Eco-Friendly Biogenic Synthesis, Characterization of Au/Fe_3O_4Magnetic Nanoparticles and its Catalytic Activity Towards Degradation of Rhodamine-B

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ABSTRACT:

Eco-Friendly biogenic synthesis of gold and iron oxide (Au/Fe_3O_4) Magnetic nanoparticles (MNPs) using Lepidagathis cristata (LC) leaf extract act as capping and reducing agent. The prepared MNPs was characterized by different analytical techniques such as UV-Vis, FT-IR, XRD, TEM,VSM and BET adsorption-desorption methods. The XRD revealed the formation of $LC/Au/Fe_3O_4$ MNPs with crystallite size of about~30 nm. The synthesized $LC/Au/Fe_3O_4$MNPs were found to be ferromagnetic nature, which was confirmed by vibrating sample magnetometer (VSM) at room temperature. Besides, the prepared composite exhibits high specific surface area of23.6 m^2g^{-1}. As well as, the $LC/Au/Fe_3O_4$ MNPs showed a good catalytic nature for the degradation of Rhodamine-B (Rh-B) in the presence of Sodium borohydride ($NaBH_4$) in aqueous solution.

Keywords: Lepidagathis cristata (LC), $LC/Au/Fe_3O_4$ catalyst, VSM, BET, Rhodamine B and Sodium borohydride.

1. Introduction

Due to globalization, modernization and expansion of industrialization, large number of toxic, hazardous harmful chemical substance and dyes are released gradually from day by day and consequently results in pollution. During the last few decades, worldwide environmental pollution is a major problem for all the living organism on the planet earth due to releasing the highly toxic, organic or inorganic pollutants from pharmaceutical, paper, plastic, food and cosmetics industries [1-2]. At present, water pollution is the major problem which mainly caused by the dyes and chemical industries. Typically, the metal nanoparticles are worn for the degradation of organic dyes. Therefore, varies methods including sol-gel, solid state reaction, hydrothermal/solvothermal, quick precipitation, sonochemical methods and microwave-irradiation have been applied for the synthesis of metal nanoparticles [3-11].Nevertheless, majority of these methods suffer from some drawbacks such as expensive reagents, long reaction time, harsh reaction conditions, high pressure/temperature /energy requirement, harmful hazardous and toxic capping agents [12-22].

Owing to the several disadvantages of the physical and chemical methods for nanoparticles preparation, improved attention is paid to the green methods to overcome the above mentioned problems (raised from physical and chemical methods) eco-friendly, non-toxic, clean, biocompatible and economically viable biogenic (green) chemistry approach is utilized. Hence, turning researcher’s focus towards the biogenic approaches for the synthesis of various NPs. the size of the synthesized NPs size and surface morphological nature mainly depend on capping agents, reducing agents and solvents. In chemical method, large amount of chemical substrates used directly effects on the environment but in biogenic method witch use nontoxic agents, it is eco-friendly to the environment. In biogenic syntheses, NPs commonly preferred from the microorganisms and plant extracts as they are relatively economical, non-toxic and eco-friendly. Here plants and microorganisms are referred as nature factories for the synthesis of various NPs.

Biogenic method is eco-friendly approach that fulfills the green chemistry morality, where the invention, design and processing of the developed products are involved with lesser or completely exclusion of utilize and generation of harmful substances. Biogenic synthesis involves the choice about solvents, reactants and reaction maintaining conditions which are planned for minimizing resource expenditure and waste generation. This method is aimed at controling large scale quantity of toxic or its by-products involving in minute reaction circumstances which reduce the utilization of natural energy resources[23-26]. For this reasons, we have selected green method for synthesis of nanoparticles especially metal/metal oxide nanoparticles. Hitherto, there is no report on synthesis of Au/Fe_3O_4MNPs. Therefore, we have report a facile and completely green method for preparation of Au/Fe_3O_4 MNPs by using Lepidagathis cristata (LC) leaf extract it contain active biomolecules such as polyphenols, alkaloids, flavonoids, proteins, enzymes, sugars and secondary metabolites act as reducing and capping agents for synthesis of various NPs. Active biomolecules function as both reducing and capping agents in the preparation of LC/Au/Fe_3O_4 MNPs. In addition, the main objective of this work is to explore the degradation of Rhodamine B dye using LC/Au/Fe_3O_4 MNPs catalyst. The as-synthesized LC/Au/Fe_3O_4 MNPs are characterized by different analytical techniques. The organic dyes are characteristic representative of high toxicity and common organic pollutants in industrial and agricultural wastewater. Therefore, we have selected Rhodamine B (Rh-B) dye as an organic pollutant in this study. These are readily soluble in water. Eventually, the catalytic activity of OS/Au/Fe_3O_4MNPs studied with Rh-B dye degradation.

2. Experimental

2.1. Preparation of the extract

The LC leaves were clean and broadly washed in running tap water, followed by distilled water to take away fine dust particles present on the surface of the leaves then chopped into small pieces. The leaf powder solution was prepared by taking 10 g of finely grinded powder was taken in a in a 250 mL conical flask with 100 mL of deionised water and boiling the mixture at 60°C for 45 Min. After cooling, filter the leaf extract and stored in a refrigerator at 4 ºC for further experimental studies.

1.2. Preparation of the LC/Au/Fe_3O_4 MNPs

Biogenic synthesis of Au supported iron oxide magnetic nanoparticles (Fe_3O_4), 1.62 g of $FeCl_3$. $6H_2O$ and 0.01 M $HAuCl_4.3H_2O$ were dissolved in 100 ml water and add30 mL extract of the LC leaf at 60ºC under vigorous stirring and adjusted 9 pH using sodium carbonate solution. After stirring of the solution1h, the color of the mixture was gradually changed to dark and a suspension of LC/Au/Fe_3O_4MNPs was formed these NPs were centrifugation and separate the MNPs.

1.3.Reduction of Rhodamine B by LC/Au/Fe_3O_4 MNPs

In a dye degradation study experiment, 30 mL 0.2 mM Rh-B aqueous solution was added with 8 mg of the catalyst and the obtained mixture was stirred at room temperature. Subsequently, $NaBH_4$ solution (3 mM, 20 mL) was mixed and continued stirring. The reaction was explored by using UV-visible absorption spectroscopy in fixed time intervals.

2.4. Characterization techniques

FT-IR spectra were observed for *LC* plant leaf extract and synthesize nano composites with Thermo Nicolet FTIR-200 thermo Electron Corporation. X-ray diffraction (XRD) patterns were carried out by using Bruker AXS D8 advanced diffractometer instrument. The shape and size of the LC/Au/Fe_3O_4 MNPs were revealed by transmission electron microscopy (TEM) images, which were obtained by JEOL JEM-3010 machine operated at 200kV. The synthesized LC/Au/Fe_3O_4 MNPs were studied by with vibrational sample magnetometer (VSM-7410). The N_2adsorption-desorption experiment was determined by the Micromeritics analyzer. The explicit surface area was considered using Brunauer-Emmet-Teller (BET) method.

3. Results and discussion

3.1. FT-IR Analysis

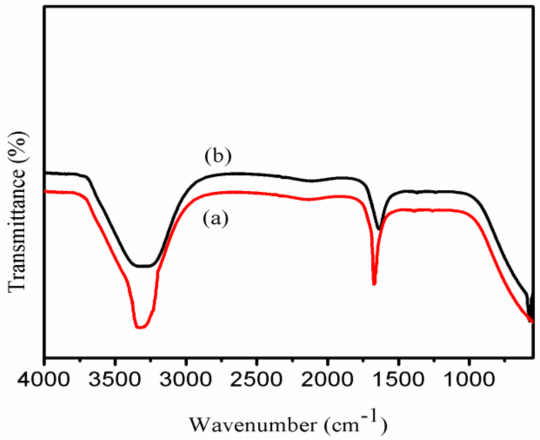

Figure 1: FT-IR spectrum of (a) *LC* leaves extract and (b) LC/Au/Fe_3O_4 MNPs samples.

The FT-IR spectrum (Fig.1a) showed a few peaks at 3335, 1670 cm^{-1}, due to poly phenolic hydroxide and carbonyl group in the molecule. The peaks suggested that the exist flavonoids, alkaloids, sterols, carbohydrates, proteins and terpenoids [27]. The possible bio-molecules responsible for the reduction of the LC/Au/Fe_3O_4MNPs were examined using the FT-IR techniques which clearly demonstrate the interaction between the metals and leaf extract on the surface of metal nanoparticles (Fig.1b). The peaks sited at 3330 and 1635, cm^{-1}correspond to the poly phenolic hydroxide in molecule and carbonyl group. Also, the peak at 579 cm^{-1} in Fig. 1b can be ascribed to Fe-O bond suggesting the formation of Fe_3O_4 nanoparticles [28].

3.2. XRD analysis

The structure of the LC/Au/Fe_3O_4 MNPs was analyzed by powder XRD and results are represented in Fig. 2. The diffraction peaks observed at 2θ values of 30.04,35.41,43.21, 56.90 and 62.50°which corresponds to the (222), (311), (400), (511) and (440) planes offace-centered cubic Fe_3O_4(JCPDC card no: 89-0950), whereas (111), (210) and (211) diffraction peaks of Fe_2O_3 (JCPDS39-1346) could not be experimental [29].

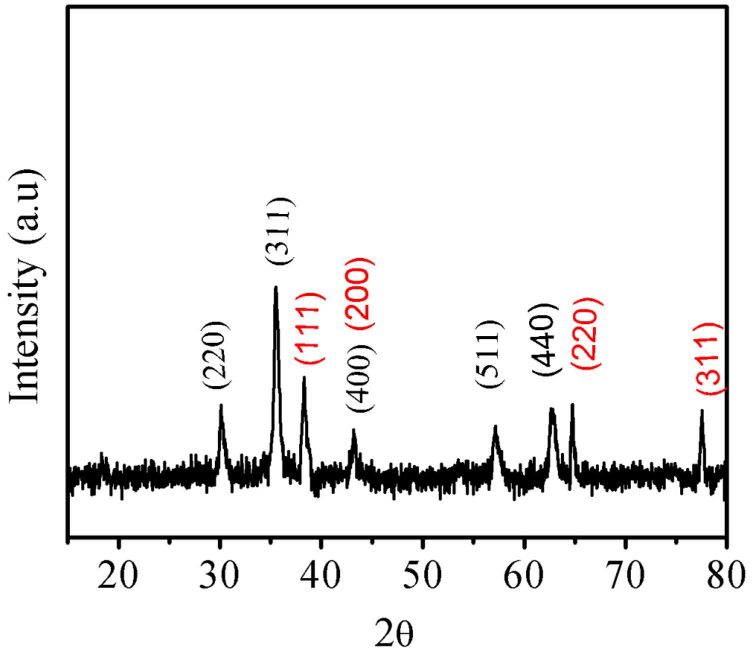

Figure 2: Powder XRD pattern of the OS/Au/Fe_3O_4 MNPs.

The diffraction pattern showing that iron nanoparticles are very easily oxidized to Fe_3O_4. Moreover, the existence of Fe_3O_4 nanoparticles and as well four peaks sited at 2θ of 38.29, 43.21, 64.68 and 77.59°corresponds (111), (200),(220) and (311) planes a face-centered cubic (fcc) structure of the gold (Au) nanoparticles. Further, we have determine the crystallite size of Fe_3O_4 nanoparticles by Scherer equation [30]:

$$D = 0.89 \frac{\lambda}{\beta \cos\theta}$$

where?

D is the average particle size,

λ is the wave length of the Cu-Kα irradiation,

β is the full width at half maximum intensity of the diffraction peak

θ is the diffraction angle

θ is the diffraction angle for the (311) peak of the core shell nanoparticles. The calculated crystalline size for Fe_3O_4 particles was about~30 nm.

3.3. Particle size analysis

The size and morphology of the OS/AuFe_3O_4 MNPs were studied by TEM analysis, which are displayed in Fig. 3A. The size of NPs range between 15 and 30 nm. Moreover, the MNPs exhibits nearly spherical morphology with some agglomeration, it is recognizable due to the magnetic nature of the particles. Furthermore, we employed EDS technique to find out the chemical composition of the LC/Au/Fe_3O_4 MNPs. Fig. 3(B) proved that the product is composed of only Au, O, and Fe in the LC/Au/Fe_3O_4 MNPs. The EDS analysis of MNPs indicates that AuNPs were decorated on the surface of the Fe_3O_4 MNPs.

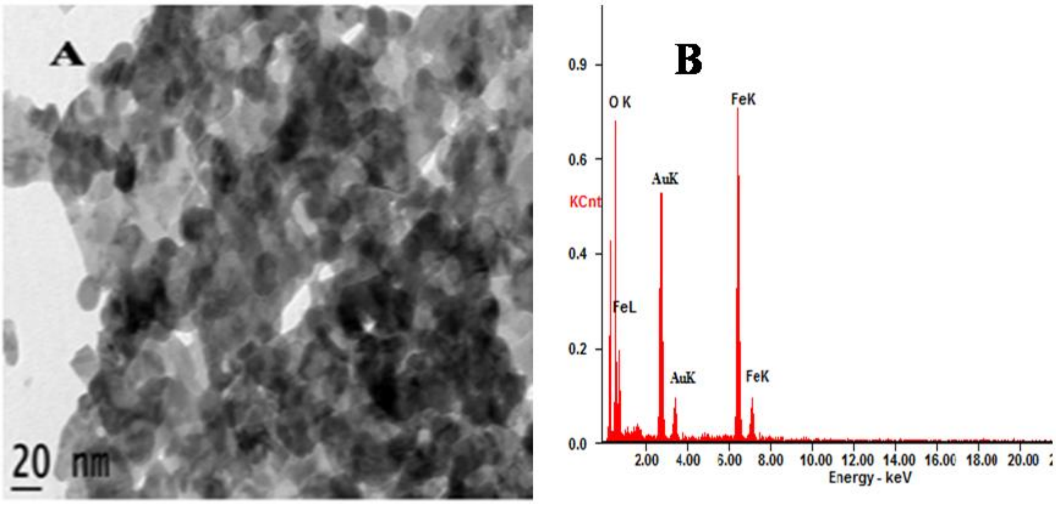

Figure 3: TEM images(A) and EDS analysis of LC/Au/Fe_3O_4 MNPs.

3.4. BET sorption isotherms

The size dependent mesoporous structure was studied by N_2 adsorption-desorption isotherms at 77 K using liquid N_2 as an adsorbent, as shown in Fig.4. The delegate isotherm of the corresponding sample was typed IV, which is a distinguishing of mesoporous nature of respective sample [31]. The intended BET specific surface area of the consequential sample is about 23.6 m^2g^{-1}which is higher than the formerreportedFe_3O_4NPs [32]. Besides, the average pore diameter was investigated through the Barrett-Joyner-Halenda (BJH) method. The result reported that sample have the total pore volume of 0.142 cm^3/g and the pore size allocation was displayed in Fig. 4 (inset), indicating that the product is a mesoporous material with pore sizes ranging from 6-20 nm. Overall, the high surface area and pore-size distribution of the LS/Au/Fe_3O_4 MNPs sample is an advantage for catalysis and biomedical applications.

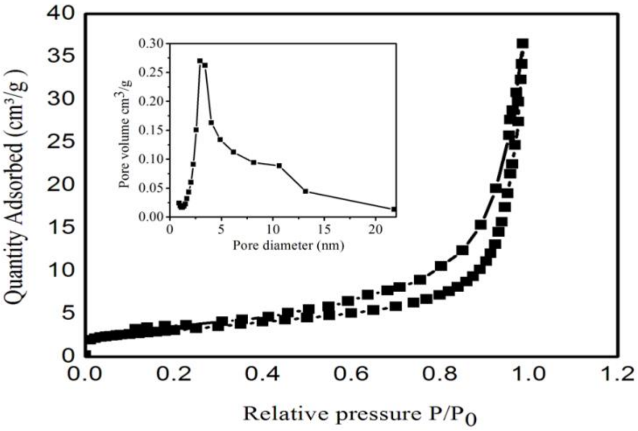

Figure 4: N_2 adsorption-desorption isotherm of OS/Au/Fe_3O_4 MNPs.

3.5. Magnetic measurements

The magnetic activity of the OS/Au/Fe_3O_4 MNPs was investigated using VSM analysis at 300 K (Fig.5). The representative M-H hysteresis curve showed that the ferromagnetic nature of the catalyst. Based on the resulting M-H curves, we can obtain the magnetic parameters such as saturation magnetization (M_s). remnant magnetization (M_r) and intrinsic coercivity (H_c), the calculated M_s, M_r and H_c values are 16.2 emu/g, 2. 2 emu/g and 96 Oe, respectively. The VSM results of OS/Au/Fe_3O_4nanoparticles were similar to the results of other [33].

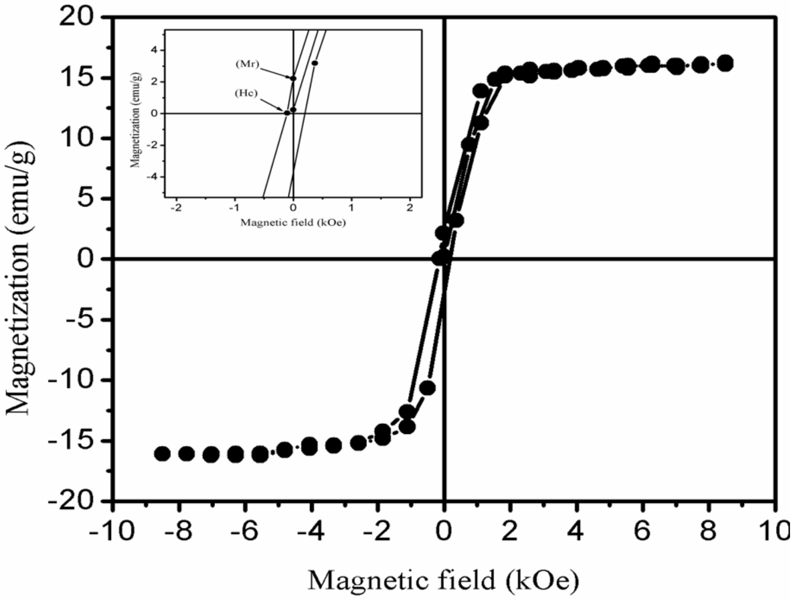

Figure 5: M-H hysteresis loop of OS/Au/Fe_3O_4 MNPs measures at 300 K

3.6. Rhodamine B catalytic degradation in presence of the LC/Au/Fe_3O_4MNPs

Further, as-synthesized LC/Au/Fe_3O_4MNPs was used to explore their application in organic dyes removal in aqueous solution. The reaction evolution was examined by UV–vis spectroscopy. As shown in Fig.6, the solution containing $NaBH_4$ and Rhodamine B was mixed with the LS/Au/Fe_3O_4 MNPs intensity of the strong absorption peak at about 560 nm. To begin to add $NaBH_4$ alone to the organic dye did not reduce, but add LC/Au/Fe_3O_4 nano catalyst degraded dye within 30 min the peak disappeared. After 30 minutes, the LC/Au/Fe_3O_4 MNPs sample could remove ~91% of total Rhodamine B in the presence of $NaBH_4$in the aqueous solution (Fig.7 B). The LC/Au/Fe_3O_4 MNPs catalyst is more reactive than Au NPs(removed only 8%) due to the MNPs showed apparently catalytic activity, this could be attributed to the effect of increased surface area and the unique advantage of easy separation under external magnetic fields. Also, the MNPs facilitates electron transfer from BH_4^- donor to the acceptor Rh-B. Further, the catalytic performance of the synthesized LC/Au/Fe_3O_4 MNPs is compared with earlier reported catalysts for the degradation of Rhodamine B, which are listed in Table. 1.

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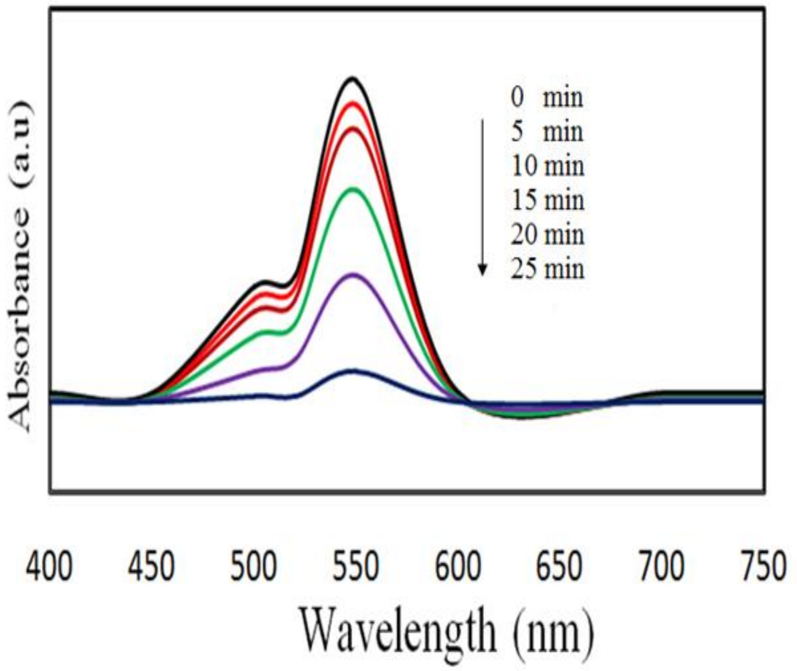

Figure 6: UV-vis spectrophotometer spectrums of Rhodamine B dye in the presence of LC/Au/Fe_3O_4 MNPs with different time intervals 0 to 25 min.

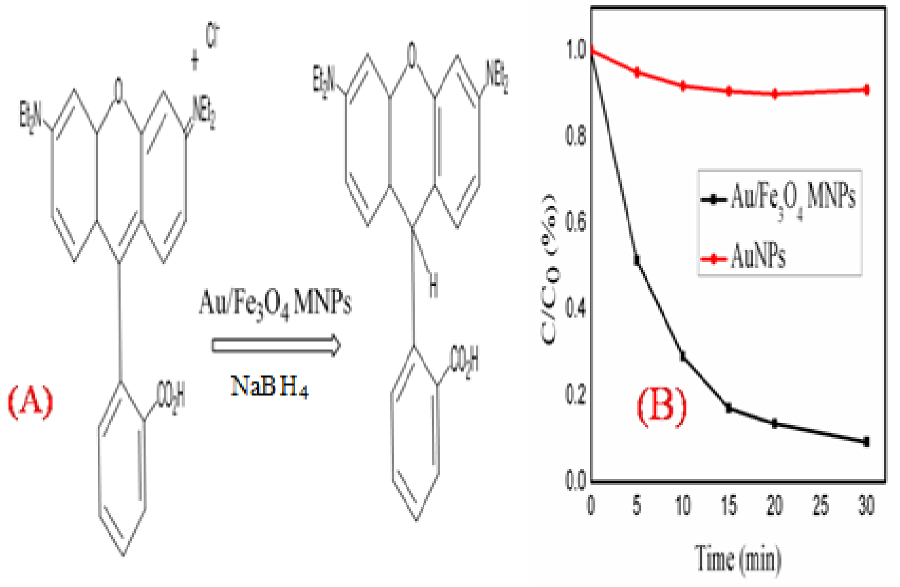

Figure 7: (A) Possible mechanism of Rhodamine B and (B) Adsorption rate of Rhodamine B on LC/Au/Fe_3O_4 MNPs and Au NPs.

Table 1.Comparison of our catalyst activity of reduction of Rh-B with previous reports.

Adsorbent	Time(min)	Reference
Ultrathin MnO_2 nanosheets	90	34
Sn-doped CuO nanoplates	120	35
Agnanoparticles supported on silica spheres	14.5	36

m-Ag/ZnO–TiO_2	20	37
LC/Au/Fe_3O_4 MNPs	25	Present work

4. Conclusion

In summary, we have successfully synthesized LC/Au/Fe_3O_4 MNPs *via* a facile green route using *LC* leaves extract as the reducing and capping agent. The as-synthesized Au/Fe_3O_4 MNPs attributed fcc structure with the crystallite size of ~30 nm, which was confirmed by powder XRD. The LC/Au/Fe_3O_4 MNPs exhibits ferromagnetic nature with magnetic parameters of M_s, M_r and H_c values are16.2 emu/g, 2.2 emu/g and 96 Oe, respectively. Besides, the LC/Au/Fe_3O_4 MNPs were highly capable, magnetically recoverable catalyst for the RhB dye degradation. The experiment was good with respect to selectivity, efficiency and showed its ability to be an efficient catalyst for dyes degradation and reduce their hazardous impact. In all, the synthesis and catalytic studies were non-toxic, economically viable and environmentally benign.

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