

Efficient photodegradation of neutral red chloride dye in aqueous medium using graphene/cobalt–manganese oxides nanocomposite

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Abstract: Graphene/cobalt–manganese oxides nanocomposites were prepared from their precursor through chemical reduction where NaOH was used as a reducing agent. The obtained GNs/Co-Mn nanocomposites were used as photocatalyst for the photodegradation of Neutral Red Chloride (NRC) dye in aqueous solution under sunlight as a function of time and catalyst dosage. The morphology and photodegradation study was carried out using scanning electron microscopy (SEM) and UV-VIS spectrophotometry, respectively. The SEM image showed the presence of Co-Mn nanoparticles on the surface of GNs, which were also confirmed by energy dispersive X-ray analysis. The photodegradation study of NRC showed that the degradation of dye increased with an increase in irradiation time, and 94% of dye was degraded within 5 min by GNs/Co-Mn. Photodegradation was also carried out with recovered catalyst, which degraded about 90% of dye within 5 min. The effect of catalyst dosage on the degradation of dye was also studied.

Key words: Graphene nanosheets, photodegradation, Neutral Red Chloride, photocatalyst

1. Introduction

Dyes and pigments are general water pollutants commonly found in industrial wastewater. These pollutants can be removed by different chemical, physical, and biological methods like adsorption, precipitation, ozonization, reverse osmosis, flocculation, and ultrafiltration. Among these techniques, photodegradation is superior because it not only removes the toxic materials but also degrades these pollutants.^{1–3} Photodegradation is an oxidation process widely used for the degradation of pollutants by light-based processes.⁴ During this process, photochemical breakdown of a molecule occurs into nontoxic, simple, and lower molecular weight fragments due to light exposure. During photodegradation, reactive radical species such as hydroxyl radicals ($\cdot\text{OH}$) and superoxide anions ($\cdot\text{O}_2^-$) are produced, which can effectively oxidize organic pollutants.⁵ Photodegradation is a photocatalytic process usually carried out in the presence of photocatalyst. Photocatalyst is a semiconductor substance that is activated by absorbing a photon, which is capable of accelerating photodegradation reaction rate and degradation efficiency without being consumed.^{6,7} Different photocatalysts have been used for the photodegradation of organic dyes, among which metals nanoparticles are the most common and advance photocatalyst.

Nanoparticles have received increased attention due to their exceptionally small sizes, large specific surface area, and unique electrical, optical, magnetic, and catalytic properties. Due to these unique characteristics, nanoparticles have various potential applications in catalysis, medicine, optical, electronic devices, dyes, pig-

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ments, and superconductors.^{8,9} Among these applications, the photocatalytic activity of nanoparticles is the most advance application. Metals and metal oxides are used as a good heterogeneous photocatalyst due to its chemical stability, low corrosion, and high surface area.⁵ Different metals and metal oxides nanoparticles are reported for the photodegradation of organic contaminants; for example, silver nanoparticles are used for the photodegradation of methyl orange dye under sunlight irradiation.¹⁰ TiO₂ nanoparticles are used for the photodegradation of organic dyes with different chromophores.¹¹ The photocatalytic properties of metals and metal oxides can be improved when nanoparticles are synthesized on supporting materials. Different supporting materials are used for nanoparticles, among which graphene is the most widely used.¹² Graphene is a monolayer hexagonal lattice of sp² hybridized carbon atoms having two-dimensional structures. Graphene exhibits a very high surface area (2630 m² g⁻¹) much higher than that of graphite and carbon nanotubes. The two-dimensional basal plane structure, potential utilizations in catalysts, and high specific surface area make graphene a good supporting substrate for catalytic nanoparticles. Graphene is the most stable supporting material that strengthens its interaction with catalyst, which can improve catalyst stability.^{12,13} Graphene/nanoparticles nanocomposites show high catalytic activity and can be used as a photocatalyst for the photodegradation of dye such as graphene/Ag/TiO₂ hybrid nanocomposites.¹⁴

In the present study, GNs/Co-Mn nanocomposites were prepared by synthesizing bimetallic nanoparticles on the surface of functionalized GNs by reduction process. The GNs/Co-Mn nanocomposite was used as a photocatalyst for the sunlight photodegradation of Neutral Red Chloride (NRC) dye in aqueous medium. NRC is an important coloring agent used as a linsey-woolsey coloring agent, biological stain, and acid–base indicator. Therefore, NRC is not only an important component of dyeing wastewater but also showed a cytotoxicity effect in living organisms.^{15,16} The photodegradation of NRC in aqueous medium was also studied as a function of time and catalyst amount.

2. Results and discussion

2.1. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) study

The morphological study of GNs/Co-Mn photocatalyst is shown in Figure 1. The SEM study showed that Co-Mn nanoparticles were well dispersed on the surface of GNs. The presence of Co and Mn nanoparticles on the surface of GNs was confirmed by EDX (Figure 2). The percentage of carbon, oxygen, manganese, and cobalt was 34.5, 22.7, 15.16, and 20.9, respectively. The result also indicated that both Mn and Co nanoparticles were synthesized in large quantities on the surface of GNs. It is clear from the EDX spectrum that oxygen is present in large quantity, which showed that GNs were well functionalized by treating with concentrated HNO₃.

2.2. Photodegradation study of NRC by GNs/Co-Mn photocatalyst

The photocatalytic properties of the synthesized GNs/Co-Mn photocatalyst were studied by degrading NRC in aqueous medium under sunlight as a function of time. Figure 3 shows the UV/vis spectra of NRC in aqueous medium before and after sunlight irradiation. The spectra showed that the photodegradation of NRC in the presence of GNs/Co-Mn gradually increased with an increase in irradiation time, which is also clear from Figure 4. Figure 4 shows a digital photograph of a photodegraded sample of NRC under sunlight irradiation. The results (Figure 4) show that about 94% of dye was degraded within 5 min under sunlight irradiation, which then slowly increased, and about 96.4% of dye was degraded within 30 min. The degradation of NRC in aqueous medium was due to the photocatalytic activities of GNs/Co-Mn nanocomposite.

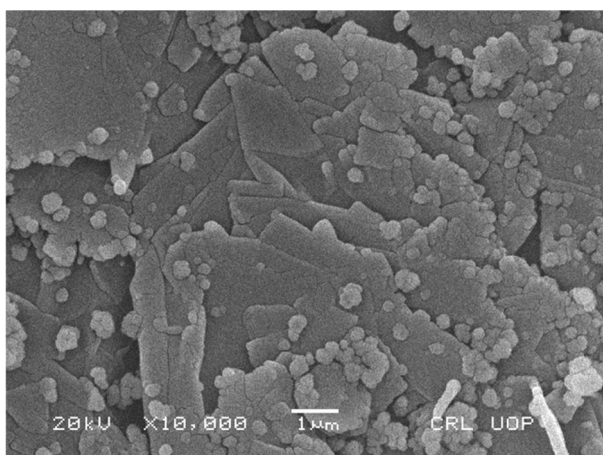


Figure 1. SEM images of Graphene/Co-Mn photocatalyst.

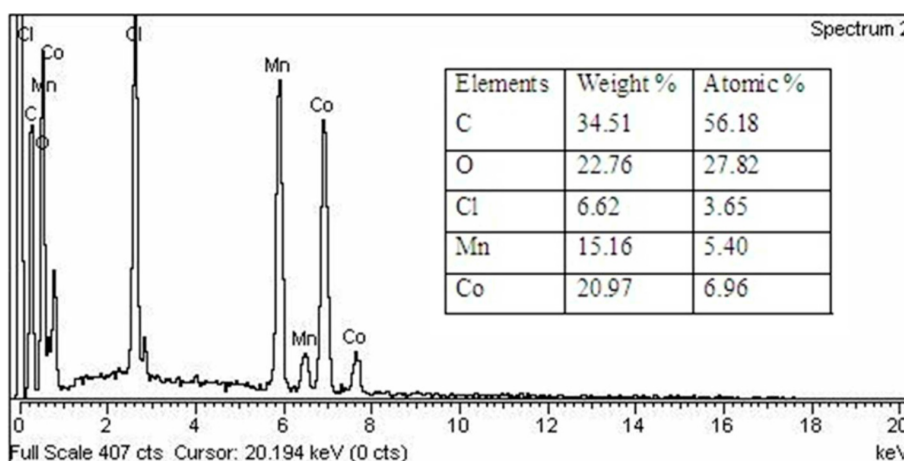


Figure 2. EDX study of GNs/Co-Mn photocatalyst.

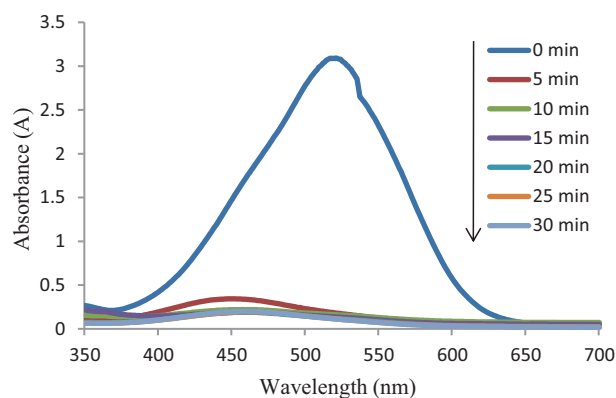


Figure 3. UV-vis absorbance spectra of NRC photodegraded by GNs/Co-Mn photocatalyst under sunlight irradiation vs. time.



Figure 4. Digital photograph of photodegradation of NRC vs. time irradiation.

The effect of GNs/Co and GNs/Mn photocatalysts on photodegradation of NRC was also studied as a function of time and its activity compared with that of GNs/Co-Mn photocatalysts. Figure 5 shows the

comparison of %degradation of NRC in the absence of photocatalyst and presence of GNs/Co-Mn, GNs/Co, and GNs/Mn photocatalysts. Figure 5 shows that GNs/Co and GNs/Mn separately significantly degraded NRC dye, while without any photocatalysts degradation was not observed. The results also showed that GNs/Co-Mn photocatalysts are more efficient and degraded more dye in aqueous solution as compared to GNs/Co and GNs/Mn photocatalysts. The results verify that GNs/Co-Mn degraded 96.37% dye within 30 min while GNs/Co and GNs/Mn degraded 90.1% and 87.7% dye within the same irradiation time, respectively.

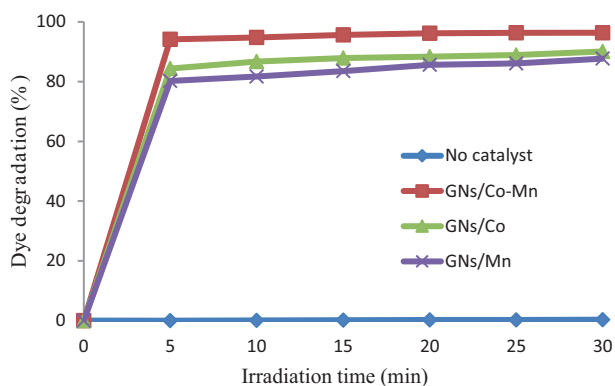
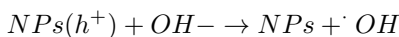
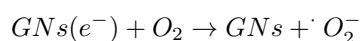


Figure 5. Comparison of %degradation of NRC without photocatalyst and by GNs/Co-Mn, GNs/Co, and GNs/Mn photocatalysts.

Figure 6 shows the proposed mechanism of degradation of NRC dye. When sunlight falls on GNs/Co-Mn, the electrons (e^-) in metallic nanoparticles are excited from the valence band to the conduction band, which create holes (h^+) in the valence band. Normally, a greater quantity of these created charges quickly recombines and the remaining fraction of electrons and holes participate in the photocatalytic reaction of dye. The photo-induced electrons are smoothly transferred from the conduction band to GNs because GNs are good acceptors of electron due to the sp^2 conjugated bond in the carbon lattice of GNs. The transfer of electrons from the conduction band to the GNs effectively retards the recombination of photo-induced electrons and holes. The separated electrons and holes take part in a chemical reaction and generate highly reactive radicals. For example, the holes present in the valence band react with the water molecules to form hydroxyl radicals ($\cdot OH$), while the electrons stored in the GNs are trapped by the O_2 molecule to form a reactive superoxide radical ion ($\cdot O_2^-$). Both radicals are highly reactive towards degradation of dye. The possible reaction steps in this mechanism under sunlight irradiation are summarized in the following equations:^{17,18}



2.3. Photodegradation study of NRC by recovered GNs/Co-Mn photocatalyst

Figure 7 shows the UV/vis spectra of NRC in aqueous solution before and after sunlight irradiation by the recovered catalyst. The results showed that the recovered GNs/Co-Mn photocatalyst significantly degraded

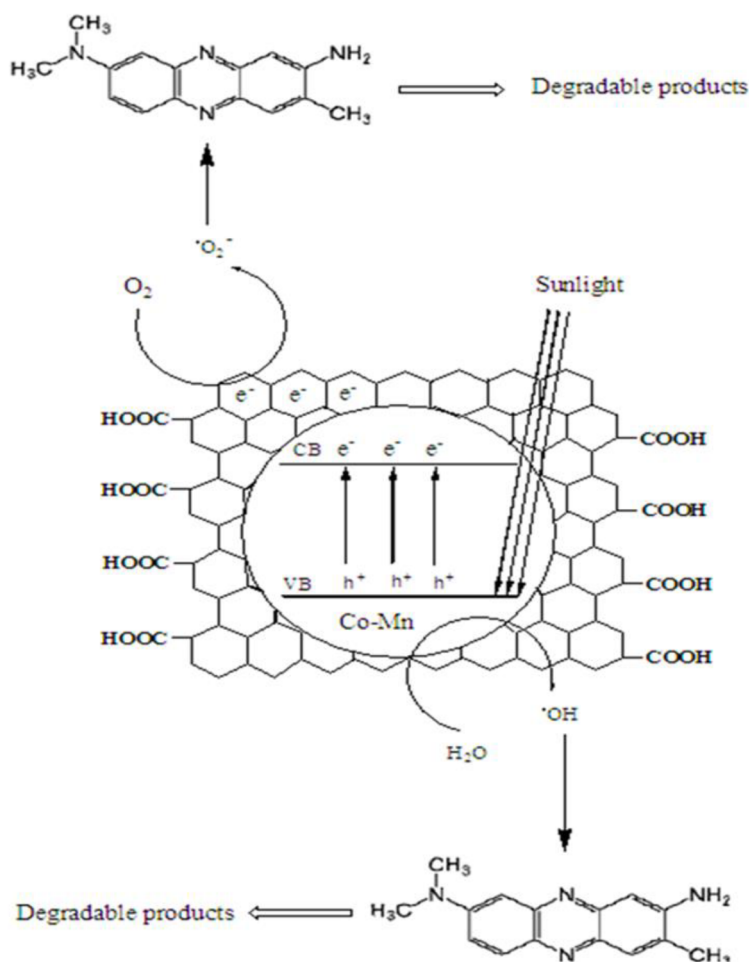


Figure 6. Schematic diagram of NRC dye degradation by GNs/Co-Mn photocatalyst under sunlight.

NRC but had less catalytic activity as compared to the original catalyst. This decrease in the photocatalytic activity of the recovered catalyst might be attributed to the deposition of photoinsensitive hydroxides on the photocatalysts surface, which block its active site.¹⁹ The recovered catalyst degraded about 91% in 5 min and 93% of dye within 30 min. The comparison of %degradation of NRC by original and recovered catalysts is shown in Figure 8. Figure 9 shows a plot of $\ln C_o/C$ versus irradiation time, which presented a linear relationship. The linear relationship indicates that the photodegradation of NRC by GNs/Co-Mn obeys first pseudo-first-order kinetics. The correlation coefficient (R^2) values are also presented in the graph.

3. Effect of photocatalyst dosage

The effect of photocatalyst dosage on the photodegradation rate of NRC under sunlight was also studied by taking different amount of photocatalyst (0.010, 0.015, 0.020, 0.025, and 0.030 g), where the dye concentration and irradiation time were 50 ppm and 5 min, respectively. Figure 10 shows the UV/vis spectra of NRC in aqueous solution before and after sunlight irradiation using different amounts of catalyst. The spectra illustrated that the photodegradation of NRC in aqueous medium increased as the quantity of catalyst was increased. Figure 11 shows the %degradation of NRC degraded by different amounts of photocatalyst. The results showed that

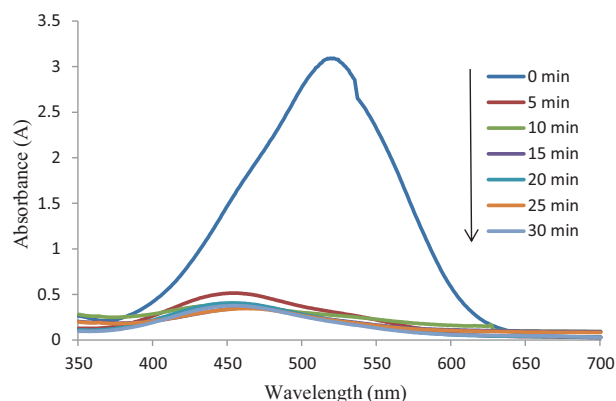


Figure 7. UV-vis absorbance spectra of NRC photodegraded by recovered GNs/Co-Mn photocatalyst under sunlight irradiation vs time.

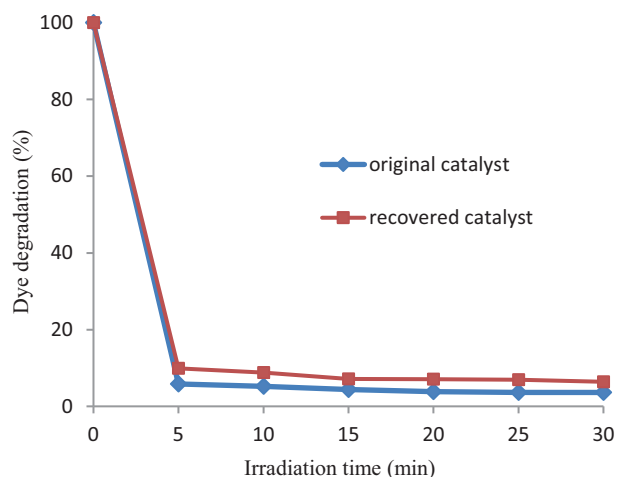


Figure 8. %Degradation of NRC with original and recovered GNs/Co-Mn photocatalyst.

0.010 g degraded 93% dye, which increased gradually as the amount of catalyst increased and about 95.5% of dye was degraded by adding 0.030 g of catalyst.

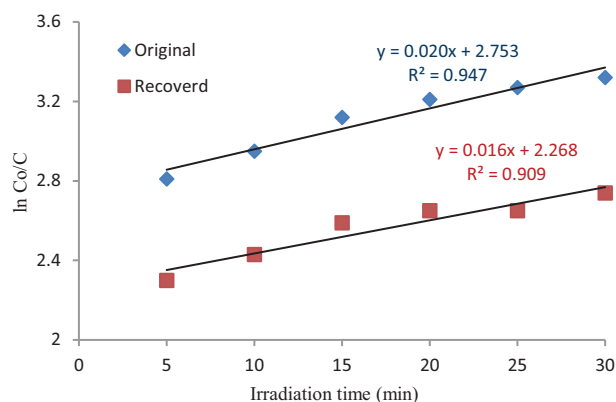


Figure 9. Kinetic study of NRC degradation reaction.

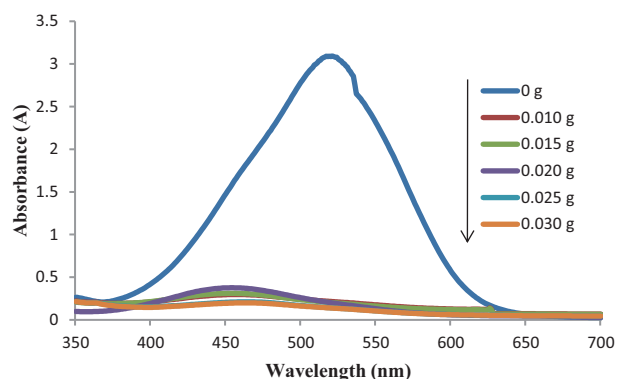


Figure 10. UV-vis absorbance spectra of NRC photodegraded by GNs/Co-Mn photocatalyst under sunlight irradiation vs. catalyst dosage.

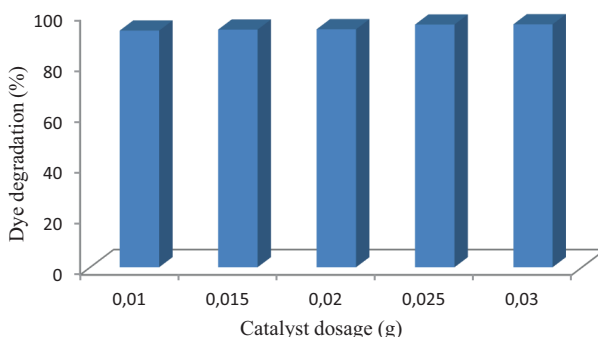


Figure 11. %Degradation of NRC with different amounts of catalyst.

4. Experimental

4.1. Materials

GNs were purchased from Chengdu Organic Chemicals Co., Ltd. Chinese Academy of Sciences. $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were supplied by Merck (Darmstadt, Germany) and used as such without any further purification. The NaOH and HNO_3 were purchased from Scharlau Chemicals and Sigma Aldrich, respectively. The NRC was purchased from the British Drug Houses Ltd. (London, UK).

4.2. Functionalization of GNs

First 3 g of GNs was sonicated in 160 mL of HNO_3 (10 M) solution for 1 h and then refluxed at 125°C for 6 h. The acid-treated GNs were separated from HNO_3 solution by filtration, washed with distilled water until freed from acid, and then dried in an oven at 100°C .

4.3. Synthesis of GNs/Co-Mn nanocomposite photocatalyst

First 0.7 g of functionalized GNs and 50 mL of 1 M solution of each $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were stirred for 20 min. The reaction mixture was also sonicated for 10 min for better dispersion of GNs. After sonication, 4 M NaOH solution (as reducing) was added dropwise to the reaction flask until the pH reached 10. The solution was then refluxed at 100°C for 2 h, cooled, and filtered. The GNs/Co-Mn nanocomposite was washed several times with distilled water in order to remove unreacted chemical reagents. The GNs/Co-Mn nanoparticles were dried in an oven at 100°C and stored for further use.

4.4. Photodegradation of NRC

First 10 mL of NRC (50 ppm) solution and 0.02 g of GNs/Co-Mn nanocomposite photocatalyst were taken in a 50-mL flask and sealed with a colorless cover to allow light and avoid evaporation. Then the solution mixture was placed under sunlight on a magnetic stirrer and was stirred with constant stirring. After a specific irradiation time, the catalyst was separated from the dye solution by centrifugation. The dye degradation study was performed by UV-vis spectrophotometer. The photodegradation of NRC was also studied with recovered catalyst. The percent degradation of NRC in aqueous media was calculated by the following equation:²⁰

$$\text{Degradation rate (\%)} = \left(\frac{C_0 - C}{C_0} \right) \times 100$$

$$\text{Degradation rate (\%)} = \left(\frac{A_0 - A}{A_0} \right) \times 100,$$

where C_o is the initial dye concentration, C is the dye concentration after UV irradiation, A_o shows initial absorbance, and A shows the dye absorbance after UV irradiation.

4.5. Instrumentation

The morphological study of gold-coated GNs/Co-Mn nanocomposite was carried out by JEOL, JSM-5910 SEM. The EDX spectrometric analysis of GNs/Co-Mn was performed on EDX (Model INCA 200/Oxford Instruments, Oxford, UK), in order to investigate the elemental composition of the samples. The photodegradation study of NRC was performed using a UV-vis spectrophotometer (UV-1800, Shimadzu, Japan).

5. Conclusion

GNs/Co-Mn nanocomposite was synthesized by reduction method from their precursors. GNs/Co-Mn shows novel photocatalytic activity because Co and Mn nanoparticles were well dispersed on the surface of GNs as confirmed by SEM. The photodegradation rate of NRC increased in aqueous solution as irradiation time increased and about 94% of dye was degraded within 5 min. The photocatalytic activity of recovered catalyst was also high and about 90% of dye was degraded within 5 min.

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