SO_2 ADSORPTION ENHANCEMENT OVER AMINE/AMIDE PROMOTED MCM-41

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Abstract

Amine/amide-support mesoporous material has been proven to enhance the acidic gas uptake. Herein, MCM-41 synthesized from rice-husk (RH) was employed as a molecular sieve supporter for dynamic SO_2 adsorption. Four species of classified amine/amide including urea (U), monoethanolamine (MEA), triethylenetetramine (TETA), and dimethylformamide (DMF) were comparatively impregnated with RM. The SO_2 adsorption was carried out in a fixed bed column at 42,000 hr^{-1} WHSV. DMF impregnated RM (DMF-RM) provided higher uptake capacity than other impregnated RMs. The SO_2 favors adsorbed on tertiary amine/amide rather than primary and secondary ones. The higher DMF content could enhance SO_2 adsorbability. The condition ranges of using 3%wt of DMF loading, initial concentration of SO_2 in synthetic waste gas less than 120 ppm, and room temperature up to $60^{\circ}C$ provided the optimal adsorption capacity toward SO_2. The regeneration of adsorbent performed completely at moderate temperature of $200^{\circ}C$. DMF-RM showed 4% capacity declination after 8 cycles consecutively uses.

Keywords: SO_2 Adsorption, MCM-41, Breakthrough Curve, Regeneration

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Introduction

SO_2 have been considered for one of serious pollutants from any combustion processes, especially for coal-fired power plant, petroleum and petrochemical plants. Due to the great concern in environmental issues, many alternative technologies have been deeply purposed. Dry and wet scrubbing processes are practically used to treat this harmful gas. One drawback of the scrubbing processes relies on amount of scrubbing agents (lime, $Ca(OH)_2$ and limestone, $CaCO_3$) used. Moreover, the processes are very energy-intensive, and all scrubbing agents are turned to be a huge amount of solid waste of $CaSO_4$, which requires further treatments. Moreover, used absorbents cannot be regenerated. Intensive studies on regenerable adsorbents and/or reactive catalysts of SO_2 are very interesting approaches (Gang et al., 2022; Berger et al., 2018; Rahmaninejad et al., 2012; Kylhammar et al., 2008).

Even though adsorption of SO_2 on activated carbon, zeolites, metallic oxides, etc. have been studied, the performance was not reached to a satisfactory level. Modified surface of adsorbents is one of emerging interests for regenerable SO_2 adsorption technologies. Abdulrasheed et al. (2018) purposed amine modified AC as an appropriate adsorbent for the sulfur-lean flue gas system, like coal fire power plant. The doping of N-substances provided significant effect to SO_2 uptake. However, with strong chemisorption between SO_2 and amine sites, the sorption of CO_2 could be offensive. To overcome this phenomena, small loading of N-doping has been recommended (Hanif et al., 2020; Yu et al., 2019; Tailor et al., 2014; Tailor & Sayari, 2016; Zhi et al., 2011; Xu et al., 2005).

Residues from burnt rice husk biomass have been known as a precursor to synthesize zeolites. Fly ash and rice husk ash containing a large portion of silica are recently utilized for mesoporous material MCM-41 and SBA-15 (Bhagiyalakshmi et al., 2010; Dhokte et al., 2011; Kumar et al., 2001; Li et al., 2017). The materials possess uniform pores, large surface area, high thermal stability, and readily for a modification, therefore they are able to be used as adsorbent supports. According to their properties, the functionalized materials by amine/amide of highly basic sites, should favor the acidic SO_2 uptake. Amine/amide groups including primarily-, secondary-, and tertiary-, have been studied to enhance the acid gas sorption uptake (Uyanga & Idem, 2007; Aaron & Tsouris, 2005; Diaf & Beckman, 1995). The information of amine-modified adsorbent is limited to CO_2 capture rather than SO_2 sorption. The acid gas CO_2 adsorption capacity depends on the number of amine groups and type of amine groups in the loading. It was mentioned that nucleophilicity of anion and basicity of amine groups play key role for SO_2 adsorption (Xu et al., 2019). A series of the results were reported on using amine modified SBA-15 for SO_2 adsorption. The removal of SO_2 over SBA-15 loaded polyethylene glycol was reported effectively from 500 to 2 ppm at flow rate of 60 ml/min under atmospheric pressure, with the breakthrough adsorption capacity of 5.4 mg SO_2/g (Wang et al., 2009). The selection of amine/amide for the surface modification affects to the basicity of the obtained materials. Tertiary amine are known to provide low affinity toward CO_2, which is readily interact with SO_2. Zhi et al. (2011) showed the significant improvement on SO_2 adsorption after impregnating triethanolamine (TEA) on SBA-15. Pore enlargement for PE-MCM-41 (PME) and SBA-15PL and then modified with polypropyleneimine dendrite and polyethyleneimine (PEI) was studied by [9]. He claimed that PEI-PME provided the highest adsorption capacity of 4.68 mmol SO_2/g. However, the reusability of SO_2 adsorbents has not been studied widely.

In this work, MCM-41 mesoporous materials synthesized from rice husk ash was used to study the SO_2 adsorption. The effects of functionalized amine/amide and their reversible ability were investigated. Studied variables of loading of amine/amide, temperature condition, initial concentration, and flow rate were performed. Moreover, the studied adsorbent was tested for its reusability.

Materials and method

1) Preparation of MCM-41 and modified MCM-41

The synthesis of MCM-41 mesoporous silica has been described elsewhere (Areerob et al., 2011). Silica was extracted directly from rice husk (RH) under a refluxing technique in HCl solution, Afterward, it was calcined at 700°C for 4 hours. Obtained silica was used to prepare sodium silicate solution. The mesoporous material was prepared by using hexadecyl (trimethyl) ammonium bromide (CTAB) as a template and sodium silicate obtained previously. The synthesis was done in hydrothermal condition at 90°C for 3 days and calcined at 600°C for 6 hours. MCM-41 from rice husk silica (assigned as RM) in white powder was obtained.

Urea (U), Monoethanolamine (MEA), triethylenetetramine (TETA) and dimethylformamide (DMF) were loaded on RM by an impregnation technique. A solution of amine/amide was prepared in a dispersing agent; acetone. The impregnation was carried out in a sonication condition. After that the soaked material was heated up to 65°C to expel acetone out. The materials were assigned as X-RM; where X represents amine/amide loading species. For example: U-RM represents MCM-41 from rice husk silica promoted by urea.

2) Dynamic adsorption experiments.

The dynamic study of SO_2 adsorption was carried out in a fixed bed unit. Studied adsorbent was sieved to 2 mm in equivalent diameter before loading into a quartz tube with an internal diameter of 6 mm. Approximately 1 g of adsorbent was used. The condition provided the packing length long enough compared to the tube diameter ($L/D > 20$) to overcome the external mass transfer effect. The experiment was tested in atmospheric pressure using the starting gas of 1,000 ppm SO_2 in balance of nitrogen. The inlet gas was further mixed with nitrogen to adjust the inlet SO_2 concentration. The tests were carried out under the WHSV of 42,000 hr^{-1}. The concentration of SO_2 in the effluent line was monitored online by SO_2 analyzer, model: SOA-7000 Shimadzu, Japan.

The sorption capacity of each studied sorbent is calculated through the area covered by the breakthrough curve, as shown in Equation 1.

$$SC = \frac{F}{m} \int_0^{\infty} (C_{in}-C_t)\,dt \qquad \text{(Eq. 1)}$$

Where SC: Sorption capacity; mg/g of sorbent
F: Flow rate of studied exhaust; ml/min
m: Weight of sorbent; g
C_{in}: SO_2 feed inlet concentration; mg/m^3
C_t: SO_2 concentration at certain time; mg/m^3

The adsorption breakthrough time was considered at the 20% of an initial SO_2 concentration in the feed stream. For the reusability study, sorbent was regenerated by heating to 80-200°C right after the adsorption. The regeneration of adsorbent was kept for 30 min until SO_2 could not be detected (less than 0.1 ppm).

3) Material characterizations

Studied adsorbents were characterized for their physicochemical properties as presented;

Powder XRD patterns were obtained from a Bruker AXS: D8 ADVANCE A25 diffractometer, United States. The x-ray was generated from a Cu Ka target with a potential of 35 kV. The scan was performed between 2θ values of 2 and 10 degrees at a scan rate of 0.02 degrees per minute.

N_2 Adsorption-desorption was performed, by a Micromeritics ASAP 2010 sorption analyzer, United States, to evaluate the surface area and pore size distribution. Sample was pretreated with heat at 105°C in vacuum environment overnight before the measurement. Specific surface area was calculated by using the standard BET method at the relative pressure range of 0.05-0.30, while pore size distribution was computed based on the BJH equation.

The IR spectra represents surface functional groups were obtained by a Fourier Transform Infrared spectrometer (FTIR-UATR, PerkinElmer spectrum two, United States). The sample was scanned within the wavenumber range of 650 to 4,000 cm^{-1}.

The surface morphology of the materials was examined by SEM (JSM-6700F, JEOL, Japan), equipped with EDX for elemental analysis and their element distributions.

Results and discussion

1. Material properties

The N_2 adsorption-desorption isotherms of fresh adsorbents (RM) modified with amine/amide of 1% (as examples) are shown in Fig. 1. A sharp increase between relative pressure P/P_o of 0.25 and 0.35 corresponds to capillary condensation within uniform mesopores. Small hysteresis loops in the adsorption and desorption cycle upon pore condensation were observed on each adsorbent, which indicated that RM and modified RM contained mesopore size. The adsorptions of N_2 isotherms over all samples presented type IV (IUPAC) patterns, which confirmed a character of highly porous and one-dimensional material. RM sample has mesopore size distributions with the average pore size of 3.2 nm. The surface properties were in the same results discussed by others (Areerob et al., 2011; Kumar et al., 2001).

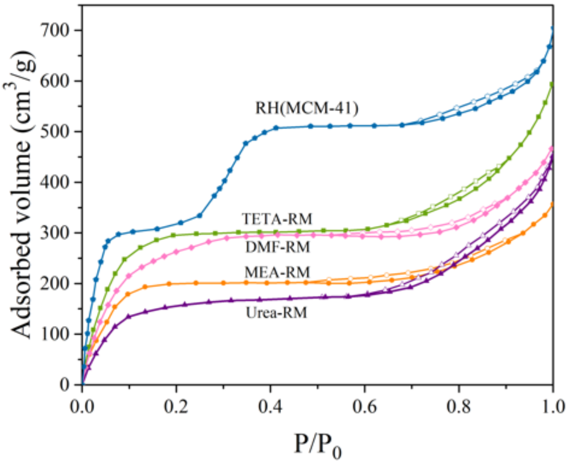


Fig. 1 N_2 adsorption-desorption of MCM-41 (RM), U-RM, MEA-RM, TETA-M, and DMF-RM (Considering the loading at 1%wt).

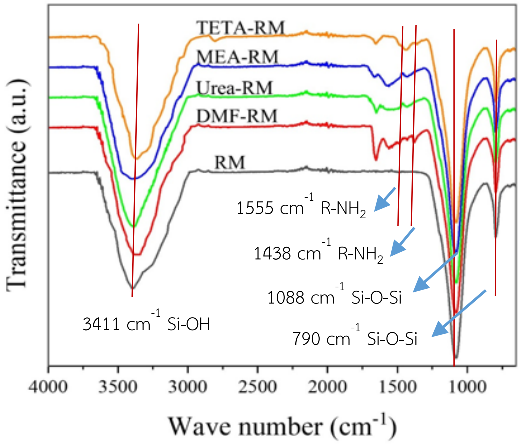


Fig. 2 FTIR spectra and of MCM-41 (RM), U-RM, MEA-RM, TETA-M, and DMF-M (Considering the loading at 1%wt).

Amine/amide modified RM samples were analyzed for their surface area and average pore size. The data is tabulated in Table 1. The surface area of all amine/amide modified RM contained less surface area, while the average pore size was little smaller compared to that of pristine RM. This was probably caused by the blocking of amine/amide species on top and or inside the pore structures.

Table 1 Surface properties of studied adsorbents

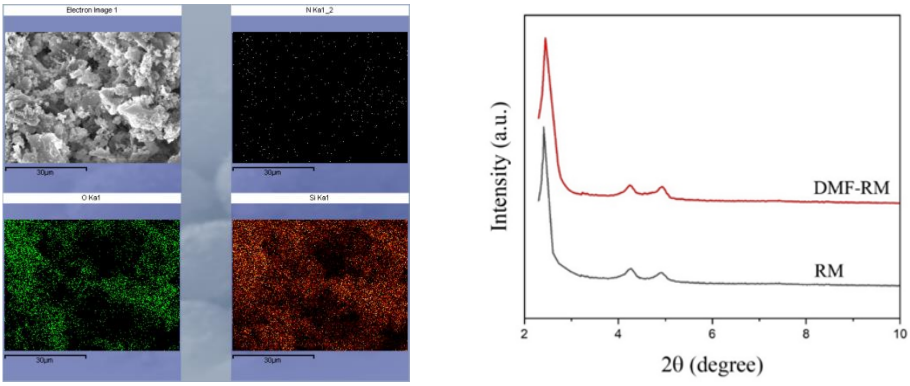
Adsorbent	BET Surface area (m²/g)	Pore volume (cm³/g)	Pore size (nm)	N- component (wt%)
MCM-41	715	0.49	3.2	--
1% U-RM	420	0.36	2.91	0.77
1% MEA-RM	448	0.34	2.95	1.44
1% TETA-RM	491	0.34	2.98	0.85
1% DMF-RM	480	0.35	2.89	0.94

To confirm the availability of amine/amide species in the modified RM, they were analyzed through an elemental analysis. Nitrogen compositions grafted onto the material considering samples with 1% loading on each amine/amide modified RM are presented in Table 1. The amounts of N are 0.77, 1.44, 0.85, and 0.94 were observed after modifying with urea, MEA, TETA, and DMF, respectively. The results corresponded with their stoichiometric reaction of silinol groups (Si-OH) on RM surface and amine species.

Fig. 2 shows FTIR spectra of RM and RM modified TETA, DMF, MEA, and urea with 1%wt loading. It was observed that the RM displayed a large availability of –OH group around 3411 cm^{-1}, which corresponded to Si-OH hydrogen-bonded OH. They were absorption bands at 1088 cm^{-1} and 790 cm^{-1}, which could be attributed to Si-O-Si strong siloxanes, and Si-O-Si, respectively. The amine/amide modified RM displayed similar spectrum patterns to the pristine RM, as described. It indicated the impregnation of TETA, DMF, MEA, and urea, did not affect the structure of RM. In addition, the FTIR spectrum of TETA-RM showed the characteristic bands at 1555 and 1438 cm^{-1} were observed. They corresponded to N-H bending of primary amine (R-NH_2) composed in TETA structure. For amide modifications, bands at 1560, 1653 cm^{-1} were observed corresponded to the availability of C=O stretching for 1^{o} and 3^{o} amide, respectively. Bands of 1085 1135 1636 and 1480 cm^{-1} were presented for DMF-RM and U-RM. They indicated the presence of C-N stretching and N-H bending of amine species, respectively. The EDS analysis showed uniform dispersion of N ions on DMF-RM (as an example). This confirms that the impregnation technique provides good dispersion of loading over supported material.

SEM images and XRD patterns are shown in Fig. 3. Only DMF-RM was selected as an example, and its element mapping of Si, N, and O. Fig. 3a illustrates particles with irregular shape and dimensions. The EDS analysis showed uniform dispersion of N ions on DMF-RM. This confirms that the preparation technique provides good dispersion of nitrogen loading over supported material.

Fig. 3b presents the XRD spectra of RM and DMF-RM. It was found that 3 peaks for both samples; the first peak was the emphatic peak at 2.5 degree, representing the hexagonal structure, the second peak at 4.3 degree and the last one at 4.9 degree. The results confirmed the form of MCM-41 material structure (ICDD#49-1712).



a)   b)

Fig. 3 a) SEM-EDX of 3% DMF-RM (Including EDS for N, O and Si), b) XRD spectra of RM and DMF-RM.

2. Adsorption tests

MCM-41 synthesized from rice husk (RM) is a highly ordered mesoporous structure with availability of high surface area. It also has a large number of silinol group as the main functional group. RM and its modified ones were tested the adsorption of SO_2 in a packed column. The total flow rate of mixed gas was introduced continuously 500 ml/min, corresponding to 42,000 hr^{-1} of WHSV. The breakthrough curves of SO_2 capture performed at $30^{\circ}C$ are shown in Fig. 4a. In this study, the loading of amine/amide was fixed at 3%wt. The sorption capacity of DMF-RM, TETA-RM, MEA-RM, and U-RM were calculated (by Eq. 1) to be 9.325, 4.772, 3.53, and 3.31 mg_{SO2}/g_{ads}, respectively. The sorption capacity on amine/amide modified RM were also higher than RM. Their capacities were higher than RM itself, 2.92 mg_{SO2}/g_{ads}, as presented in Fig. 4b. The SO_2 breakthrough time on amine/amide modified RM were longer than that on pristine RM. Considering the amine/amide modified RM, they possessed the surface area less than RM, however, the constitutions of amine and amide groups on the surface of modified samples might play a role on adsorption improvement. Considering on the highest SOx caption capacity, we showed two profiles of breakthrough curves of DMF-RM. One of the profiles was not complete after adsorption time after 60 min. This might be caused by the channeling package problem on the top part of the column.

The results revealed that species containing 3° amine/amide was able to increase the adsorption units higher than those containing 2° and 1° amine and amide. The results corresponded with the results described by Yu et al., (2019). The performance of DMF-RM was considered further in loading, temperature, initial concentration effects and the reusability of the adsorbent.

2.1 Effect of loading

DMF was impregnated onto RM with different weight percent (1, 3, 5%wt). They were performed at 30°C and 42,000 hr^{-1} of WHSV. The higher DMF loading, the sorption capacity and breakthrough time are extended higher and longer, as shown in Fig. 4b. DMF-RM loading varied 1-5%wt provided the SO_2 sorption capacity in similar range of 11.6 to 12.7 mg/g, while the breakthrough time moved from 40 min to 120 min ca. The higher amount of amine loaded affected highly to the SO_2 removal. However, the leading of 5%wt might give some inconsistent results, caused by the agglomerated particles.

2.2 Temperature effect

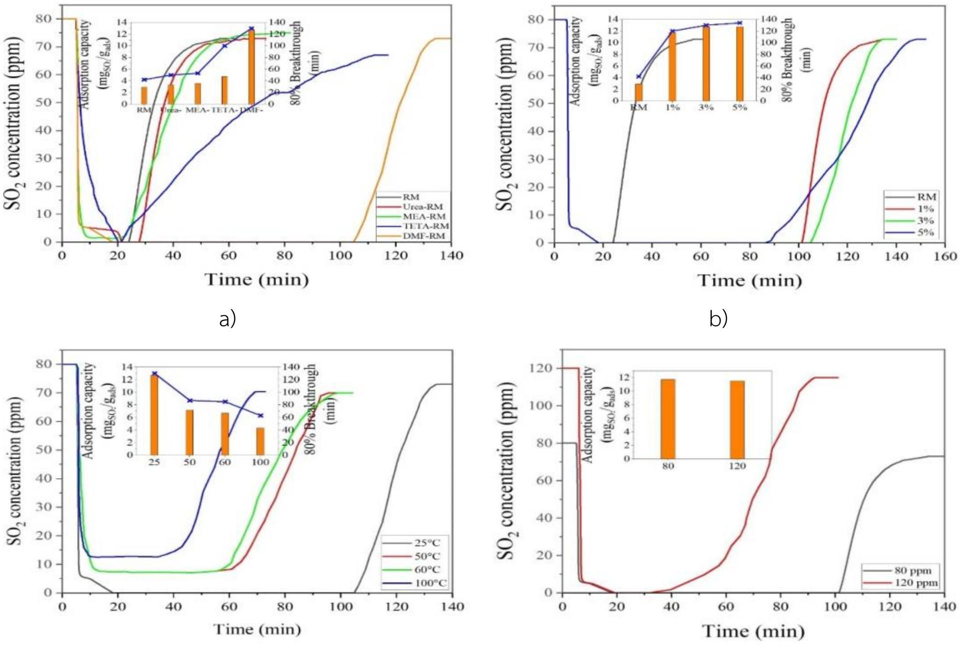
The effect of adsorption temperature was performed at 25, 50, 60, and 100°C. It was conducted with an initial SO_2 concentration of 100 ppm and WHSV 42,000 hr^{-1}. Results of breakthrough curves and capacities are presented in Fig. 4c. The adsorption capacity decreased dramatically from 9.4 to 7.1, 6.7, and 4.3 mg/g, respectively. The breakthrough time therefore reduced from 100 min to 62 min. It was obvious that adsorption bonding of SO_2 molecules with the adsorbent sites possibly became weaker at higher temperature. Consequently, the adsorption capacity became lower, and the breakthrough curves became suddenly dropped.

2.3 Initial concentration effect

Initial concentration of SO_2 was studied under the same WHSV. Using an initial concentration ranged between 80-120 ppm, it can be seen, in Fig. 4d, the breakthrough time was greatly reduced with higher concentration. Considering the sorption capacity, they provided very similar values, which were 11.7 and 11.4 mg/g, respectively. As observed that the uptake amount was little lower with high initial concentration. Moreover, the adsorption of high concentration performed completely within the shorter period (∼83 min.) compared to that of low concentration (∼112 min.). Besides, the breakthrough curve of higher initial concentration did not sharply rise as that of lower initial concentration. This indicated that higher concentration might not be recommended under this WHSV conditions.

3. Reusable potential of adsorbent

One focusing point of this work was on the stability and repeatability of selected adsorbent. To study the regeneration of adsorbent, the adsorbent was saturated by SO_2 were desorbed after a breakthrough experiment. The desorption of SO_2 out from the adsorbent surface (3%DMF-RM) was done through higher temperature swing process. Temperature was raised to 80, 120 and 150°C and kept for 30 min. The column was cooled down, afterward, before running for the next consecutive round. It was observed the desorption peaks observed with temperature at 80, 120 and 150°C, were found smaller compared to the uptake one, as shown in Fig. 5. It, therefore, indicated that with these temperatures was unable to desorb SO_2 species attached to adsorbent completely. The condition at 200°C was then recommended. The material (3%DMF-RM) was exposed to eight consecutive cycles of 80 ppm SO_2. Little change in SO_2 adsorption capacity was observed over eight cycles. It is approximated that the sorption capacity declined about 4% of the initial capacity after the 8th cycle.



a)

b)

c)

d)

Fig. 4 a) SO_2 breakthrough curves on different kinds of modified –RM, b-d) SO_2 breakthrough curves over DMF-RM on the study of loading, temperature, and initial concentration, respectively, and their corresponding uptake capacities and breakthrough times (insets).

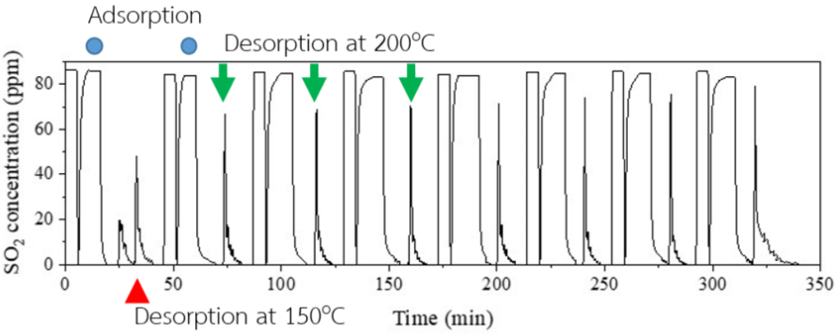


Fig. 5 Adsorption-regeneration of SO_2 over DMF-RM for 8 cycles.

Conclusions

Rice husk was utilized as a potent precursor for the preparation of MCM-41 (RM). Surface area and average pore diameter of the synthesized MCM-41 were found to be 600-800 m^2g^{-1}, and 3.2 Å. RM was modified by amine/amide (urea (U), monoethanolamine (MEA), triethylenetetramine (TETA) and dimethylformamide (DMF)). Microcrystalline structure of hexagonal for both pristine and modified RM was examined by XRD. The loading of amine/amide had no significant effect to the structure of RM. The loading distribution was found uniformly through SEM-EDS. Amine/amide modified RM adsorbents were tested for SO_2 removal in synthetic waste gas. At the optimal conditions (42,000 hr^{-1} WHSV, initial SO_2 concentration <120 ppm, temperature <60°C), the DMF-RM exhibited a maximum removal of 12 $mg_{SO2}/g_{adsorbent}$. The regeneration of adsorbent was completely exhibited at 200°C.

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