

## Adsorption of dimethylamine from aqueous solution by manganese dioxide

L. Yang, Z. Chen, D. Zhang, Y. Liu, Y. Han and J. Shen

### ABSTRACT

Removal of precursors of *N*-nitrosodimethylamine (NDMA), such as the most direct precursor dimethylamine (DMA), might be an effective method to control NDMA formation during practical water treatment process. Adsorption of DMA onto manganese dioxide ( $\text{MnO}_2$ ) from aqueous solution has been investigated using batch experiments in this study. Results indicate that DMA adsorption is initially rapid (in the first 5 h) and the adsorption process reaches a steady state after 15 h. The adsorption isotherms are well described by the Freundlich models. The desorption shows an irreversibility of DMA adsorption onto  $\text{MnO}_2$ . The effects of temperature, pH, ionic strength, humic acid, and the presence of other secondary aliphatic amines on adsorption processes are also examined. According to the experimental results, the amount of DMA adsorbed increases with an increase of temperature from 288 to 308 K, and with a decrease of ionic strength from 1 to 10 mM. The maximum adsorption appeared at pH 7.0. However, the amount of DMA adsorbed onto  $\text{MnO}_2$  does not show obvious difference in the presence of humic acid. According to the results, it suggests that the adsorption is primarily brought about by electrostatic interaction between DMA and  $\text{MnO}_2$  surface.

**Key words** | adsorption, dimethylamine, manganese dioxide

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### INTRODUCTION

In spite of many recent efforts in the mechanisms of *N*-nitrosodimethylamine (NDMA) formation, the most effective precursor of NDMA has remained unknown until now. As the most direct precursor, dimethylamine (DMA) was often used in the study of NDMA formation mechanism (Mitch *et al.* 2003) and control strategy (Lee *et al.* 2007, 2008). DMA is a simple short-chain secondary aliphatic amine which is frequently present in environmental samples, biological fluids and industrial waste materials at trace level (Zhao *et al.* 2003). According to the investigation of water in a city of northern China (Ben 2009), the concentration of DMA in the source water and the effluent of water-supply plant were 101.2  $\mu\text{g/L}$  and 63.5  $\mu\text{g/L}$ , respectively.

To control the yield of NDMA formation in treated waters, two different strategies, i.e. removal of NDMA after its formation or degradation NDMA precursors to prevent NDMA formation, can be applied. Due to the special physi-

cochemical characteristics of NDMA, it cannot be removed well from the water by conventional treatment technologies, such as air-stripping, activated carbon and biodegradation (Fleming *et al.* 1996). Currently, the most commonly applied treatment method for aqueous NDMA is photolysis by ultraviolet (UV) radiation (Liang *et al.* 2003; Lee *et al.* 2005), which is not quite cost-effective. Therefore, removal of precursors would be beneficial to decrease NDMA formation during water treatment process.

DMA is readily removed by secondary biological treatment, during which DMA concentrations could be reduced by at least an order of magnitude (Mitch & Sedlak 2002). Since nitrite is commonly present in biological wastewater treatment systems as a metabolite of the nitrification and denitrification processes, NDMA can be formed *via* nitrosation during secondary biological wastewater treatment (Valentine *et al.* 2005).

Lee *et al.* (2007, 2008) reported that NDMA precursors could be removed effectively by strong oxidants, such as ozone, chlorine dioxide and ferrate. And with the pre-oxidation, remarkably reduction in the NDMA formation potentials (NDMA-FP) was observed. Tertiary amines containing a DMA functional group could produce DMA after pre-oxidation, and NDMA-FPs were relevant with the yield of DMA formation. But it was reported that NDMA was detected after ozonation (Andrzejewski *et al.* 2008), potassium permanganate (KMnO<sub>4</sub>) reaction (Andrzejewski & Nawrocki 2009) and other oxidation treatment (Andrzejewski & Nawrocki 2007) of aqueous solutions of DMA with high dosage of oxidants, and nitrosation was assumed to be the main NDMA-formation pathway.

Since chemical methods have a potential risk on NDMA formation with the removal of DMA, effective physical treatment process would be the solution for both precursor elimination and NDMA yield control. DMA, like many nitrogen-containing NDMA precursors, is charged at neutral pH, so it should be even less susceptible to treatment by air stripping or adsorption compared to NDMA. Hwang *et al.* (1994) reported that DMA was removed poorly by granular activated carbon.

In our earlier study on removal of DMA by O<sub>3</sub> combined with KMnO<sub>4</sub>, removing the MnO<sub>2</sub> suspensions formed during pre-oxidation process was beneficial for the reduction of NDMA yield in post-chloramination process. Andrzejewski & Nawrocki (2009) identified the suspensions generated during KMnO<sub>4</sub> reaction with DMA as MnO<sub>2</sub>, and indicated that MnO<sub>2</sub> suspension might catalyze NDMA formation through nitrosation pathway. But according to our results, the effect of MnO<sub>2</sub> on DMA might be removal by adsorption rather than catalyzed nitrosation. Numerous authors have documented that natural or synthetic MnO<sub>2</sub> could be used to remove heavy metals (Feng *et al.* 2007), phenol, chlorophenols (Zhang *et al.* 2002) and natural organic matters (Liu *et al.* 2005; Zhang *et al.* 2009) in aqueous as adsorbent because of its high adsorptivity.

The purpose of this study is to investigate the adsorption characteristics of DMA from aqueous solutions onto MnO<sub>2</sub>. As a first step in the adsorption of DMA, the adsorption equilibrium time is quantified. Then adsorption isotherms are conducted at batch experiments under different temperatures, the desorption of DMA by MnO<sub>2</sub> also has been studied to determine the reversibility of adsorption. Influencing parameters such as pH, ionic strength, humic acid, and the presence of other two secondary aliphatic amines are evaluated to characterize the extent of DMA adsorption.

## MATERIALS AND METHODS

### Materials

All experiments were conducted using deionized water. Dimethylamine hydrochloride (99%), methylethylamine (94%, MEA) and diethylamine ( $\geq 99\%$ , DEA) were purchased from Acros Organics. Potassium permanganate (99.5%), sodium thiosulfate (99.0%), sodium silicate and all other reagents were purchased from Tianjin Baishi Chemical and used without further purification.

### Preparation of MnO<sub>2</sub>

The adsorbent, MnO<sub>2</sub>, was prepared in the laboratory by the chemical precipitation method. The precipitate was obtained by slowly mixing aqueous solutions of 0.24 mol/L KMnO<sub>4</sub> and 0.09 mol/L Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> with magnetic stirring. After reaction for 2 h, Na<sub>2</sub>SiO<sub>3</sub> was slowly added to the solution to improve strength and sedimentation effect of the MnO<sub>2</sub> precipitate. The precipitate was aged at 313 K over 48 h, and then collected and repeatedly rinsed with water until the pH and conductivity of the rinse water remained constant in three consecutive rinses. The precipitate was dried at 333 K for 24 h. Before using as the adsorbent, the dried precipitate was grinded to 75–125  $\mu\text{m}$ .

### Characterization

X-ray diffraction (XRD) powder patterns were recorded on a diffractometer (D/max-rB, Japan) using Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm, 40 kV voltage, 150 mA electric current, 0.02° of step, and 10–90° of scanning range).

FT-IR spectra of the adsorbent recorded using FT-IR spectrometer (Perkin Elmer, USA) with a resolution of 2 cm<sup>-1</sup> and a spectral range of 4000–400 cm<sup>-1</sup>.

Metals leaching from the adsorbent into the solution were determined by inductively coupled plasma atomic emission spectrometer (ICP-AES, Optima5300DV, Perkin Elmer, USA).

### Adsorption experiments

The effect of contact time on DMA adsorption onto MnO<sub>2</sub> was studied based on the DMA concentration in the range from 0.01 mM to 0.5 mM. The adsorption experiments were carried out by mixing 125 mg MnO<sub>2</sub> samples with a 250 mL aqueous solution in a 500 mL stirred flask at temperature of 298 K. Samples were taken out and filtrated by a glass fiber

with 0.45  $\mu\text{m}$  pore size at different times. Then the residual concentration of DMA was determined.

The adsorption isotherm experiments of DMA onto  $\text{MnO}_2$  were performed on the basis of a batch experiment. A given amount of adsorbent (25 mg) was placed in a 100 mL flask, into which 50 mL of a DMA solution with varying concentrations was added. The experiments were performed in a temperature-controlled water bath shaker for 24 h at a mixing speed of 170 rpm. After the adsorption reached equilibrium, the solutions were filtered and analyzed for the remaining concentration of DMA. The amount of DMA adsorbed onto  $\text{MnO}_2$  was calculated from the mass balance equation as

$$q_e = \frac{(c_0 - c_e)V}{M}, \quad (1)$$

where  $q_e$  (mg/g) is the amount of DMA adsorbed per gram of  $\text{MnO}_2$  at equilibrium;  $c_0$  (mg/L) and  $c_e$  (mg/L) are the initial and equilibrium liquid phase concentration of DMA, respectively;  $V$  (L) is the volume of DMA solution, and  $M$  (g) is the mass of  $\text{MnO}_2$  used. To check reproducibility, DMA adsorption was carried out in duplicate. The relative deviations met with the requirement of less than 5%.

### Desorption experiments

Desorption isotherm were obtained from the adsorption samples in equilibrium. Solution containing  $\text{MnO}_2$  was transferred into centrifuge tubes that were centrifuged at 3000 g for 10 minutes with the centrifuge temperature being set at the incubation temperature. Then, 25 mL of the supernatant was removed and compensated for sampling by adding 25 mL pure water or 10 mM NaCl solution. The tubes were placed on a reciprocating shaker for 1 hour at 298 K. Preliminary kinetic studies showed that desorption could reach equilibrium state within a time of 24 h. After shaking, the suspensions were centrifuged and 25 mL of the supernatant was collected for analysis.

### DMA analysis

DMA was detected using a gas chromatogram method after derivatization with benzenesulfonyl chloride (Frank et al. 1997). In this study, the derivatization was conducted in a 22 mL extraction vial, the volume of sample used was 10 mL, and the amounts of all other reagents were scaled down accordingly.

## RESULTS AND DISCUSSION

### Characterization of the adsorbent

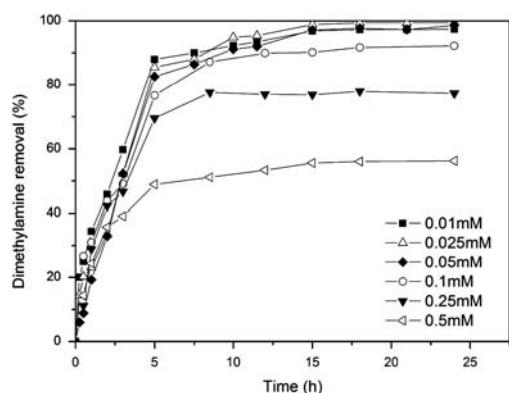
In the preliminary experiments, *in situ*  $\text{MnO}_2$  (17.4 mg/L) formed by the reaction of  $\text{KMnO}_4$  and  $\text{Na}_2\text{S}_2\text{O}_3$  was used to adsorb DMA, but only 5% DMA ( $[\text{DMA}]_0 = 0.01 \text{ mM} = 0.45 \text{ mg/L}$ ) could be removed after 10 h adsorption. When increasing the concentration of  $\text{MnO}_2$  to 0.696 g/L, nearly 30% DMA was eliminated from the water, but the  $\text{MnO}_2$  suspensions are difficult to settle, while 0.028 mg/L Mn could be detected after 10 h adsorption which was lower than the limit of drinking water standard of China (0.1 mg/L) and that of USA (0.5 mg/L). Therefore, previously prepared  $\text{MnO}_2$  was used in the following experiments, and prepared by three different methods which were different in aging time and additive: (i) without aging; (ii) aged for 48 h; (iii) added  $\text{Na}_2\text{SiO}_3$  after formation of  $\text{MnO}_2$ , then aged for 48 h. The adsorbents formed by method (i) and (ii) both have high adsorptivity, over 51% DMA ( $[\text{DMA}]_0 = 0.01 \text{ mM} = 0.45 \text{ mg/L}$ ) could be removed within 15 min and 97.3% after 5 h, but the Mn concentration in the solution is still higher than 0.1 mg/L. The adsorption rate of adsorbent (iii) was slower than adsorbent (i) and (ii), but it had less Mn leaching (0.04 mg/L) and better sedimentation effect.

The crystal structure of  $\text{MnO}_2$  was examined by XRD (data not shown), and all three  $\text{MnO}_2$  adsorbents were amorphous, so these adsorbents should have large specific surface area. To validate this hypothesis, further research is need to determine Brunauer-Emmet-Teller (BET) specific surface area, pore volume and pore size of the adsorbent.

All three pre-synthesized  $\text{MnO}_2$  adsorbents were characterized by the FT-IR. In the FT-IR spectra, the shoulder bands at  $3411 \text{ cm}^{-1}$  corresponded to the structural  $-\text{OH}$  stretching vibration ( $\nu\text{OH}$ ). The bands at  $1635 \text{ cm}^{-1}$  were related to the H-O-H bending ( $\delta\text{OH}$ ), indicating the deformation of adsorbed water molecules. The bands at  $527 \text{ cm}^{-1}$  should be caused by the vibration of Mn-O. We assumed that condensation dehydration occurred between Si-OH with Mn-OH, leading to the formation of Si-O-Mn. The band at  $923 \text{ cm}^{-1}$  (adsorbent (iii)) may be due to the Si-O-Mn stretching.

### Effect of contact time on DMA adsorption

As shown in Figure 1, the removal rate of DMA is fast in the first 5 h, then DMA is eliminated slowly in the next 10 h, and apparent adsorption equilibrium is obtained after 15 h for all the six initial DMA concentration. Thereafter, no detectable concentration changed occurred (<7 hours) after adsorption

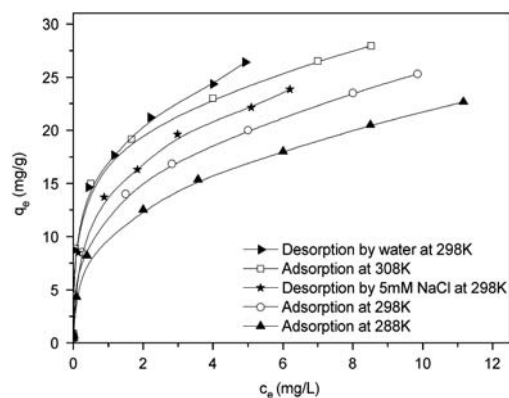


**Figure 1** | Effect of contact time on DMA adsorption by MnO<sub>2</sub> (adsorption conditions: adsorbent dosage = 0.5 g/L, pH 7.0, and temperature = 298 K).

equilibrium and average removal efficiency of DMA reaches from 99.38% to 56.22% when the initial concentration of DMA is from 0.01 to 0.5 mM (i.e. from 0.45 mg/L to 22.5 mg/L), during this period. It is hypothesized that the adsorption takes place not only at easily accessible surface sites, but also in micropores. It also can be seen in the [Figure 1](#) that the removal of DMA at adsorption equilibrium decreases with increasing initial DMA concentration. The limited number of adsorption sites available for the uptake of DMA at a fixed adsorbent dosage might be the main reason for this phenomenon.

### Adsorption isotherms

The adsorption isotherms of DMA onto MnO<sub>2</sub> at temperatures of 288, 298, and 308 K are shown in [Figure 2](#). All adsorption isotherms are nonlinear with curvatures concave to the x-axis. The adsorption of DMA onto MnO<sub>2</sub> increases from 22.66 mg/g (50.4% removal) to 27.95 mg/g (62.1% removal) when temperature is increased from 288 to 308 K at an initial concentration of 22.5 mg/L. The increase in the equilibrium adsorption with temperature demonstrates that



**Figure 2** | Adsorption isotherm of DMA onto MnO<sub>2</sub> at different temperatures (adsorption conditions: adsorbent dosage = 0.5 g/L, and pH 7.0).

DMA removal by adsorption onto MnO<sub>2</sub> favors high temperature. The adsorption isotherms at different temperatures can be fitted well using Freundlich isotherm model (reflected with the correlation coefficients, >0.990). The Freundlich constants ( $K_F$ ) at 288 K, 298 K and 308 K are 10.10, 12.62 and 17.15 (mg/g)(L/mg)<sup>1/n</sup>, respectively. And it suggests that the adsorbent MnO<sub>2</sub> is inhomogeneous, and the adsorption film is monomolecular.

In order to evaluate the reversibility of DMA adsorption onto MnO<sub>2</sub>, desorption characteristics were also determined, also shown in [Figure 2](#). There is obvious hysteresis in deionized water between adsorption and desorption. The lag angle of the two desorption isotherms are 63.4° (with pH 7.0 water) and 23.4° (with pH 7.0, 5 mM NaCl), respectively. It suggests that the adsorption and desorption are irreversible. Since the pH value of saturation adsorption solution was above 9, most of DMA existed in the form unprotonated DMA ( $pK_{a,DMA} = 10.7$ ). With the addition of neutral pH water/NaCl solution, certain concentration of the residual DMA converted into DMA<sup>+</sup>, and then adsorbed by negatively charged MnO<sub>2</sub>.

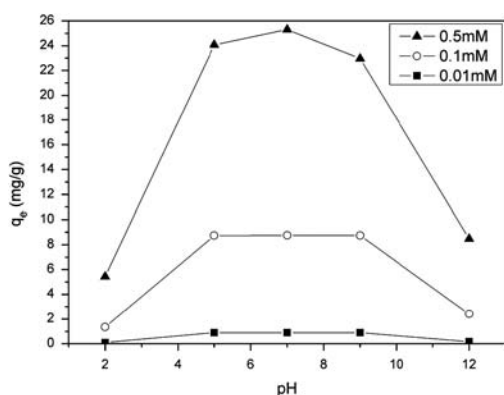
### Effect of pH on DMA adsorption

Since pH value governs both the presence of charges on mineral surfaces and the fraction of adsorbate in an ionized form, the extent of charged organic compounds to solid association is expected to depend on pH. To determine the effect of pH on adsorption capacity of MnO<sub>2</sub>, solutions were prepared at different pH values ranging from 2.0 to 11.0 (shown in [Figure 3](#)). At pH 2.0, 5.0, 9.0 and 12.0, the uptakes of DMA ( $[DMA]_0 = 22.5$  mg/L) are 12.1%, 53.5%, 51.0% and 18.8%, respectively, and the maximum amount of absorbed DMA is appeared at pH 7.0 (56.2%).

There are six adsorption mechanisms used to explain the adsorption onto a solid surface, i.e., electrostatic interaction, ion exchange, ion-dipole interactions, coordination by surface metal cations, hydrogen bonding, and hydrophobic interaction ([Lu et al. 1996](#)). Almost all mineral particles in natural waters are charged, and every solid could present a charged surface to the aqueous solution due to the ionizable surface groups ([Schwarzenbach et al. 2003](#)). The water-wet surface of MnO<sub>2</sub> is covered by hydroxyl groups. These hydroxyl moieties can undergo proton-exchange reactions with the aqueous solution:



where Mn refers to an atom Mn in the surface of MnO<sub>2</sub>. The



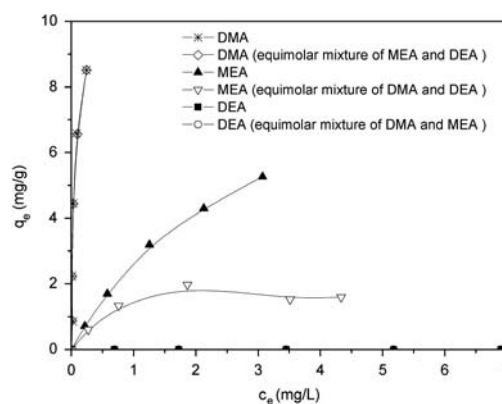
**Figure 3** | Effect of solution pH on the adsorption of DMA onto MnO<sub>2</sub> (adsorption conditions: adsorbent dosage = 0.5 g/L, temperature = 298 K).

$pK_a$  value of DMA is 10.7, so the share of DMA<sup>+</sup> decreases with the increasing pH, at pH 6.5, 7.5 and 8.5 is 99.5%, 97.5% and 82.5% respectively and in relation to the total amine content (Andrzejewski & Nawrocki 2009). Only protonated DMA can be adsorbed on the negatively charged surface of MnO<sub>2</sub>. The lower DMA adsorption at alkaline can be attributed to the increasing amount of unprotonated DMA in the total amine content with increasing pH. At acidic pH, the negative charge on MnO<sub>2</sub> decreased with the decreasing pH, leading to less adsorption of DMA.

### Effect of Ionic strength and humic acid on DMA adsorption

Ionic composition and ionic strength of the solution are also factors which affect the sorption of charged organic chemicals, especially when inorganic ions compete with organic ones for binding sites.

Our experiment results show that the amount of adsorbed DMA onto MnO<sub>2</sub> decreases with the increase of NaCl concentration in the solution. The Freundlich constants ( $K_F$ ) at NaCl concentrations of 1, 2, 5, 10 mM are 10.85, 7.18, 2.99 and 1.53 (mg/g)(L/mg)<sup>1/n</sup>, respectively. As discussed in the last section, the surface of MnO<sub>2</sub> is negatively charged at neutral pH. The interaction force drawing DMA<sup>+</sup> also draws inorganic counter ions like Na<sup>+</sup> near the negatively charged surface of MnO<sub>2</sub> in water. To the contrary, inorganic molecules with negatively charges, such as Cl<sup>-</sup>, will be repulsed from the near-surface water. The organic ions, DMA<sup>+</sup> in this study, will accumulate in the thin film of water surrounding the particle as part of the population of charges in solution balancing the charges on the solid surface. According to the experiments results, it infers that NaCl prefers to occupy the strongest sites on MnO<sub>2</sub>, and competes with DMA<sup>+</sup> for space in MnO<sub>2</sub> due to the surface



**Figure 4** | Adsorption isotherm of DMA, MEA and DEA onto MnO<sub>2</sub> at 298 K (adsorbent dosage = 0.5 g/L, and pH 7.0).

heterogeneity, which leads to the decrease in the amount of DMA adsorption.

Humic acid, the representative of natural organic material (NOM), exists widely in surface water and it interferes with the adsorption of trace organic compounds on porous adsorbents by pore blockage and direct competition for adsorption sites (Ho & Newcombe 2005). However, our experiment results suggest that the existence of humic acid at a concentration of 1.2 to 10 mg/L does not significantly affect the extent of DMA adsorption.

### Effect of MEA and DEA on DMA adsorption

According to the experiment results (shown in Figure 4), the adsorption isotherm of DMA is not influenced by the equimolar of MEA and DEA coexisted, 94.6% DMA ( $[DMA]_0 = 0.1 \text{ mM} = 4.5 \text{ mg/L}$ ) is removed by MnO<sub>2</sub> after 24 h. It also can be seen that 46.2% MEA ( $[MEA]_0 = 0.1 \text{ mM} = 5.7 \text{ mg/L}$ ) is adsorbed onto the MnO<sub>2</sub> without the presence of DMA and DEA, and the adsorption isotherm of MEA is also well described by the Freundlich models (the correlation coefficients is 0.9914). It is noteworthy that the adsorption amount of MEA is much less than DMA, and it decreases obviously with the competition of DMA. The phenomenon indicates that DMA prefers to dominate the strongest sites on MnO<sub>2</sub>, and it competes with MEA for space in MnO<sub>2</sub>. The mechanism might be explained through further characterization of the adsorbent. Unfortunately, there is no evidently adsorption of DEA on MnO<sub>2</sub>.

## CONCLUSIONS

Synthetic MnO<sub>2</sub>, produced by a chemical precipitation method was demonstrated to adsorb DMA from aqueous

solution. The results showed that DMA could be adsorbed onto  $\text{MnO}_2$  quickly. The data observed from adsorption isotherms at different temperatures were fit to the Freundlich model. It was found that neutral pH is beneficial for adsorption of DMA. This phenomenon can be attributed to the amount of protonated DMA in the total amine content and the amount of negative charge on the surface of  $\text{MnO}_2$ . Increasing ionic strength from 1 to 10 mM decreased the extent of DMA adsorption from 7.37 to 3.6 mg/g for ions mainly occupied the strongest sites on  $\text{MnO}_2$ . The presence of humic acid and other secondary aliphatic amines (MEA and DEA) had no obvious influence on DMA adsorption. Desorption isotherms showed that adsorption and desorption of DMA were irreversible. Combined with all experiments results, it was concluded that electrostatic interaction was the main force to adsorb DMA from aqueous solution. Further characterization of the adsorbent should be done in the future.

## ACKNOWLEDGMENT

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