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Magnetic Multi-Walled Carbon Nanotube as an Adsorbent for Toluidine Blue O Removal from Aqueous Solution

F. Hamidi Malayeri[1,2], M. R. Sohrabi[2], H. Ghourchian[1,3*]

1- Department of Biophysics, Institute of Biochemistry and Biophysics, University of Tehran, Tehran, I. R. Iran
2- Department of Chemistry, Islamic Azad University, North Tehran Branch, Tehran, I. R. Iran
3- Nanobiomedicine Center of Excellence, Nanoscience and Nanotechnology Research Center, University of Tehran, Tehran, I. R. Iran

(*) Corresponding author: hadi@ibb.ut.ac.ir
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Abstract:
Toluidine Blue O (TBO) is a cationic dye which is extensively used in the industries. In the present paper a simple and efficient wet chemical method was introduced for removal of TBO from waste aqueous solution. Magnetic multi-walled carbon nanotubes were synthesized using commercially available multi-wall carbon nanotubes and magnetic iron oxide nanoparticles which were examined for removal of TBO. The magnetic adsorbents were easily manipulated using an external magnetic field for desired separation, causing the removal of dyes from polluted water. The experimental results revealed that after 30 min, the separation process for TBO absorption reaches to equilibrium at pH 7.0. The optimum condition for removal of TBO was reported.
Keywords: *Magnetic Carbon nano-tubes, Adsorption, Magnetic separation, Toluidine Blue O, Nanocomposite.*

1. INTRODUCTION

Since industrial organic materials such as dyes are toxic to organisms and mammals, contamination of waste waters in environment by these materials is one of the most serious problems. Dyes are in a steadily growing demand. They are widely used in various industrial fields such as textiles, paper, rubber, plastics, leather, cosmetics, pharmaceuticals and food productions and their discharge into water causes environmental pollution [16].
So far different methods including biological treatment [19], coagulation/flocculation [15], ozone treatment [38], chemical oxidation [10], membrane filtration [4], ion-exchange [22], photocatalytic degradation [26] and adsorption [9] have been used for the removal of chemicals from waste water. Among them, adsorption technology is attractive due to its merits of effectiveness, efficiency and economy [12,2,6].
The common adsorbents are including activated carbons, clays, zeolites, industrial by-products, agricultural wastes, polymeric materials and biomass [7]. However, these primarily adsorbents suffer from low capacity in adsorption and inconvenience in separation process. Therefore, the researchers still make effort to develop new promising adsorbents. Carbon nanotubes (CNTs) have been the focus of an intensive study by researchers since their discovery in 1991 [17]. Due to the relatively large specific surface area, small size, hollow and layered structures, [24,25], CNTs have attracted increasing attention as a new type of powerful solid-phase extraction

adsorbent. CNTs have been applied as an effective adsorbent for the removal of organic and inorganic contaminants including 1,2-dichlorobenzene [28], trihalomethanes [20], microcystins [36], fluoride [23], lead [24], nickel [5], arsenate [29], Cd^{2+}, Cu^{2+} and Pb^{2+} [34] from water. However, some disadvantages such as the poor solubility of CNTs and difficulty in collecting them from their dispersing media by tedious centrifugation process [11] cause much inconvenience in their practical application. To overcome these problems, magnetic and functionalized CNTs were introduced which are able to fully disperse in aqueous media and can be easily separated from the medium. Magnetic separation technology has been gradually attracted the attention of scientists and technicians as a rapid and effective technology for separation of materials. Due to its capability of treating large amount of wastewater within a short time and producing no contaminants, it has been used for many applications including environmental technology [18,27].

So far different adsorbents have been developed for dye removal from aqueous solutions. Applying magnetic Fe_3O_4-activated carbon for methylene blue [35], magnetic alginate beads [33] and magnetic CNTs for organic dyes [14,30] are some examples of dye removal from water solutions. But to our knowledge, applying the magnetic-carboxilic acid functionalized CNTs for the removal of Toluidine Blue O (TBO) has not been yet reported.

In the present report a simple and efficient wet chemical method was introduced for the removal of TBO as an example of cationic dye from aqueous solution. A magnetic nanocomposite adsorbent consists of carboxilic acid functionalized multi-wall carbon nanotubes and magnetic iron oxide nanoparticles (Fe_3O_4-MWCNTs-COOH) were applied for the removal of TBO which is extensively used in the industries.

2. EXPERIMENTAL

2.1. Materials

MWCNTs with outer diameter of 40–60 nm and length of 5–15 μm were purchased from Shenzhen

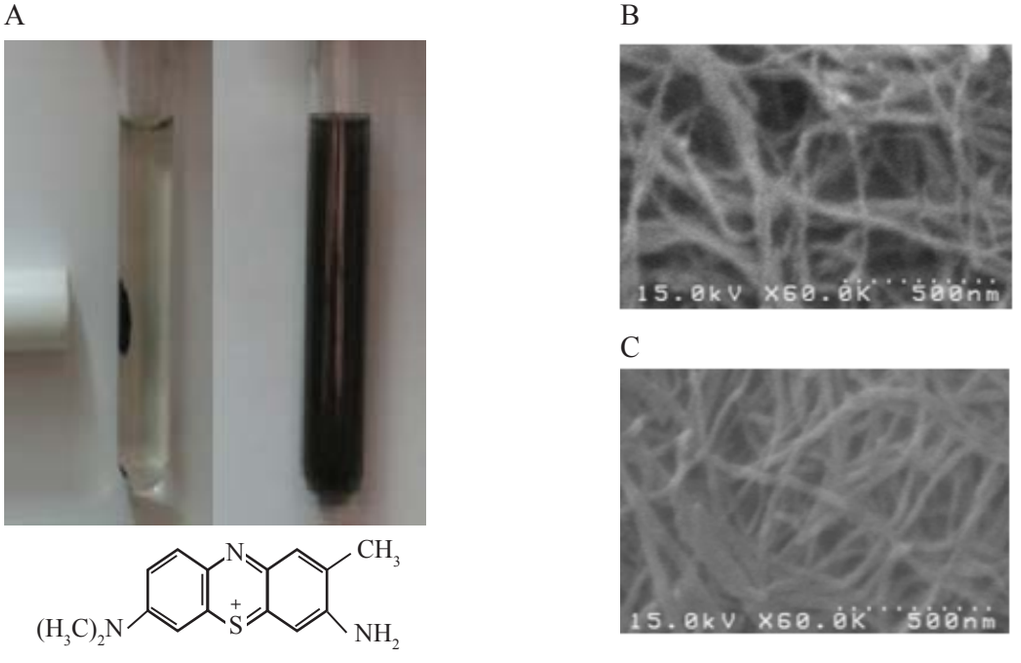

Figure 1: *A) The image of Fe_3O_4-MWCNTs-COOH, dispersed in water (right) and manipulated by an external permanent magnet (left). B) The chemical structure of TBO. C) FESEM images of MWCNTs-COOH (left) and Fe_3O_4-MWCNTs-COOH (right).*

Nanoport Company (Shenzhen, China). TBO, potassium di-hydrogen phosphate, di-potassium hydrogen phosphate and other chemicals were obtained from Merck (Germany). Poly (tetra-fluoroethylene) (PTFE) membrane with 0.45 μm in pore size was purchased from Schleicher & Schüll (Germany).

2.2. Apparatus

Field emission scanning electron microscopic (FESEM) images were obtained using a FESEM (model S4160, Hitachi, Japan) at 15 kV. The samples for FESEM analysis were obtained by dropping modified MWCNTs on a gold plate and drying the sample in air at room temperature. X-ray diffraction (XRD) measurements were performed using a Philips Diffractometer of X'pert Company with mono chromatized Co kα radiation. The dye concentration was measured by using UV–Visible spectrophotomer (Kontron-922) at 633 nm. For the adsorption experiments a shaker from Gesells Chaft Fur Labortechnik MBH, Germany was used. A F-12 pH meter (Horriba) was used for pH tests.

2.3. MWCNTs functionalization

MWCNTs were functionalized according to our previous works [32,37]. Briefly, purified MWCNTs were sonicating in HNO_3 (35%) for 5 h. Then, they were filtered using a 0.45 mm hydrophilized PTFE membrane in extensive deionized water until no residual acid was detected. The process was followed by drying the HOOC-MWCNTs under infrared lamp.

2.4. Preparation of magnetic CNTs

Fe_3O_4 was deposited on MWCNTs by a co-precipitation process. 10 mg COOH-MWCNTs was added to 2 mL solution containing 17 mg (4.33 mmol) $(NH_4)_2\ Fe(SO_4)_2.6H_2O$ and 25 mg (8.66 mmol) $NH_4Fe(SO_4)_2.12H_2O$ and sonicated at 50°C for 10 minute under ultrasonic bath (30 W, 40 kHz). While the mixture was sonicating, 10 mL of NH_3 aqueous solution (8 M) was added drop wise to it. The pH of the final mixture should be in alkaline range to Fe_3O_4 nanoparticle precipitate on MWCNTs surface. For removing impurities (such as sulfate, ammonia and non-magnetized MWCNTs) and neutrality of the obtained Fe_3O_4-MWCNTs-COOH nano-composite, it was washed with double-distilled water and the precipitate was isolated by a permanent magnet [31,37].

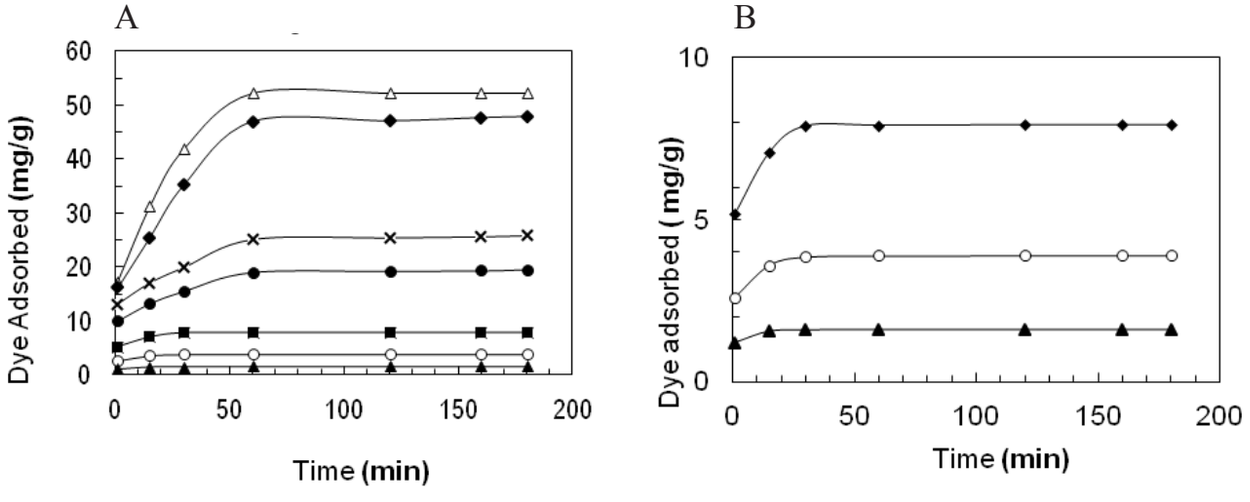

Figure 2: *A) Time course for TBO adsorption on Fe_3O_4-MWCNTs-COOH. (▲) 0.2, (O) 0.5, (■) 1, (●) 3, (×) 5, (◆) 8 and (△) 10 mg/L of dye sample solutions in water were added to 1 mg adsorbent suspension. B) Scale up of (A) for concentrations of: 0.2, 0.5, and 1 mg/L.*

2.5. Adsorption experiments

Stock solution of dye was prepared by dissolving the TBO powder in distilled water. The dye solutions of different concentrations were prepared by diluting the dye stock solution in appropriate rates. Adsorption experiments were carried out at room temperature in a glass bottle containing 10 ml of different concentration of dye samples exposed to 1-3 mg Fe_3O_4-MWCNTs-COOH as adsorbent while the solution was shaking on a shaker at 200 rpm. After the adsorption process being completed the Fe_3O_4-MWCNTs-COOH were separated from dye solution using a permanent magnet. At this stage, the equilibrium concentration of TBO was measured using the UV–Vis spectrophotometer at 633 nm, corresponding to the maximum absorbance of dye. The amount of dye adsorbed was calculated using the equation 1 [1]:

$$(A_0 - A_t)/M \times 116.2 = Qe \quad (1)$$

Where, A_0 and A_t are initial and equilibrium adsorption of dye, M is the mass of Fe_3O_4-MWCNTs-COOH (mg) and Q_e is the amount of dye adsorbed on Fe_3O_4-MWCNTs-COOH at equilibrium condition (mg/g).

2.6. pH effect

The influence of pH on adsorption capacity of Fe_3O_4-MWCNTs-COOH was studied over a pH range from 5 to 8. At first phosphate buffer solutions of different pHs (5.0, 5.5, 6.0, 6.5, 7.0, 7.5 and 8.0) were prepared using. Then the amount of dye adsorbed on Fe_3O_4-MWCNTs-COOH (mg/g) was measured using the procedure explained in previous section (*Adsorption experiments*).

3. RESULTS AND DISCUSSION

3.1. Fe_3O_4-MWCNTs-COOH manipulation

By using acid treatment the hydrophilic groups of carboxylic acids can be introduced on the sidewall of MWCNTs thus enhancing the solubility and dispersion of MWCNTs in aqueous solution [22]. Moreover, by connection of magnetic iron oxide nano-particles (Fe_3O_4) to MWCNTs the solubility and dispersion of MWCNTs in aqueous solution is more enhanced. Then, the produced magnetic MWCNTs rapidly respond to the permanent magnet. As shown in Figure 1-A, the magnetic MWCNTs are easily manipulated by an external magnetic field. The re-dispersion process can be readily repeated by switching the external magnetic field off.

3.2. Characterization of the Fe_3O_4-MWCNTs-COOH

The morphology of the Fe_3O_4-MWCNTs-COOH adsorbent was studied using FESEM (Figure 1-B). By comparison of the image obtained from MWCNTs-COOH (Figure 1-B, left) and Fe_3O_4-MWCNTs-COOH (Figure 1-B, right) it was revealed that the thickness of modified MWCNTs has increased after magnetization. This indicates that iron oxide nanoparticles were successfully attached to the surface of MWCNTs. Also the XRD patterns of Fe_3O_4-MWCNTs-COOH showed that in the magnetization process Fe_3O_4 commonly formed in a pure crystal containing Maghemite (Fe_2O_3) and Geothite (FeO.OH) (Data not shown).

3.3. Dye adsorption on Fe_3O_4-MWCNTs-COOH

It seems that TBO can be adsorbed on Fe_3O_4-MWCNTs-COOH due to both hydrophobic-hydrophobic and electrostatic interactions. As seen in Figure 1-C, the chemical structure of TBO contains an aromatic backbone. Therefore, the adsorption of TBO on Fe_3O_4-MWCNTs-COOH might be based on Van-der Waals interactions between the hexagonally arrayed carbon atoms in the graphite sheet of MWCNT and the dye aromatic backbone [11]. Also the electrostatic interaction between the positive cationic group in dye structure and the negative charge of carboxylic functional groups on MWCNTs surface might be the other reason for such an adsorption.

3.4. Effect of contact time

The effect of contact time on the removal of TBO by magnetic MWCNT nano-composite was studied

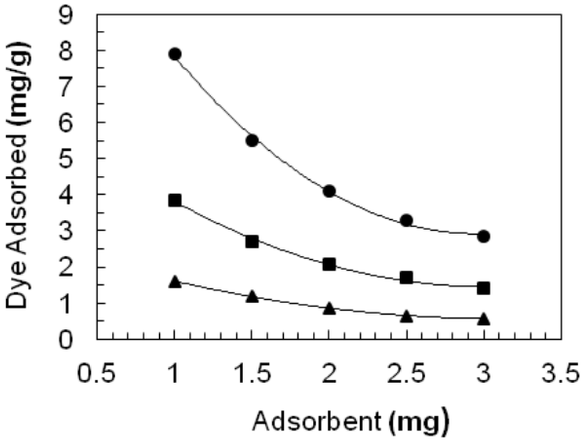

Figure 3: *Dependency of dyes adsorbed on Fe_3O_4-MWCNTs-COOH dosage. Each point designates the maximum dye absorption after 30 min exposure of dye to magnetic MWCNTs. The signs (●), (■) and (▲) stand for 1, 0.5 and 0.2 mg/L of dye, respectively.*

over a range of 0.2 to 10 mg/L. As shown in Figure 2, it was observed that at higher concentration of dye samples (3-10 mg/L, Figure 2-A) the optimum equilibrium time for TBO absorption on Fe_3O_4-MWCNTs-COOH is about 60 min. While at lower concentration of dye samples (0.2-1 mg/L, Figure 2-B) the optimum equilibrium time for TBO absorption on Fe_3O_4-MWCNTs-COOH is about 30 min. The shorter equilibrium time suggests that Fe_3O_4-MWCNTs-COOH have higher adsorption efficiency to the removal of dyes from water. Therefore, the low concentration range of TBO was selected for further studies.

3.5. Effect of adsorbent dosage

To investigate the effect of Fe_3O_4-MWCNTs-COOH dosage on dye adsorption, different concentrations of dye (0.2, 0.5 and 1 mg/L) were exposed to Fe_3O_4-MWCNTs-COOH over a range from 1 to 3 mg. As shown in Figure 3, the amount of dye adsorbed (mg/g) decreased as Fe_3O_4-MWCNTs-COOH dosage was increased over the range from 1 to 3 mg. The maximum amount of dye removal was obtained using 1 mg of Fe_3O_4-MWCNTs-COOH. Since the adsorption capacity was greatest when 1 mg nano-composite was added to 1 mg/L of dye sample, this amount was used as optimum dosage.

3.6. Effect of pH

The influence of pH on adsorption capacity of Fe_3O_4-MWCNTs-COOH was studied over a pH range from 5 to 9. The pH of the solutions was fixed using 0.1 M phosphate buffer solutions having certain pH value. It was observed that dyes adsorbed increased when pH changed from 5 to 7, and then dye adsorbed decreased beyond 7. It is well known that the surface of CNTs contain some oxygen groups such as carboxylic groups (-COOH) and hydroxylic groups (-OH) after acid treatment [1]. At lower pH values, due to the protonation of electron rich regions on the surface of MWCNTs, the surface carboxylic groups are neutral. Under these conditions, the uptake of positive charged dye will be low. As shown in Figure 4 at pH 7, the carboxylic groups are ionized and the negative charge density on the surface increases, resulting in enhanced removal of dyes. Therefore, the pH 7 was selected as optimum pH for dye adsorption on magnetic MWCNTs.

3.6. Adsorption kinetics

The adsorption kinetics was described by a pseudo second-order equation 2 [8,13]:

$$dq_t/dt = k_2(q_e - q_t)^2 \quad (2)$$

In this model, k_2 (g/mg.min) is the rate constant of the pseudo second-order adsorption, q_e and q_t (mg/g) are the amount of TBO adsorbed at equilibrium time and time t, respectively. Integrating Eq. 2 and applying limit times from 0 to t and TBO adsorbed at equilibrium from 0 to q_t gives the equation 3.

$$t/q_t = 1/k_2q_e^2 + t/q_e \quad (3)$$

Figure 5 shows the pseudo second-order kinetics of TBO adsorption on to magnetic-MWCNTs for different initial dye concentrations. The rate parameters of k_2 (0.142), and q_e (0.125) were obtained from the intercept and slope of t/q_t against t. It is clear that the adsorption kinetics of TBO on to magnetic-MWCNTs follows this model, with regression coefficients 0.99.

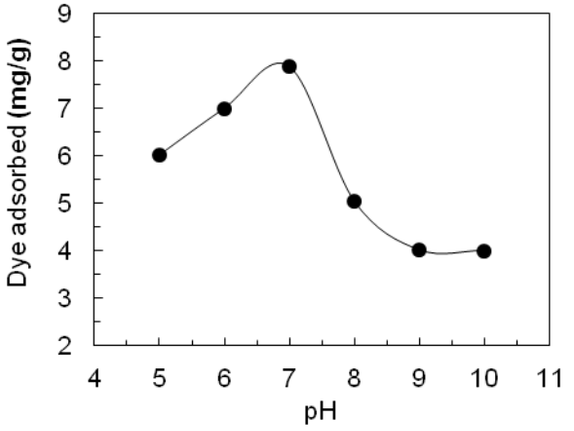

Figure 4: *pH effect on TBO removal.*

3.7. Adsorption isotherms

The adsorption capacity of the Fe_3O_4-MWCNTs-COOH adsorbent for the cationic dye was evaluated using Freundlich Model (4):

$$\log q_e = \log K_F + \log c_e/n \quad (4)$$

Where, q_e is the dye concentration on magnetic MWCNTs at equilibrium (mg/g); c_e denotes the dye concentration in solution at equilibrium (mg/L). The adsorption capacity (K_F = 0.89) and the adsorption strength (n = 1.0) were obtained from the intercept and slope of the linear plot of log q_e versus log c_e [3] (Data not shown).

3.8. Desorption studies

To examine the desorption, 1 mg Fe_3O_4-MWCNTs-COOH nano-composite adsorbent was added to 10 mL of dye solution and the mixture was shaken at room temperature on a rotary shaker at 200 rpm for 150 min. The initial dye concentration and pH were 1 mgL^{-1} and 7.0, respectively. At the end of the adsorption period, the dye-adsorbed on Fe_3O_4-MWCNTs-COOH adsorbent was isolated from the mixture with a magnet and then added into 10 mL ethanol. The suspension was shaken on a rotary shaker at 200 rpm at room temperature for different time intervals. After each interval, the Fe_3O_4-MWCNTs-COOH was isolated from the mixture with a magnet and the absorbance of supernatant was analyzed by UV–Vis spectrometer. The recovery percent of nano-composite (R%) were calculated using the Eq. (5):

$$R\% = (A_t/A_o)100 \quad (5)$$

Where, A_o is the initial absorbance of dye solution (before treatment with nano-composite) and A_t is absorbance of dye solution desorbed from nano-composite at each interval. As seen in Figure 6, at beginning the dye molecules were rapidly desorbed but after about 50 min the desorption rate was gradually lessened and it finally reached to a plateau at 90 min. This means that desorption value and consequently the recovery percent reaches to a maximum (84%) at 90 min.

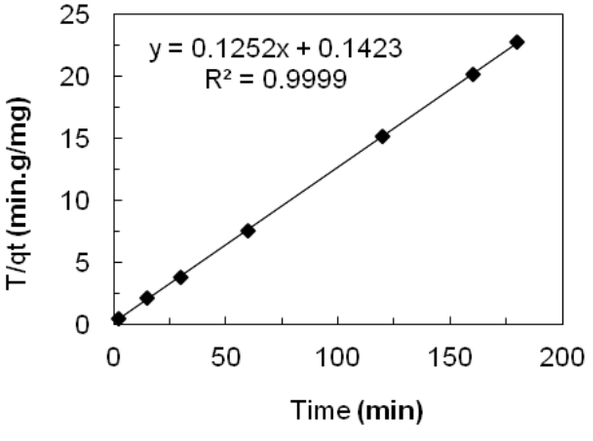

Figure 5: *Pseudo second-order plots for the adsorption of TBO at C_o 1 ppm, pH 7.*

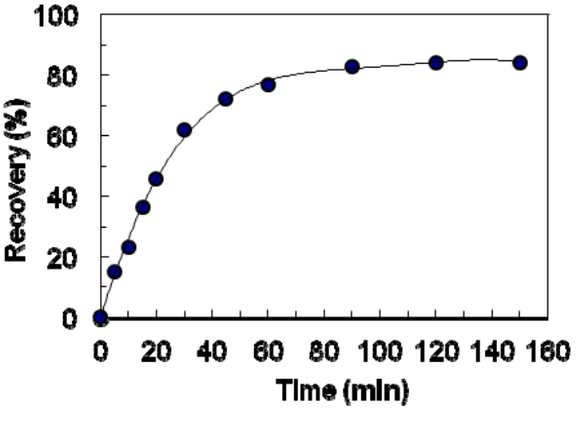

Figure 6: *Recovery percentage of dye from Fe_3O_4-MWCNTs-COOH.*

4. CONCLUSION

A simple and efficient wet chemical method was introduced for the removal of TBO dye from aqueous solution. The magnetic nano-composite adsorbent consisted of commercially available MWCNTs and magnetic iron oxide nanoparticles. Combination of the high adsorption capacity of CNTs and the separation convenience of magnetic materials showed a satisfactory potential for the removal of TBO. This method could be a potential alternative method for the removal of cationic dye from industrial waste water.

5. ACKNOWLEDGMENT

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