cr, Cd and Pb) concentrations on percent removal at equilibrium at laboratory room temperature, pH = 10, contact time = 120 min, adsorbent size: fresh *Opuntiaf. indica* (FC) = 1 cm and AE = 0.25 - 0.50 mm, Volume of solution = 100 mL, activated carbon (AE) made from *acacia etbiaca* dose = 1 g and FC dose = 7.5 g.

#### 3.5.1. Langmuir Isotherm

The most widely used isotherm equation for modeling of the sorption equilibrium data is the Langmuir isotherm. This model assumes the uniform energies of adsorption onto the surface without any transmigration of adsorbate in the surface of adsorbents. Langmuir sorption is a model based on the physical hypothesis that there are no interaction between adsorbed molecules or ions and the adsorption energy over the entire coverage surface. This model imposes that a particular site of the adsorbent is occupied by an adsorbate molecule or ion; no further adsorption takes place at that site, i.e. forming a monolayer of adsorbed species. The linear form of Langmuir isotherm equation is given by the equation 5 (Langmuir, 1916):

 $\frac{C_e}{q_e} = \frac{1}{qmK_L} + \frac{C_e}{qm} - \dots - (Eq.5)$ 

Where, *C*e is the equilibrium concentration of the of heavy metals (Cr, Cd and Pb) (mg/L), qe is the amount of heavy metal adsorbed per unit mass of FC and AE (g g-1), qm and *K*L are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The Langmuir constants can be evaluated from the slope and the intercept of linear equation (Table 1).

#### 3.5.2. Freundlich Isotherm

This model considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption (Freundlich, 1906) and can be represented by equation 6:

Where,  $K_f$  (g/g) and *n* are Freundlich constants giving an indication of how favorable the adsorption process.  $K_f$  can be defined as the adsorption or distribution coefficient and represents the quantity of heavy metal (Cr, Cd and Pb) adsorbed onto the adsorbents (FC and AE) for a unit equilibrium concentration. The slope of 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Al Duri, 1995; Ayranci and Hoda, 2005).

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To compare the Langmuir and Freundlich isotherm models, the experimental data have been statistically processed by linear regression. The regression equations of y=ax+b type and the obtained values of the correlation coefficient,  $R^2$ , are given in table 1. It can be seen (Table1) that the obtained data fit better to the Freundlich model than the Langmuir model (higher values for  $R^2$ ), so the formation of more than one molecular layer of heavy metals (Cr, Cd and Pb) on the surface of fresh cactus (FC) and activated carbon made from woods of *acacia etbiaca* (AE) appears to be achieved.

Table 1.Langmuir and Freundlich adsorption constants for adsorption of heavy metals (Cr, Cd and Pb) on Fresh cactus (FC) and activated charcoal made from woods of *acacia etbiaca* (AE).

Adsorbent	Adsorbate	Langmuir Constants			Freundlich Constants		
		qm(g/g)	KL	R2	Kf	n	R2
FC	Cr	0.865	1.13	0.763	0.88	1.581	0.95
	Cd	0.843	1.42	0.784	0.91	1.434	0.96
	Pb	0.824	1.33	0.775	0.79	1.653	0.97
AE	Cr	0.988	1.32	0.842	0.74	1.874	0.99
	Cd	0.993	1.21	0.773	0.85	1.862	0.99
	Pb	0.899	1.17	0.851	0.78	1.923	0.99

## 4. CONCLUSION

The present study was carried out to examine the ability of fresh cactus (FC) and activated carbon made from woods of *acacia etbiaca* to adsorb Cr, Cd and Pb from synthetic aqueous solutions. Thus, the results of the findings indicated that the adsorbents prepared from the locally available materials appeared to be a promising adsorbent for the removal of toxic heavy metal contaminants of Cr, Cd and Pb from aqueous solutions under laboratory conditions. The optimum pH obtained for removal process was around 10. The results of this study also showed that the extent of toxic heavy metal removal (Cr, Cd and Pb) increased with decreased initial concentration of the heavy metals and also increased with increased contact time and doses of FC and AE. The adsorption process of the two studied adsorbents (FC and AE) occurred in a moderate time and reached equilibrium at about 120 min. In comparison of the two adsorbents, AE showed a higher adsorption capacity than FC under the same conditions. In addition, the results obtained were well fitted in the linear forms of Freundlich than Langmuir adsorption (© CNCS, Mekelle University 214

isotherms for both FC and AE. Thus, the low cost and locally available adsorbents of FC and AE appeared very prospective and promising adsorbents for the removal of toxic heavy metal contaminants such as Cr, Cd and Pb from industrial effluents of textile and tannery industries which are found in the basic forms.

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