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Adsorption of Copper Metal Ions from aqueous Solution Using Rice Husk and Groundnut Shell

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Abstract: ***The pollution of water resources due to the disposal of heavy metal ions has been an increasing worldwide concern for the last few decades. Batch experiments were conducted to know the influence of various parameters of adsorption on removal of Copper metal ions by agricultural byproducts (Groundnut shell, Rice husk and combined adsorbents). It has been found that the percentage of adsorption increases with increase in pH and decreases with the increase in metal ions concentration. Equilibrium time required for the adsorption of Copper metal ions by agricultural byproducts was found to be 2 hrs. The obtained results show that the adsorption of Copper by Rice husk and Groundnut shell are of second order.***

Keywords: Adsorption, Rice husk, Groundnut shell, Copper, Kinetics.

1. Introduction

The pollution of water resources due to the disposal of heavy metal ions has been an increasing worldwide concern for the last few decades. Heavy metals pollution occurs in much industrial wastewater such as that produced by metal plating facilities, mining operations, battery manufacturing processes, the production of paints and pigments, and the ceramic and glass industries. Whenever toxic heavy metals are exposed to the natural eco-system, accumulation of metal ions in human bodies will occur through either direct intake or food chains. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products. Increasing levels of heavy metals and other pollutants in the environment pose serious threat to water quality, human health, and living organisms. Hence heavy metals should be prevented from reaching the environment [1].

There are various conventional methods applied for removing heavy metal ions, and they include chemical precipitation, membrane process, ion exchange, solvent extraction, electrodialysis, and reverse osmosis. These methods are non economical and have many disadvantages such as incomplete metal removal, high reagent and energy consumption, and generation of toxic sludge or other waste products that require treatment before disposal [2].

Biosorption is a process that utilizes low-cost biosorbent to sequester toxic heavy metals. Biosorption has distinct advantages over the conventional methods, which include reusability of biomaterial, low operating cost, selectivity for specific metal, short operation time and no chemical sludge. In the recent years many biosorbent materials of agricultural based have been utilized for heavy metal biosorption. These include: coconut husk and shell, sea weeds, bagasse ash, hazelnut shell, peanut hull, tree fern, black gram husk, maize leaf, maize, sun flower waste, coffee beans, *Ficus religiosa* leaves, wheat bran, almond shell, tea waste [3].

1.1 Copper

Copper, an element which has been used by man for years, can be regarded as a longstanding environmental contaminant. Several industries like mining, printing, painting, dyeing, battery manufacture and other industries discharge effluent containing Cu (II) to surface water. Copper smelting and mining are major industrial processes that lead to Copper contamination of water and soil.

Copper is an essential nutrient, required by the body in very small amounts. But if it is exceed the limit it can cause diseases. Short periods of exposure can cause gastrointestinal disturbance, including nausea and vomiting. Use of water that exceeds the permissible level over many years could cause liver or kidney damage. Copper is rarely found in source water, but copper mining and smelting operations and municipal incineration may be sources of contamination [4].

2. Materials and Methodology

2.1 Adsorbent Preparation

Rice husk and Groundnut shell were ground separately and sieved to obtain particle size of 0.6mm.The sieved adsorbents were washed with distilled water several times to remove dust and kept in an oven at 65 ^{0}C for 24 h to reduce the moisture content. Then these adsorbents were used for batch experiments.

2.2 Adsorbate

Stock solutions of Copper were prepared by dissolving 1g of Copper turnings in 20 mL Nitric acid and then make up into 1000 ml. Different initial concentrations of metal ions were prepared by diluting the stock solutions. The pH was maintained using 0.1N HCl and 0.1N NaOH solutions.

2.3 Batch experiments

The experiments were carried out under constant shaking of 100ml of synthetic solutions in conical flasks using heavy rotatory shaking apparatus. Samples were withdrawn after a definite time interval and filtered through Whatman No. 41 filter paper and then measured in ICP. The amount of metal ions adsorbed by adsorbent is calculated using the following equation:

$$qe = \frac{(C_0 - C_e)V}{M} \quad (1)$$

Where,
C_o = Initial concentration of the metal ions in solution (mg/L)
C_e = Final concentration of the metal ions solution (mg/L)
V = solution volume (L) and
M = mass of the sorbent (g)

3. Results and Discussions

3.1General

Adsorption studies are conducted for the removal of copper from aqueous solution. Batch experiments were carried out under different pH, time, initial concentration of metal ions and adsorbent doses. The results of the above study are presented in the following section.

3.2 Effect of pH

The pH of solution significantly influences the removal of heavy metals hence it is an important condition for adsorption of Copper metal ions. With the contact time of 2h batch experiments were carried out at different pH values (3-10) with 30mg/L of copper. Fig.1 and Fig. 2 reveals the adsorption capacity of metal ions. At pH 8, 1g of Rice husk was able to give copper removal efficiency of 96.72% and at pH 6, Copper removal efficiency was 93.90% using 1g of Groundnut shell.

At low pH, high concentrations of H^+ ions were present in solution that competes for vacant adsorption sites of adsorbent. This phenomenon could be confirmed by the observation of sharp increase in the final solution pH of those having low initial pH values. For each hydrolysable metal ion, there was a critical pH range where the metal uptake efficiency increased from a very low level to maximum value. Decreasing trend in uptake was observed above pH 8 due to formation of soluble hydroxyl complexes [6].

3.3 Effect of contact time

In the present study, effects of contact time (15 - 165 min) on the removal of Copper metal ions have been carried out with initial concentration of 30 mg/L at pH 7 and 8 for Groundnut shell and Rice husk respectively**.** The maximum uptake of copper was at 2h using Rice husk and Groundnut shell as adsorbents. After 2h, the % removal was negligible; hence all experiments were carried out at equilibrium time of 2h.

As can be seen from the Fig. 3 and Fig. 4, the biosorption process took place in two stages. The first stage was rapid, where about 90.99 % biosorption was completed by Rice husk and 82.31% biosorption was completed by Groundnut shell within first 15 min. The second stage represented a slower progressive biosorption. The rapid initial biosorption may be attributed to the accumulation of metals on to the surface of biosorbent, due to its large surface area. With the progressive occupation of these sites, process became slower in the second stage [3].

3.4 Effect of initial concentration of metal ions

The adsorption experiments were carried out with metal ion concentrations of 20, 40, 60, 80,100,120,140 and 160 mg/L at pH 8 and 7 using 1g of Rice husk and Groundnut shell. The effect of initial concentration of copper is shown in Fig. 5 and Fig. 6 for Rice husk and Groundnut shell respectively. Results from these plots indicate that Copper removal efficiency decreases from 97.81 % to 70.76% for Rice husk and from 94.56% to 65.38% for Groundnut shell as the initial concentration of Copper increased from 20mg/L to 160mg/L. Fig. 9 shows that removal efficiency by combined adsorbents (Rice husk and Groundnut shell) decreases from 92.90% to 68.93% as the initial concentration of copper increased from 350mg/L to 600mg/L. At low metal ion loads, adsorption involved the high energy sites. Under these conditions, the ratio of number of moles of metal ion to the available adsorption sites was low, and therefore, the amount adsorbed per unit mass increased slowly. With an increase in metal ion load, the higher energy sites would be rapidly saturated and the metal ions would gradually occupy the lower energy sites, resulting in a continuous increase in the amount adsorbed per unit mass [7].

3.5 Effect of adsorbent dose

The effect of adsorbent doses of Rice husk, Groundnut shell ranging from 2 – 9g/L and combined adsorbents(Rice husk and Groundnut shell) ranging from 2 – 7g/L on copper removal are shown in Fig.7, Fig.8 and Fig.10 respectively. The results indicate that the percentage removal of Copper metal ions increases as the adsorbent dose increases by giving removal efficiency from 88.43% to 94.12% for rice husk, from 85.66 % to 91.52% for Groundnut shell and from 89.15% to 94.96% for combined adsorbents (Rice husk and Groundnut shell).

The removal efficiency and specific uptake of metals depend on type and quantity of the biosorbent. The increase in percentage removal of Copper with increase in adsorbent dose was due to the availability of more and more adsorbent surfaces for the solutes to adsorb.

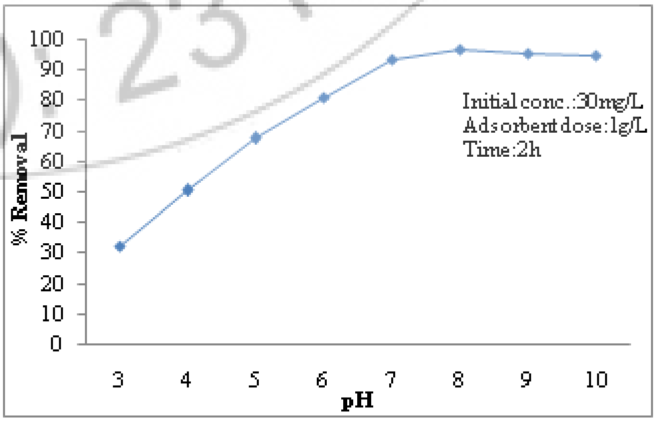

Figure 1: Effect of pH on Copper removal by Rice husk

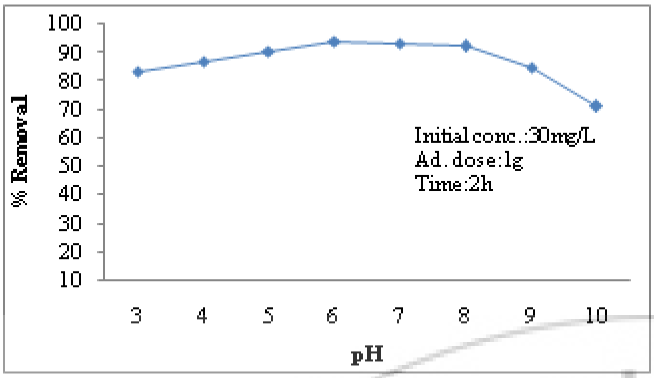

Figure 2: Effect of pH on Copper removal by Groundnut shell

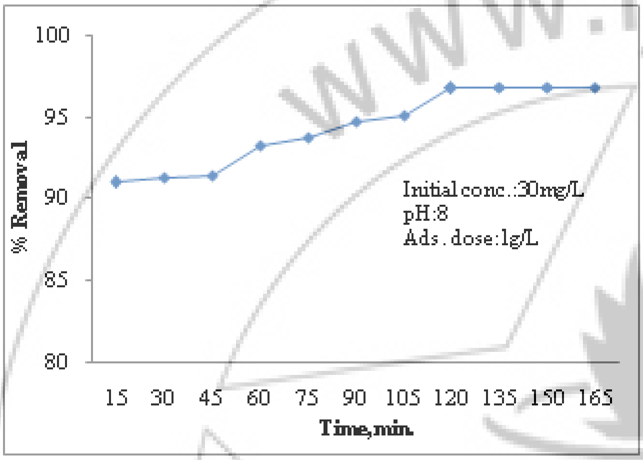

Figure 3: Effect of contact time on Copper removal by Rice husk

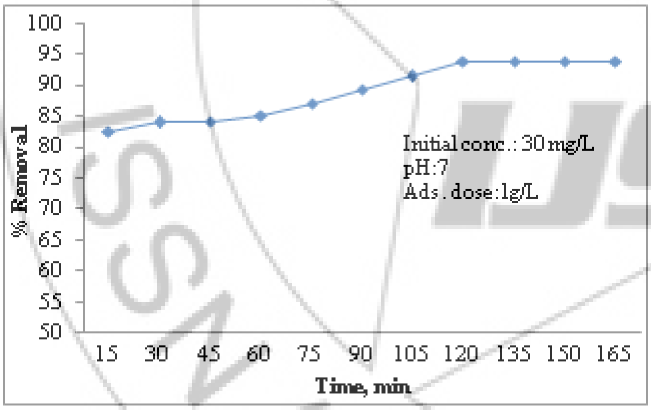

Figure 4: Effect of contact time on Copper removal by Groundnut shell

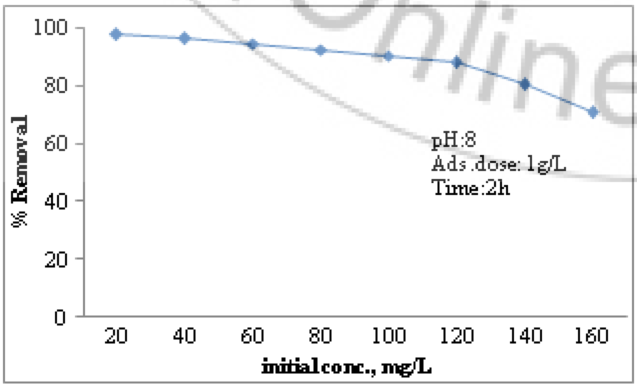

Figure 5: Effect of initial concentration on Copper removal by Rice husk

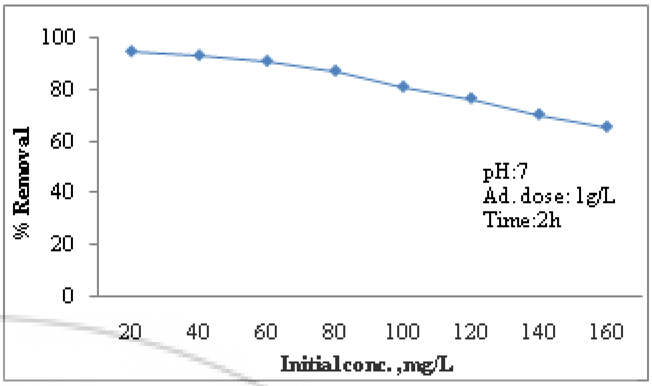

Figure 6: Effect of initial concentration on Copper removal by Groundnut shell

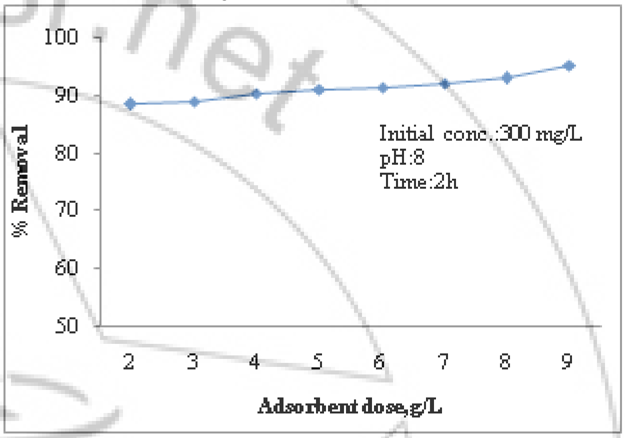

Figure 7: Effect of adsorbent dose on Copper removal by Rice husk

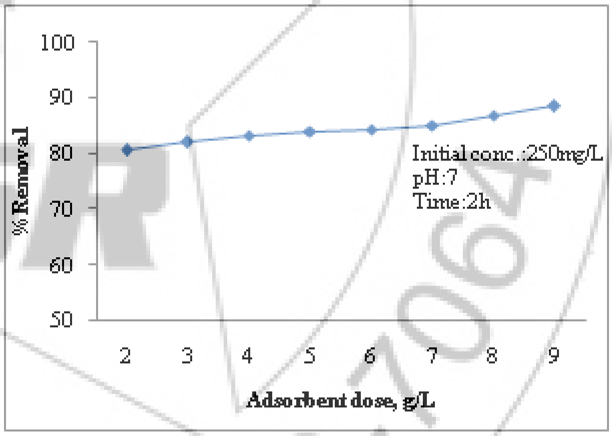

Figure 8: Effect of adsorbent dose on Copper removal by Groundnut shell

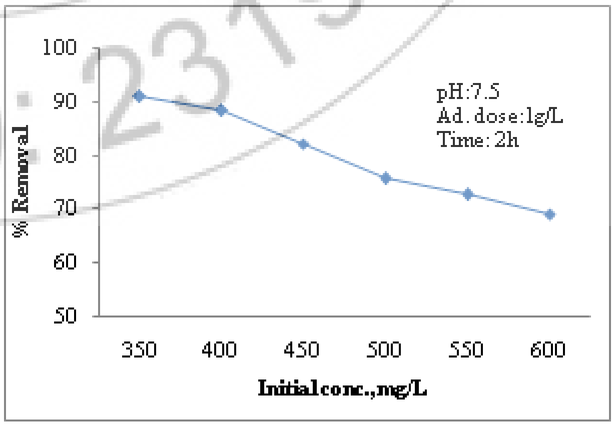

Figure 9: Effect of initial concentration on Copper removal by combined adsorbents

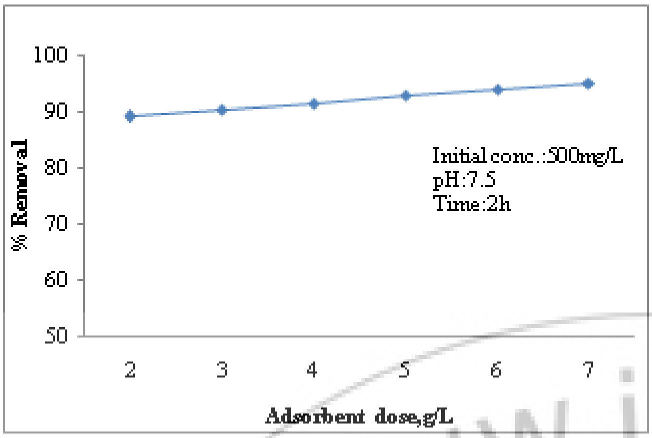

Figure10: Effect of adsorbent dose on Copper removal by combined adsorbents

3.6 Kinetic Modeling

In order to investigate the biosorption kinetics, the Lagergren first order (Lagergren, 1898) and pseudo second order kinetics models were applied.

$$\frac{dqt}{dt} = k1(qe - qt) \qquad (2)$$

This equation can be integrated to yield a linearized form as

$$Log(qe - qt) = Logqe - \frac{k1t}{2.303} \qquad (3)$$

Where,
k_1 = Lagergren rate constant for adsorption (min.$^{-1}$),
q_e = amount of metal biosorbed at equilibrium (mg g^{-1})
q_t = amount of metal biosorbed (mg g^{-1}) at any time t.

The values of k_1 and qe were determined from the slope and intercept of lines in Figure.
The equation of pseudo second order model is:

$$\frac{dqt}{dt} = k2(qe - qt)^2 \qquad (4)$$

Integration and rearrangement of the above equation yielded the following equation

$$\frac{t}{qt} = \frac{1}{k_2 (qe)^2} + \frac{1}{qe(t)} \qquad (5)$$

Where,
k_2 = equilibrium rate constant of second order kinetics model (g mg^{-1} min^{-1})
q_e = the equilibrium capacity
q_t = the biosorption capacity at any time t.

In the present study these are plotted in Fig.11, Fig.12, Fig.13 and Fig.14 for Rice husk and Groundnut shell respectively. The data from the table indicates that the adsorption of Copper by Rice husk and Groundnut shell are of second order reaction.

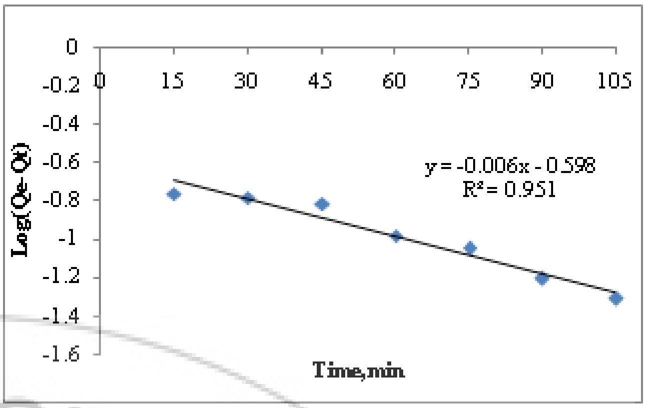

Figure 11: Pseudo first order plot for Copper adsorption onto Rice husk

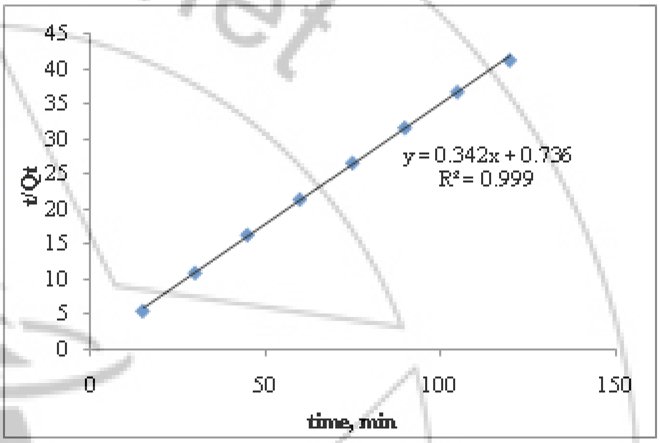

Figure 12: Pseudo second order plot for Copper adsorption onto Rice husk

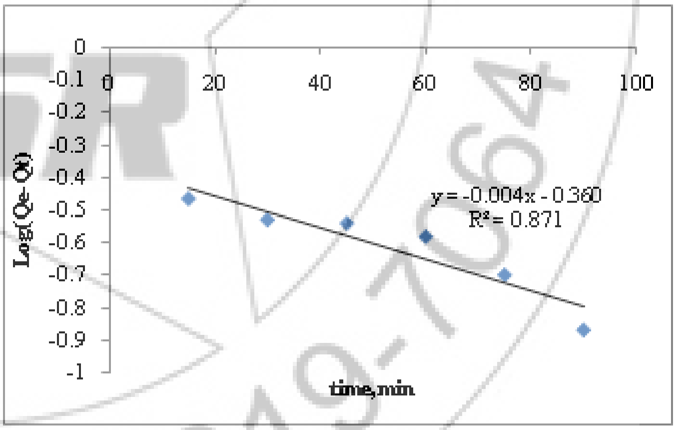

Figure 13: Pseudo first order plot for Copper adsorption onto Groundnut shell

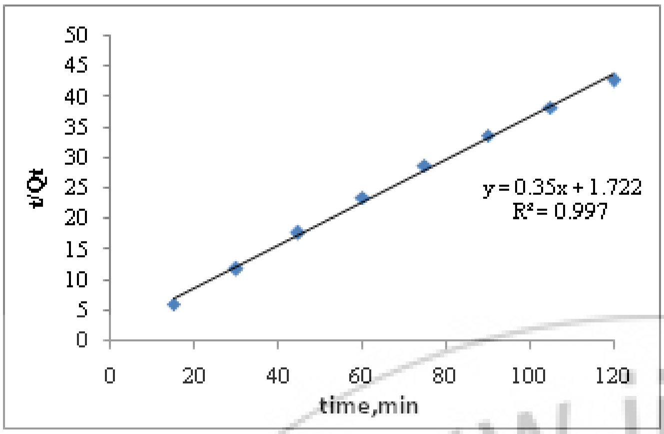

Figure 14: Pseudo second order plot for Copper adsorption onto Groundnut shell

Table 1: The first order and second order sorption rate constants

Adsorbents	Pseudo 1st order			Pseudo 2nd order			Exp. qe (mg/g)
	K^1 (min^{-1})	qe (mg/g)	R^2	K^2 (g/mg min)	qe (mg/g)	R^2	
Rice husk	0.014	3.963	0.951	0.159	2.924	0.999	2.902
Groundnut shell	0.009	2.290	0.871	0.071	2.857	0.997	2.810

4. Conclusions

Batch experiments were conducted to know the potentiality of Rice husk and Groundnut shell as adsorbents for the removal of heavy metal (Copper) from synthetic wastewater. Based on the results and discussions the following conclusions can be derived.

- The maximum removal efficiency of Copper was 96.72 % and 93.90% at pH of 8 and 6 using Rice husk and Groundnut shell respectively.
- The contact time necessary for maximum adsorption was found to be 2 hrs.
- For adsorbent dose of 9 g Copper removal was 94.12% of copper conc. of 300mg/L, 9 g of Groundnut shell was able to remove 91.52% of Copper concentration of 250 mg/L and 7g of combined adsorbents was able to remove 94.96 % of 500mg/L of copper metal ions.
- These results shown that the percentage removal of Copper metal ions was high in case of Groundnut shell when compared with Rice husk.
- From the kinetic study models the adsorption of Copper by Rice husk and Groundnut shell are of second order reaction.
- As low cost adsorbents Rice husk and Groundnut shell can be efficiently used for removal of heavy metals without giving any chemical treatment for adsorbents.

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Author Profile

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