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Z-Scheme g-C₃N₄/Fe₃O₄/Ag₃PO₄ @Sep magnetic nanocomposites as heterojunction photocatalysts for green malachite degradation and dynamic molecular studies

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R. Haounati, H. Ighnih, H. Ouachtak, Rahime Eshaghi Malekshah, N. Hafid, et al.. Z-Scheme g-C₃N₄/Fe₃O₄/Ag₃PO₄ @Sep magnetic nanocomposites as heterojunction photocatalysts for green malachite degradation and dynamic molecular studies. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2023, 671, pp.131509. 10.1016/j.colsurfa.2023.131509 . hal-04297898

HAL Id: hal-04297898

<https://hal.science/hal-04297898>

Submitted on 22 Nov 2023

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1 **Z-Scheme g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep magnetic nanocomposites as**
2 **heterojunction photocatalysts for green malachite degradation and**
3 **Dynamic molecular studies**

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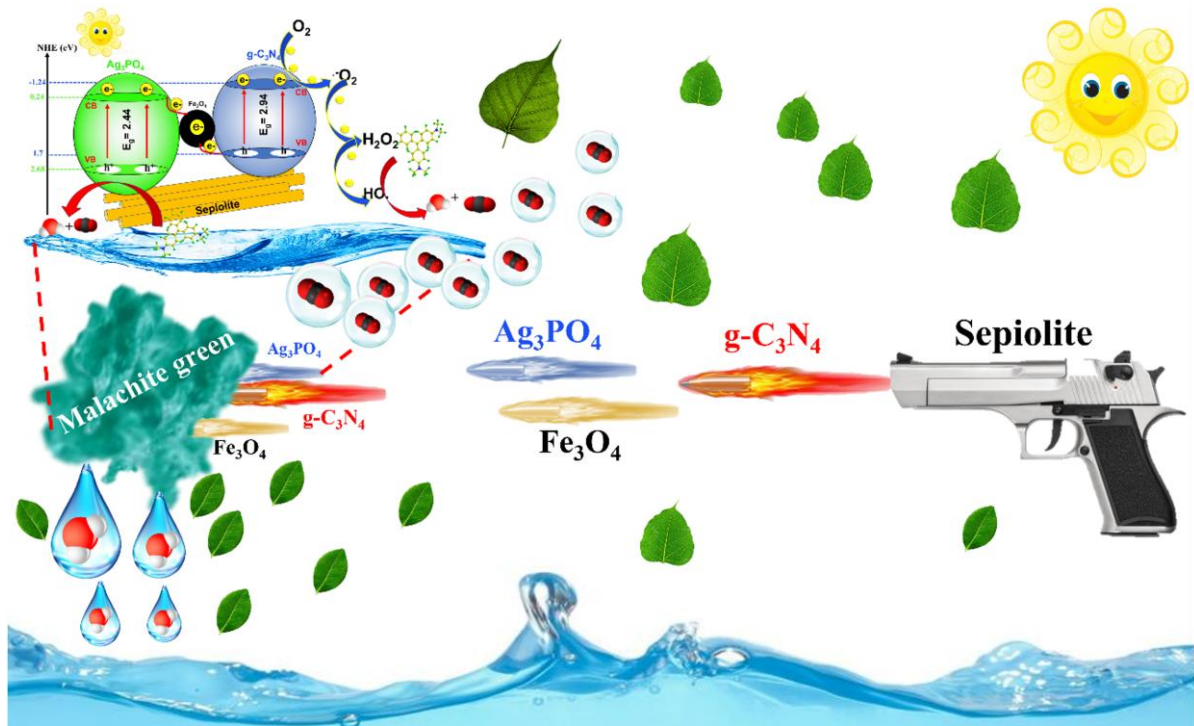
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27 **Graphical abstract**



28

29 **Abstract**

30 Recently, the synthesis of Z-scheme nanocomposite heterojunctions has received significant
31 attention. In the present work, we prepared a Z-scheme heterostructures nanocomposite by
32 using a facile co-precipitation method. Several techniques were used to characterize the
33 structures, the morphologies, the optical and the electronic properties, as well as the
34 photocatalytic performance of the nanocomposite. Thus, the scanning electron microscope
35 and the transmission electron microscope analyses showed that the sepiolite surface was well
36 occupied by the Ag_3PO_4 , the $\text{g-C}_3\text{N}_4$ and the Fe_3O_4 nanoparticles. Further, the g-
37 $\text{C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ nanocomposite, as compared to pure $\text{g-C}_3\text{N}_4$, $\text{g-C}_3\text{N}_4@\text{Sep}$ and g-
38 $\text{C}_3\text{N}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$, exhibited significantly improved photocatalytic performance for the
39 degradation of malachite green (MG) (100%, 12 min). Such photocatalytic activity was found
40 to be about 27, 26 and 1.85 times higher than that of $\text{g-C}_3\text{N}_4$, $\text{g-C}_3\text{N}_4@\text{Sep}$ and g-
41 $\text{C}_3\text{N}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$, respectively. The photocatalytic enhancement of magnetic
42 nanocomposite $\text{g-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ to degrade organic molecules such as MG dye,
43 under solar light irradiation, was attributed to the synergy effects between Ag_3PO_4 supported
44 by sepiolite clay and $\text{g-C}_3\text{N}_4$ combined with the Fe_3O_4 nanoparticles. Furthermore, the

45 photocatalytic activity of g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep remained at a high level even after four
46 cycles, suggesting that the quaternary nanocomposite has a high stability and good reusability,
47 as resulting from the suitable band structure and the Z-scheme heterojunction construction,
48 which improved the light usage and the charge carrier migration rate. DFT-D correction was
49 used to optimize all the structures. Then, MD calculations were applied to form
50 Fe₃O₄/Ag₃PO₄@Sep nano-composite, resulting the stable configuration due to the negative
51 adsorption. At last, the MG adsorption was investigated by adsorption locator module on
52 nano-composite, suggesting the thermodynamic stability system.

53 **Keywords:** Z-scheme, nanocomposite, malachite green, MD calculation.

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70 **1. Introduction**

71 In the recent years, the aquatic systems pollution has led to several humans and animals health
72 issues, impacting the economy and affecting the climate change [1–4]. Such water pollution
73 results mainly from the growing industrialization and the agricultural activities, and leads to
74 wastewater large amounts production [5]. The polluted waters may contain toxic metals,
75 organic molecules, dyes and drugs [6]. Particularly, the dye effluents originating from textile,
76 leather, cosmetics and pigments industries, are responsible for one of the major water
77 pollution problems in the world, and they should be consequently investigated [7].

78 Several methods such as the physical adsorption [8, 9], the biological process [10], and the
79 chemical oxidation [11, 12], have been applied at laboratory, as well as, at large scales, for the
80 wastewater treatment and the dye removal from the contaminated aqueous medium. Among
81 these methods, the Advanced Oxidation Processes (AOP), such as: photocatalytic degradation
82 using heterogeneous photocatalytic process, has been found to be a superior method, due to its
83 operational simplicity, its high efficiency toward the organic dyes, its economic benefits and
84 its facile mineralization of organic dyes into H_2O and CO_2 [13]. On the other hand, various
85 materials used as adsorbents and/or catalysts, for the dye removal from wastewaters using the
86 AOP method, they mainly include few high surface area materials such as zeolite, activated
87 carbon, carbon nanotubes, graphene and some other photocatalytic materials such as oxides
88 (ZnO , Bi_2O_3 , TiO_2 , YVO_4 , WO_3), hydroxides ($La(OH)_3$), sulfurs (MoS_2) and phosphates
89 ($BiPO_4$, $CePO_4$, Ag_3PO_4) [13, 14]. For the silver orthophosphate (Ag_3PO_4) based
90 semiconductor photocatalysts, due to their strong oxidation abilities, and their non-toxicities,
91 they have been widely employed for water purification [15]. In addition, to enhance the
92 catalytic activity of these silver orthophosphate (Ag_3PO_4) based materials, several
93 modifications were realized, including: homojunction construction, Z-Scheme composite
94 design, and defect generation [16]. The Z-Scheme design consist on improving the separation
95 efficiency of photogenerated electron(-)-hole(+) pairs by constructing heterojunction Z-
96 scheme photocatalysts with typical n-type semiconductors, such as: CeO_2 , TiO_2 , Fe_2O_3 , ZnO ,
97 etc.[13]. There are many problems associated with Z-scheme photocatalysts materials,
98 including the problem of charge transport at incomplete contact interfaces [17], and the
99 sufferance from the recycling process [13].

100 The present work deals with novel “g-C₃N₄ /Fe₃O₄ /Ag₃PO₄@Sep” Z-scheme based
101 photocatalysts, which were prepared, using a simple co-precipitation approach, to enhance the
102 sunlight degradation of Malachite Green MG dye in water. To the best of our knowledge,
103 there are no reported work on the preparation and the application of this material in the
104 photocatalytic decomposition performance of dyes under sunlight irradiation.

105 In the Z-scheme based photocatalyst preparation, the Fe₃O₄ was used as an n-type
106 semiconductor, due to its strong magnetic properties, the sepiolite clay (having the chemical
107 formula: Mg₄Si₆O₁₅(OH)₂·6H₂O) was used for its important benefits (environmentally
108 friendly, stable, inexpensive), and its large specific surface area, the g-C₃N₄ was used since it
109 is considered as a major component in the design of new photocatalysts for photodegradation
110 of organic molecules such as dyes under sunlight irradiation. The high photocatalytic activity
111 of the g-C₃N₄ can be explained by its band gap of 2.7 eV, yielding to an absorption edge
112 suitable for visible light capture, and band positions suitable for water oxidation-reduction,
113 and leading to high thermal and chemical stabilities[18, 19].It should be noted that the
114 sepiolite can provide more active sites for the Z-scheme “g-C₃N₄/Fe₃O₄/Ag₃PO₄”
115 photocatalyst.

116 In the present work, the structure and the morphology of the elaborated photocatalysts were
117 investigated. Further, we propose a possible enhanced Z-scheme heterojunction mechanism of
118 electron transfer. MD simulation was used to form Fe₃O₄/Ag₃PO₄@Sep nano-composite and
119 MG adsorption on this nano-composite.

120 **2. Experimental**

121 **2.1. Samples preparation**

122 **2.1.1. Chemicals**

123 The raw clay used in this work is sepiolite (Sep), is the same as used elsewhere [20].The other
124 chemicals, including melamine (C₃H₆N₆, 99%), ferric chloride hexahydrate (FeCl₃·6H₂O,
125 97%), ferrous sulfate hepta hydrate (FeSO₄·7H₂O, 99%), silver nitrate (AgNO₃, 99.8%),
126 ammonium dihydrogen phosphate (NH₄H₂PO₄, 98%),hydrochloric acid (HCl, 99%), sodium
127 hydroxide (NaOH, 98%), malachite green (MG, 99%) and ethylene glycol (HOCH₂CH₂OH,
128 99%), were all of analytical grade, purchased from Sigma-Aldrich and used as received.

129

130 **2.1.2 Synthesis of g-C₃N₄ and Fe₃O₄**

131 The g-C₃N₄ photocatalyst was synthesized through simple melamine calcination, by heating,
132 at 550 °C for 3 h (heating rate of 5 °C/min) 5g of melamine powder, and by using an alumina
133 crucible placed in a muffle furnace, as depicted in **Figure.1**.

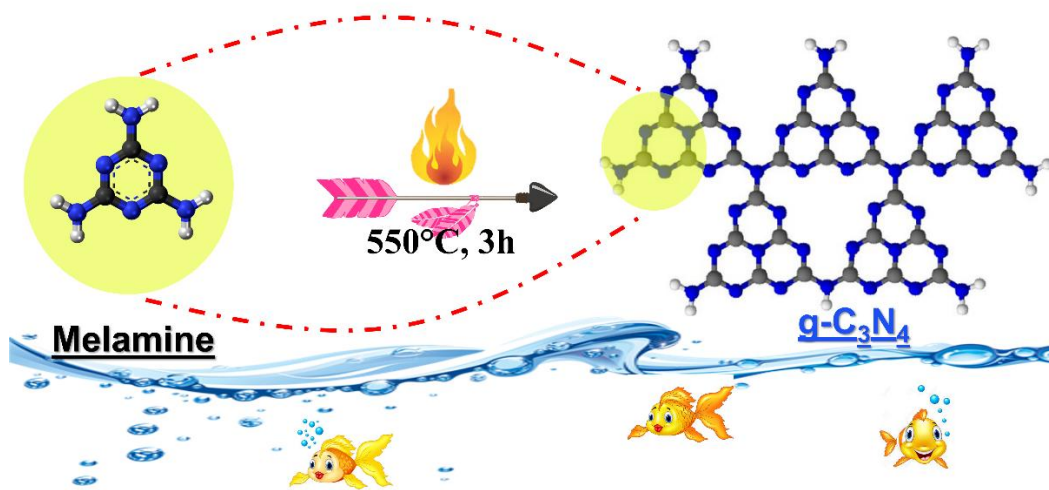


Figure. 1: Mechanism of g-C₃N₄ preparation from melamine

134
135 The magnetite Fe₃O₄ was prepared by co-precipitation method. Thus, in typical experiment,
136 4.670 g of FeCl₃.6H₂O and 2.401 g of FeSO₄.7H₂O were dissolved in 50 ml of ethylene
137 glycol/deionized water with the ratio 1/1 under vigorous magnetic stirrer at room temperature
138 for 30 min under N₂. Then amounts of NaOH 1M solution were added dropwise to the
139 previous solution, under constant magnetic stirring to adjust the pH to 9. Afterwards, the
140 mixture was magnetically stirred for 12 h more. Subsequently, the obtained mixture was
141 washed with distilled water, and the resulting black Fe₃O₄ was dried at 80 °C for 24 h as
142 shown in **Figure.2**.

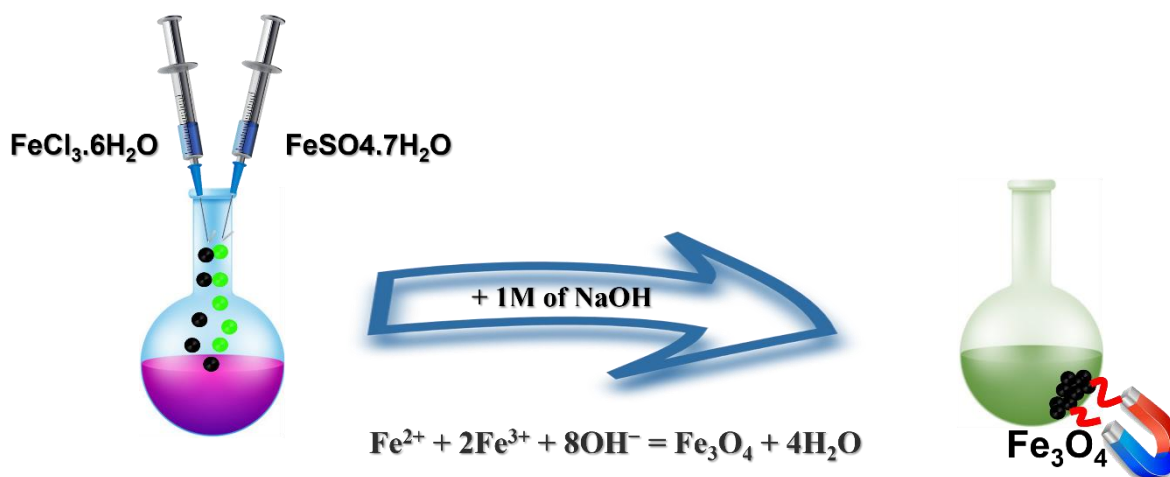


Figure. 2: The scheme for the Fe_3O_4 nanoparticles formation

143

144 2.1.3 Synthesis of quaternary $\text{g-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ nanocomposites

145 The $\text{g-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ nanocomposite was prepared by a facile heterogeneous
 146 suspension reaction procedure.

147 Firstly, the sepiolite-supported- Ag_3PO_4 ($\text{Ag}_3\text{PO}_4@\text{Sep}$) nanocomposite was synthesized
 148 through a simple electrostatically driven reaction. Thus, in a typical experimental synthesis
 149 procedure, a sepiolite suspension was obtained by dispersing 4 g of the raw sepiolite in
 150 200 mL of distilled water using ultrasonic treatment. Afterwards, a solution of AgNO_3 was
 151 added dropwise to the aqueous sepiolite dispersion in order to recover totally the negatively
 152 charged sepiolite sheets by the positive Ag^+ charges. Subsequently, 0.048 mM $\text{NH}_4\text{H}_2\text{PO}_4$
 153 was added, drop by drop, to the sepiolite- AgNO_3 mixture and NaOH 0.5M was slowly added
 154 into the resulting mixture, followed by magnetic stirring at room temperature for 4 h. At the
 155 end of the reaction, a green-yellow precipitate of $\text{Ag}_3\text{PO}_4@\text{Sep}$ was recovered by
 156 centrifugation at 5000 rpm for 10 min, washed several times with distilled water, and dried at
 157 80 °C overnight.

158 Secondly, the magnetic nanocomposite ($\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$) was prepared by dropping off
 159 Fe_3O_4 nanoparticles (10 mg/mL) on the surface of the heterogeneous $\text{Ag}_3\text{PO}_4@\text{Sep}$
 160 suspension, under vigorous stirring for 4 h. The resulting magnetic nanocomposite
 161 $\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ was collected by a permanent magnet, washed with distilled water
 162 multiple times, and dried under vacuum overnight. In the last step, a $\text{g-C}_3\text{N}_4$ suspension was
 163 dropped off the surface of the $\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ nanocomposite. Finally, the obtained
 164 magnetic nanocomposite was separated by a permanent magnet and washed several times by

165 deionized water, and then dried at 80°C. The obtained sample was denoted as g-
 166 C₃N₄/Fe₃O₄/Ag₃PO₄@Sep. **Figure. 3** shows the steps involved in the magnetic g-
 167 C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposite synthesis.

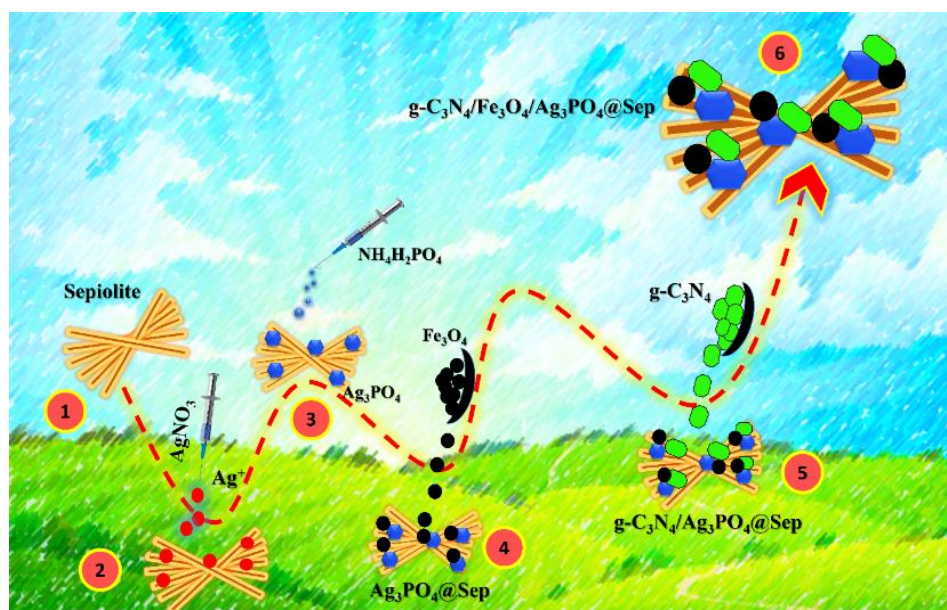


Figure. 3: The formation mechanism of quaternary g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep

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169 2.2. Photocatalytic activity

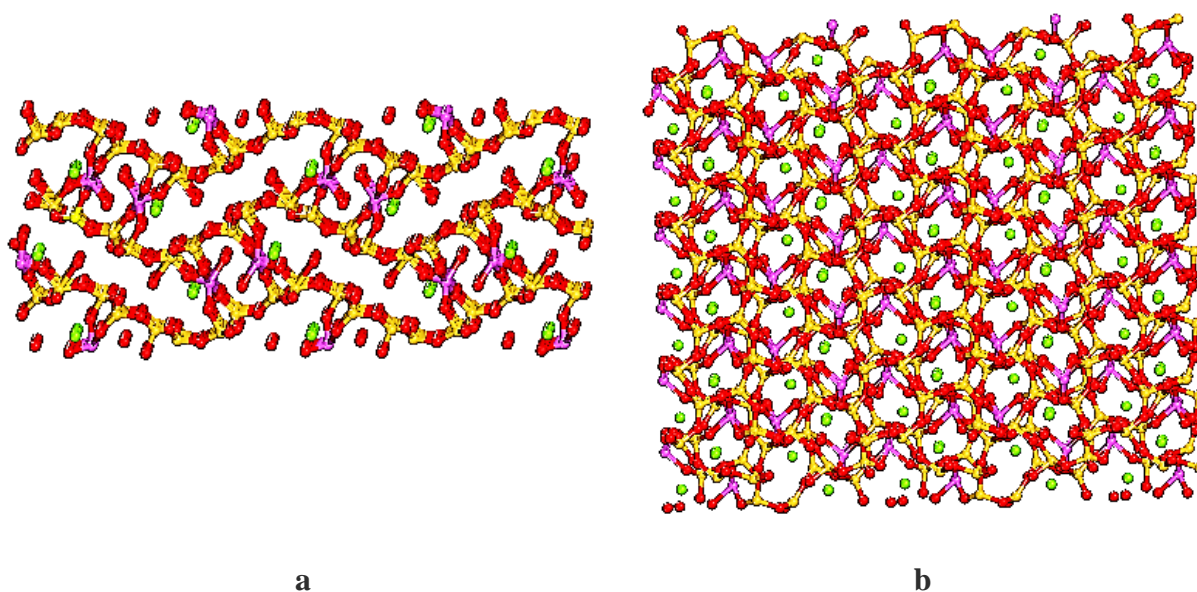
170 The photocatalytic activity of the g-C₃N₄, Ag₃PO₄, Fe₃O₄, Ag₃PO₄@Sep and g-
 171 C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposite photocatalysts were evaluated for the
 172 photodegradation of Malachite Green (MG) in aqueous media under sunlight irradiation.
 173 Hence, in typical photocatalytic experiment, an amount of 100 mg of the photocatalyst was
 174 dispersed in 100 mL MG dye solution (10 mg/L). The prepared suspensions were maintained
 175 inside the reactor, in the dark, for 1 h to reach an adsorption-desorption equilibrium between
 176 the support and MG dye molecules, then 5 mL solutions were withdrawn every 2 minutes
 177 under sunlight irradiation. Subsequently, the solution was centrifuged to separate the liquid
 178 and solid phases for determine the concentration of MG dye with the wavelength of 615 nm
 179 using UV visible JENWAY-6705 spectrophotometer. The percent degradation was measured
 180 using the expression (**Eq.1**):

$$181 \quad \% \text{ of dye degradation} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

182 where C_0 is the original absorbance value of MG dye at initial time, and C_t is the absorbance
 183 value of MG dye at a given time after sunlight irradiation.

184 **2.3. Computational details**

185 $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ (sepiolite like palygorskite: Sep) with lattice parameters $a = 13.5$, $b =$
186 27.0 , and $c = 5.30 \text{ \AA}$ and built based on (200) surface and thickness of 1.574 \AA (**Figures 4a-b**)
187 [21]. C_3N_4 , Ag_3PO_4 and MG (malachite green) was used to perform all the required
188 calculations based on Density functional theory (DFT-D) by DMol³ module, GGA/ PBE
189 functional and DND and spin-unrestricted in Materials Studio 2017 software (**Figures 4c-d**).
190 Fe_3O_4 as cubic (ID: mp-753222 and Point Group $\text{Fd}\bar{3}\text{m}$) with $a = b = c = 8.44 \text{ \AA}$, $\alpha = \beta = \gamma =$
191 90.00° and volume of 602.06 \AA^3 was downloaded from
192 <https://materialsproject.org/materials/mp-19306> (Figures 4e-f). After that, Fe_3O_4 without
193 unitcell was made based on (220) surface and thickness of 1.500 \AA and slab position (1.00)
194 (**Figure 4g**). In order construct nano-composite $\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$, dynamic calculation (by
195 the Monte Carlo adsorption locator module) was used to assess the adsorption of 6 C_3N_4 ,
196 Ag_3PO_4 and Fe_3O_4 molecules [22]. Additionally, 6 molecules of MG were adsorbed on
197 $\text{Ag}_3\text{PO}_4(\text{Ag}_3\text{PO}_4@\text{Sep})$ by the Monte Carlo adsorption locator module [23].



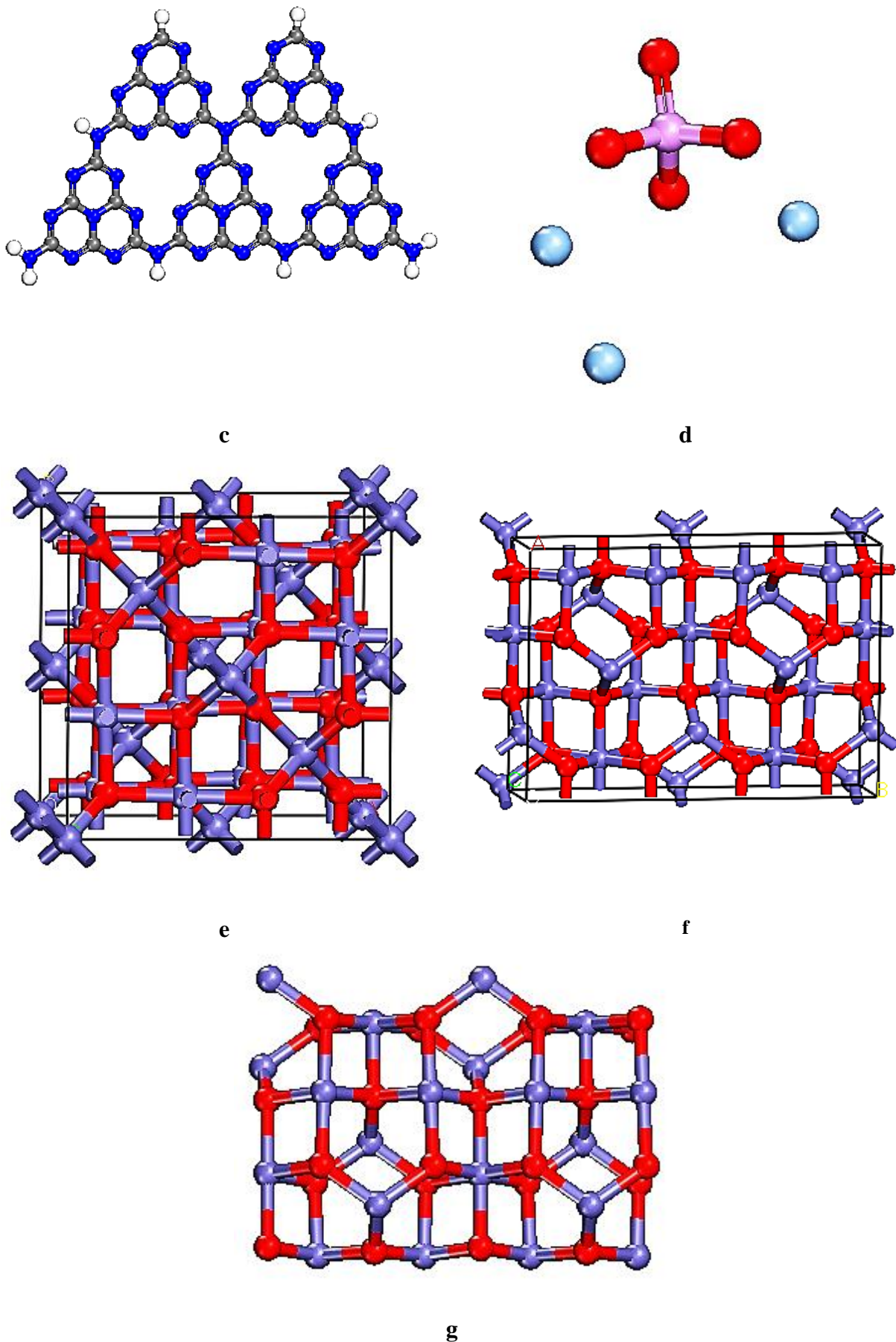


Figure 4. Snapshots of the optimized structures (a and b); $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ (sepiolite,

(c); C₃N₄, (d); Ag₃PO₄, (e); Fe₃O₄ as cubic (ID: mp-753222), (f); Fe₃O₄ (220) and (g); Fe₃O₄ (220) without unicell. Colored balls are Mg (green), oxygen (red), orange (Si), violet (Fe), pink (Al), and white (H).

198

199 3. Results and discussion

200 3.1. Characterizations of the g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposites

201 *XRD analyzes*

202 The crystalline structures of the as-prepared samples were determined by XRD. Thus, **Figure.**
203 **5** shows the XRD patterns of pure g-C₃N₄, sepiolite, Fe₃O₄ and g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep
204 nanocomposites.

205 Two distinct fundamental diffraction peaks are shown for the g-C₃N₄ sample, the great peak
206 located at ~ 27.4° corresponds to (0 0 2) planes and it is due to the stacking of the conjugated
207 double bonds with the interlayer d-spacing (0.336 nm), while the small peak at~13.1°, is
208 indexed as (1 0 0) planes, and it is attributed to the interplanar of interlayer d-spacing
209 (0.672 nm) [24]. For the sepiolite clay, all the observed diffraction peaks of the sample were
210 found to correspond to the JCPDS card (No. 75–1597) in addition to the observed few peaks
211 resulting from quartz and carbonates impurities. The characteristic diffraction peaks of the
212 synthesized Fe₃O₄ nanoparticles occurred at diffraction angles, 2θ = 30.46°, 35.60°, 43.48°,
213 53.84°, and 57.40°, which are attributed to (2 2 0), (3 1 1), (4 0 0), (4 2 2), and (5 1 1) planes,
214 respectively, confirming the formation of the Fe₃O₄ spinel cubic phase (JCPDS No. 01–076-
215 0955). Finally, the X-ray diffraction (XRD) pattern of the g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep
216 nanocomposite shows clearly all the diffraction peaks of Ag₃PO₄ which can be easily indexed
217 to the Ag₃PO₄ centered cubic structure and correspond to the JCPDS card (No. 06-0505). As
218 can be seen also in **Figure. 5**, the XRD spectrum of the nanocomposite shows the presence of
219 the sepiolite and the body cubic spinel Fe₃O₄ nanoparticles peaks, which confirm the
220 successful preparation of g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposite.

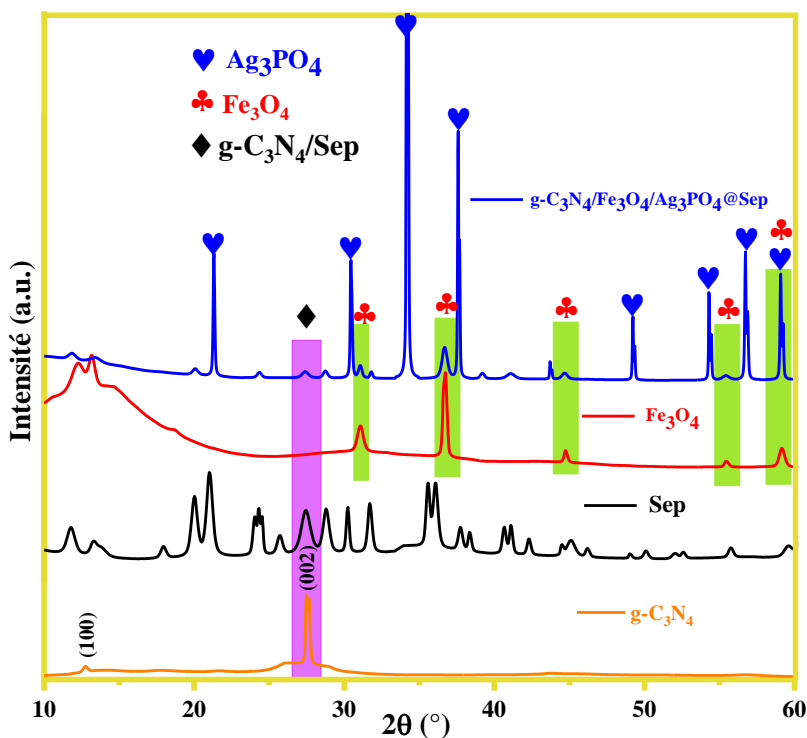


Figure. 5. XRD patterns of the prepared samples.

221

222 **FTIR analyzes**

223 In order to assess the successful formation of nanocomposites, FTIR spectroscopy was used
 224 as a tool to investigate the chemical structures of the various prepared samples. Thus, **Figure.**
 225 **6** shows the FTIR spectra of g-C₃N₄, Sepiolite, Fe₃O₄, Ag₃PO₄@Sep and g-
 226 C₃N₄/Fe₃O₄/Ag₃PO₄@Sep catalysts. As can be seen in **Figure. 6a**, the g-C₃N₄ sample shows
 227 strong IR responses. In this figure, the bands located at 1251, 1325, 1419, 1571, and 1639 cm⁻¹
 228 ¹ could be attributed to the typical stretching modes of CN heterocycles, whereas the
 229 absorption peaks at 800 cm⁻¹ and 889 cm⁻¹ are ascribed to the typical breathing mode of tri-s-
 230 triazine units and the deformation mode of N – H bonds, respectively [25, 26]. For the
 231 sepiolite, the FTIR spectrum depicted in **Figure. 6b** exhibits two absorption peaks of zeolitic
 232 water (3433 cm⁻¹ and 1644 cm⁻¹) and coordinated water (3581 cm⁻¹) present in the sepiolite
 233 nanofibers structure. Note that the absorption peaks located in the region of 788–675 cm⁻¹,
 234 were attributed to the bending and the stretching vibration of hydroxyl groups (Mg-OH),
 235 whereas the band located at 1016 cm⁻¹, 455 cm⁻¹, 1215 cm⁻¹ and 1074 cm⁻¹, they might be
 236 due to the Si-O bonds stretching[27, 28]. For the Fe₃O₄ nanoparticles spectrum, as shown in
 237 **Figure. 6c**, two characteristic peaks located at 556 cm⁻¹ and 1058 cm⁻¹ were observed,
 238 corresponding to the Fe–O stretching mode in the Fe₃O₄ confirming that the main phase is

239 magnetite[29]. In the case of $\text{Ag}_3\text{PO}_4@\text{Sep}$, as can be seen in **Figure. 6d**, the spectrum shows,
 240 in addition to all characteristic peaks of raw sepiolite, three characteristic bands located at
 241 1012 cm^{-1} , 1012 cm^{-1} and 1390 cm^{-1} , due to stretching vibration and bending vibration of P-
 242 O-P and P=O of pure Ag_3PO_4 [29].

243 For the $\text{g-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ nanocomposite FTIR spectrum shown in **Figure. 6e**, as
 244 can be observed, the presence of all the characteristic bands of sepiolite, Fe_3O_4 , Ag_3PO_4 and
 245 $\text{g-C}_3\text{N}_4$, confirms that Ag_3PO_4 nanoparticles cover the sepiolite surface of and they are joined
 246 to the $\text{g-C}_3\text{N}_4$ nano sheets by Fe_3O_4 nanoparticles. Thus, from the overall FTIR data, the
 247 successful preparation of the $\text{g-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ nanocomposite is clearly
 248 evidenced.

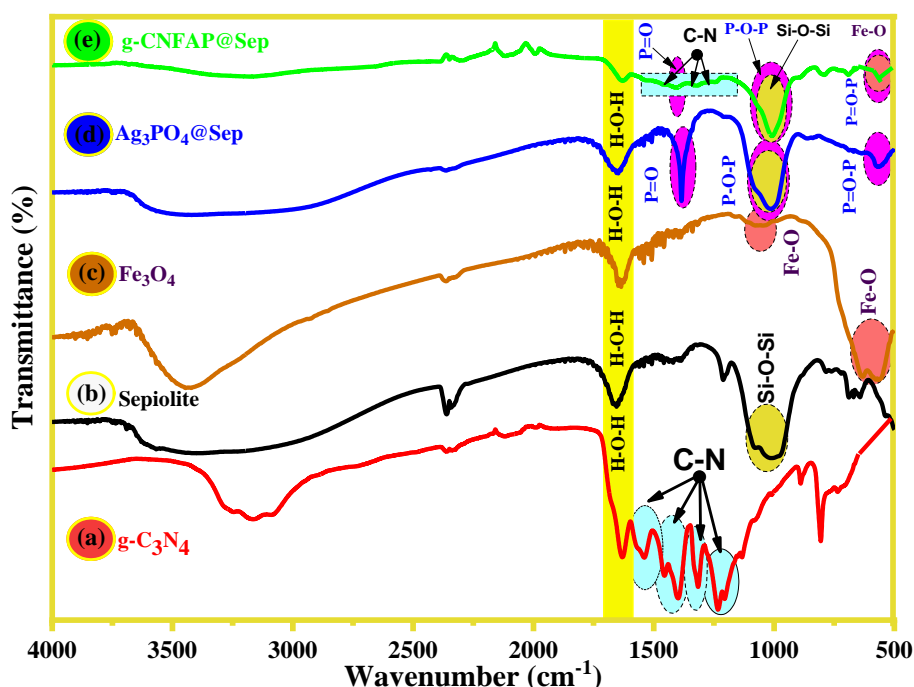


Figure. 6. FTIR spectra of photocatalysts. (a) $\text{g-C}_3\text{N}_4$, (b) Sepiolite, (c) Fe_3O_4 , (d) $\text{Ag}_3\text{PO}_4/\text{Sep}$ and (e) $\text{g-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$.

249

250 SEM analyzes

251 The surface structure and morphological characteristics of $\text{g-C}_3\text{N}_4$, Sepiolite, $\text{Ag}_3\text{PO}_4@\text{Sep}$
 252 and $\text{g-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ the composites were investigated using SEM as shown in
 253 **Figure.7**. The $\text{g-C}_3\text{N}_4$ (**Figure. 7a**) prepared directly from the calcination of the melamine
 254 shows a mesoporous structure with an irregular sheet shape. It can be observed from **Figure.**
 255 **7b** that the raw sepiolite surface reveals compact nodular with non-uniform fibrous filament

256 morphology. After surface modification of sepiolite by Ag_3PO_4 nanoparticles, as shown in
 257 **Figure. 7c**, it is obvious that the Ag_3PO_4 slightly changes the raw sepiolite by making the
 258 nanofibrous surface rougher. Note that the Ag_3PO_4 nanoparticles attachment on the sepiolite
 259 surface results from the electrostatic interaction. In addition, the image in **Figure. 7c** shows
 260 small particle sizes with sheets shapes, which are attributed to $\text{g-C}_3\text{N}_4$. According to the SEM
 261 image of $\text{g-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ nanocomposite shown in **Figure. 7d**, the Fe_3O_4
 262 nanoparticles, the Ag_3PO_4 nanoscale and the $\text{g-C}_3\text{N}_4$ nanosheets are homogeneously
 263 distributed, and cover all the sepiolite fibrous surface. In summary, the obtained SEM images
 264 show high adhesion of the prepared catalysts, mainly Ag_3PO_4 particles on the sepiolite surface,
 265 which may increase the nano composite photogenerated carriers' lifetime.

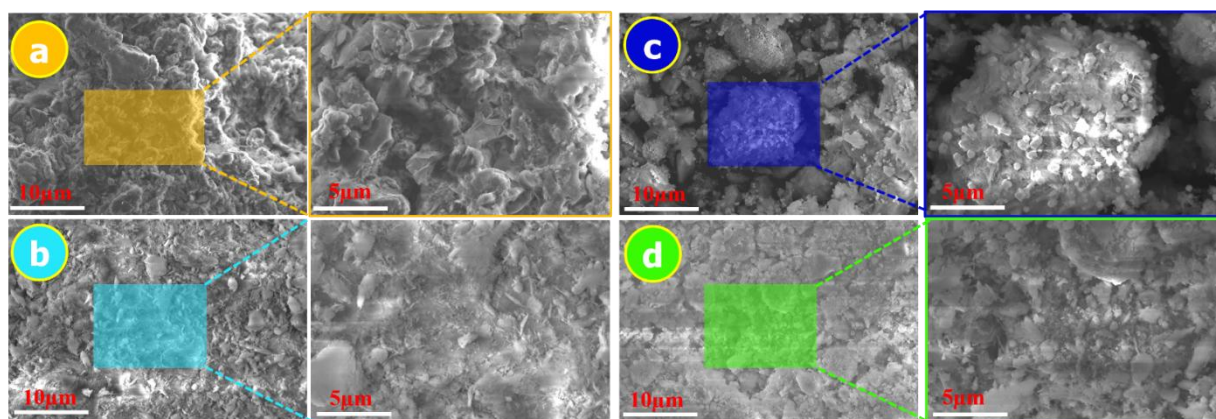


Figure. 7. SEM images of $\text{g-C}_3\text{N}_4$ (a), sepiolite (b), $\text{g-C}_3\text{N}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ (c) and $\text{g-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ (d).

266

267 *EDX and mapping analyzes*

268 The energy dispersive X-ray spectra (EDX) and the mapping are two of the effective methods
 269 for determining the sample chemical composition and its purity. The EDX spectra and image
 270 mapping of the synthesized samples, $\text{g-C}_3\text{N}_4$, sepiolite, $\text{Ag}_3\text{PO}_4@\text{Sep}$ and $\text{g-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$
 271 nanocomposite are displayed in **Figure. 8a-d**. The spectrum for the $\text{g-C}_3\text{N}_4$ shows, as expected, the presence of C and N elements. Similarly, the raw sepiolite
 272 EDX spectrum shown in **Figure. 8b**, indicates the presence in the sample of the O, Mg and Si
 273 elements. Moreover, the EDX spectrum of $\text{g-C}_3\text{N}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ nanocomposite shows that
 274 all the elements in the nanocomposite are found to be matched such as O, Mg, Si, C, N, Ag
 275 and P. The EDX spectrum of $\text{g-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ nanocomposite indicates the
 276 appearance of O, Mg, Si, C, N, Ag, P and Fe elements, and the mapping shows that the g-

278 C_3N_4 , Ag_3PO_4 , and Fe_3O_4 elements, are homogeneously distributed on the sepiolite surface.
 279 **Table 1** is presented the atomic percentages of different elements.

280

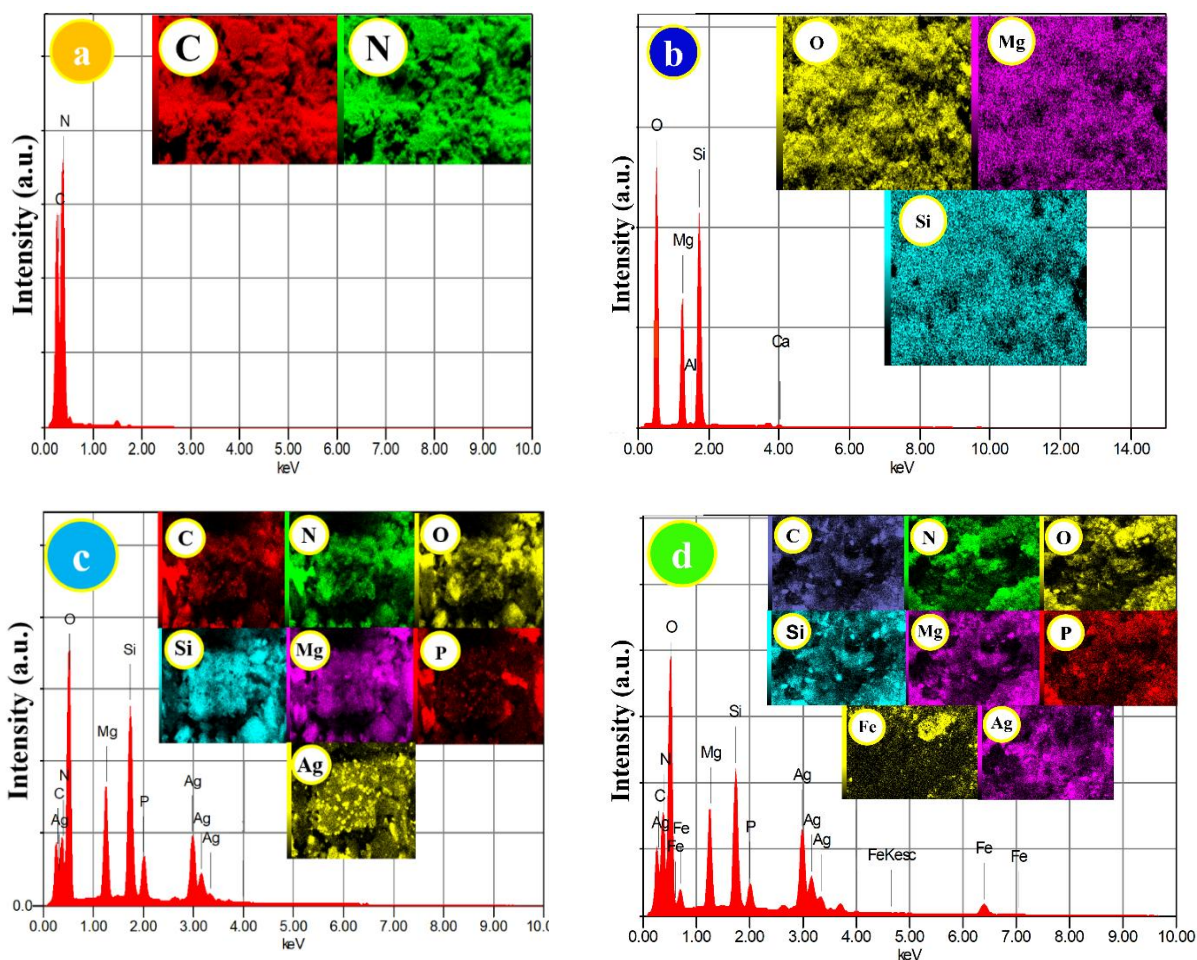


Figure.8. EDX spectra and mapping micrographs, of $g-C_3N_4$ (a), sepiolite (b), $g-C_3N_4/Ag_3PO_4@Sep$ (c) and $g-C_3N_4/Fe_3O_4/Ag_3PO_4@Sep$ (d).

281

282 **TEM analyzes**

283 Transmission electron microscopy (TEM) is an excellent analytical method in the physical,
 284 chemical, sciences can be used to find the morphology and size of different materials. In this
 285 study, TEM analysis was used to investigate the particle size and morphology of $g-C_3N_4$, $g-$
 286 $C_3N_4/sepiolite$, $g-C_3N_4/Ag_3PO_4$ and $g-C_3N_4/Fe_3O_4/Ag_3PO_4@Sep$ nanocomposites in details.
 287 As shown in **Figure. 9a**, the pristine $g-C_3N_4$ have uniform fabric-like folded nanosheets
 288 fabric-like folded nanosheets with thin thickness porous. The porous structure was favorable

289 for the catalyst to absorb pollutants and further promote the degradation and was in the size
 290 range of about 50-80 nm.

291 **Table 1.** Atomic percentages of the g-C₃N₄, sepiolite, g-C₃N₄/Ag₃PO₄@Sep and the g-
 292 C₃N₄/Fe₃O₄/Ag₃PO₄@Sep elements.

		C	N	O	Mg	Si	Ag	P	Fe	Ca	Al
g-C₃N₄	At	44.59	55.41	-	-	-	-	-	-	-	-
	%										
Sepiolite	At	-	-	63.56	20.25	15.56	-	-	-	0.4	0.
	%									3	2
g-C₃N₄/Ag₃PO₄@Sep	At	8.82	4.33	45.35	8.29	21.06	10.13	2.02	-	-	-
	%										
C₃N₄/Fe₃O₄/Ag₃PO₄@ Sep	At	9.42	12.02	41.01	7.83	19.04	6.35	2.22	2.1	-	-
	%										

293

294 The corresponding TEM image of g-C₃N₄/sepiolite is given in **Figure. 9b**. It reveals that the
 295 sepiolite shows nanotubes-like fibers having uniform diameters with an average of ~ 30 nm,
 296 which exhibited the strong contact between nanosheets g-C₃N₄. The **Figure. 9c** is clearly
 297 displayed the strong interfacial contact between g-C₃N₄ and Ag₃PO₄, which is conducive to
 298 the rapid transfer and separation of photogenerated electron-hole pairs in g-C₃N₄/ Ag₃PO₄
 299 nanocomposite. Moreover, the Ag₃PO₄ exhibited hexagonal form with a size of ~ 200 nm. In
 300 addition, it could be observed from the **Figure. 9d** that all as prepared catalysts nanoparticles
 301 g-C₃N₄, Ag₃PO₄ and Fe₃O₄ were homogeneously loaded on the nanotubes sepiolite surface.
 302 Even more important, the photocatalysts g-C₃N₄ and Ag₃PO₄ are implying the strong
 303 interfacial contact between them by Fe₃O₄ nanoparticles, which may favor the charge transfer.
 304 So, the obtained results reinforce what was previously obtained by several analysis
 305 techniques.

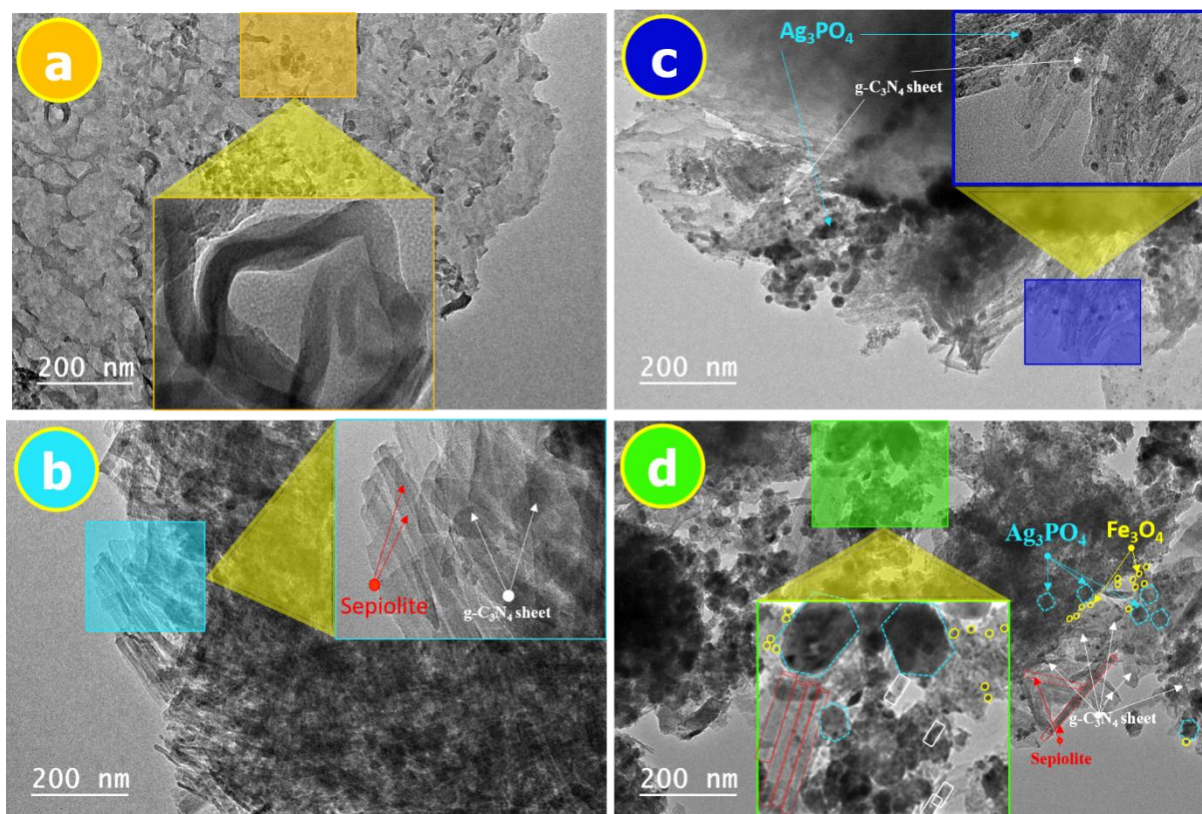


Figure. 9. TEM images of the $g\text{-C}_3\text{N}_4$ (a), $g\text{-C}_3\text{N}_4/\text{sepiolite}$ (b), $g\text{-C}_3\text{N}_4/\text{Ag}_3\text{PO}_4$ (d) and $\text{C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$

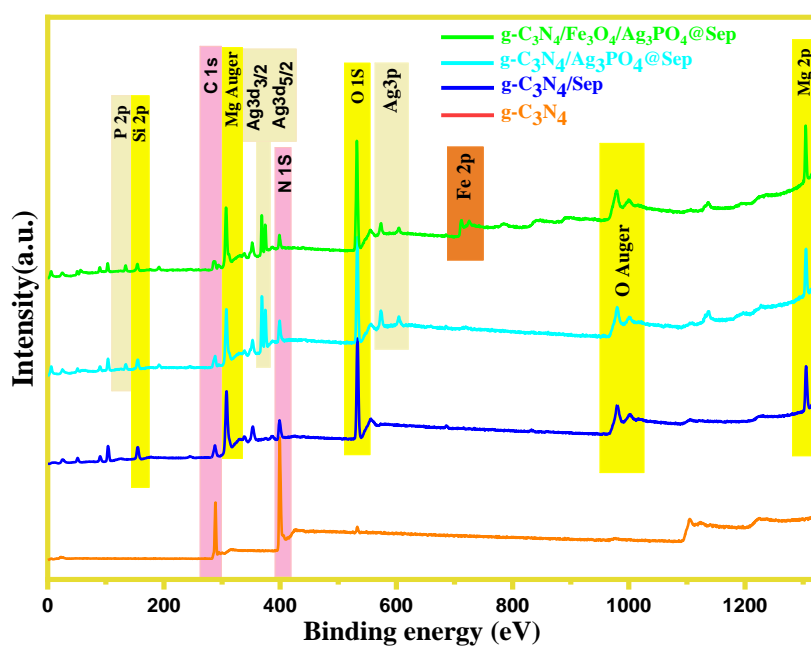
306

307 *XPS analyzes*

308 XPS is commonly quantitative technique used to provide information on the elemental
 309 composition and the valence states of constituent elements on the surface of the
 310 nanomaterials. Nevertheless, the chemical species in the surface of $g\text{-C}_3\text{N}_4$, $g\text{-C}_3\text{N}_4/\text{sepiolite}$, -
 311 $\text{C}_3\text{N}_4/\text{Ag}_3\text{PO}_4 / \text{Sep}$ and $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ nanocomposites were confirmed by XPS
 312 and reported in **Figure.10**. The XPS spectrum of $g\text{-C}_3\text{N}_4$ **10a** reveals mainly two peaks
 313 assigned to C1s and N1s, the spectrum of $g\text{-C}_3\text{N}_4/\text{sepiolite}$ **Figure. 10a** shows seven main
 314 elements C 1s, N 1s, Si 2p, O 1s, Mg 2p, O Auger and Mg Auger. Moreover, the spectrum of
 315 $g\text{-C}_3\text{N}_4/\text{Ag}_3\text{PO}_4$ (**Figure. 10a**) includes all peaks of $g\text{-C}_3\text{N}_4$ and sepiolite as well as four
 316 elements P2p, Ag 3d_{3/2}, Ag 3d_{5/2} and Ag3p. The XPS spectrum of $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$
 317 nanocomposite is reported in **Figure. 10a**, it can be seen that all peaks of $g\text{-C}_3\text{N}_4$, sepiolite
 318 and Ag_3PO_4 are existing as well as element Fe 2p, which confirm the presence of Fe_3O_4 in the
 319 surface of sepiolite. **Figure.10b** shows the high-resolution XPS spectra of the peak of Si 2p
 320 located in the region of 101.97 eV, which revealing the valence state of the silicon.

321 **Figure.10c** detects the deconvoluted Mg 2s spectra located at 1303.2 eV, which can be
 322 attributed to magnesium hydroxides Mg-OH. In **Figure. 10d**, the C 1s spectrum can be
 323 decomposed into two constituents at 284.8 and 288.3 eV for the C-C and C-N chemical
 324 bonding, respectively[30, 31].The N 1s peak of g-C₃N₄ could be deconvoluted into three
 325 Gaussian–Lorentzian fitted peaks at 398.96, 399.67, and 400.9 eV, which were attributed to
 326 pyridinic N (C-N=C), pyrrolic N (N-(C)₃), and graphitic N (C-N-H) respectively (**Figure. 10e**
 327) [32, 33].The deconvoluted Ag3d spectra demonstrate the existence of two main peaks at
 328 367.2 and 373.17 eV (**Figure. 10f**), assigned to the Ag3d_{5/2} and Ag3d_{3/2} of Ag⁺ in the
 329 nanocomposite. The deconvolution of O1s from the nanocomposite display two principal
 330 peaks at 531.1 and 532.32 eV, corresponding to and the lattice oxygen atoms (O²⁻) and H₂O
 331 molecules adsorbing on the surface of nanocomposite **Figure. 10g** [34, 35]. Deconvolution Fe
 332 2p orbital presents two main spectrum located at 711.97 and 725.56 eV, could be due to the
 333 Fe 2p_{3/2} and Fe 2p_{1/2} spin orbitals of magnetite, respectively, **Figure. 10h** [36].As can be
 334 seen in **Figure 10.i**. the peak at 132.8eV may be attributed to the P2p, which is assigned to
 335 P⁵⁺ of PO₄³⁻ [36]. Therefore, these results could confirm the coexistence of g-C₃N₄, Ag₃PO₄
 336 and Fe₃O₄ in the g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposites, and then create an important
 337 synergistic effect during the photocatalytic activity.

338



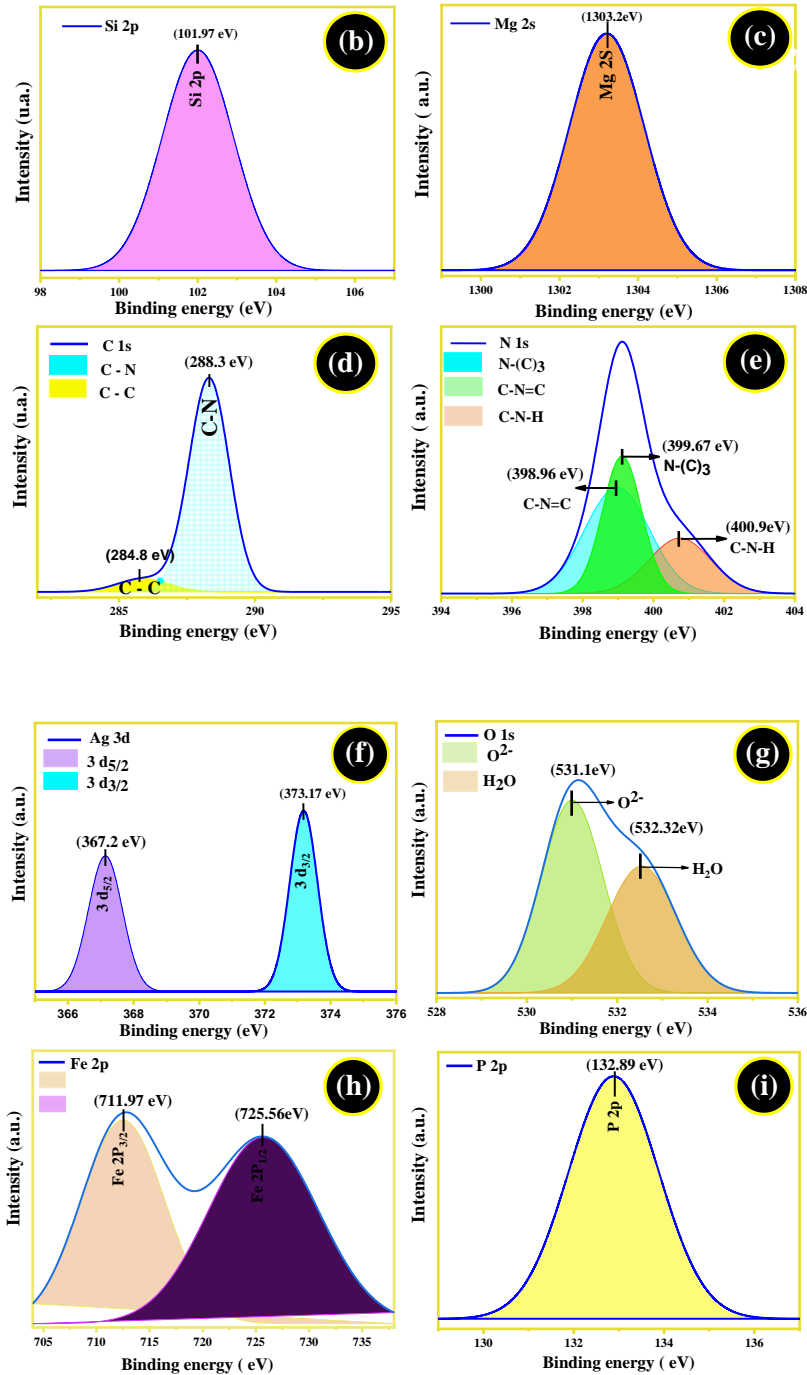


Figure. 10. XPS analyzes of g-C₃N₄, g-C₃N₄/Sep, g-C₃N₄/Ag₃PO₄@Sep and g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposite (a) HR Si 2p spectrum (b) HR Mg 2s and (c) HR C 1s (d)HR N1s (e) HR Ag 3d (f)HR O1s (g) HR Fe 2p (h) HR P 2p (i).

339 **DRS analyzes**

340 Solid-state UV-Vis or diffuse reflectance spectroscopy (DRS) is a very useful technique to
 341 investigate the electronic and optical properties of catalysts samples. It can be observed from

342 **Figure.11a** that all samples exhibited good light capture in the range of 200 to 500 nm, the
 343 DRS spectrum shows an absorption band edge at λ 440 nm corresponding to intrinsic
 344 absorption of g-C₃N₄ and Ag₃PO₄ demonstrated an absorption band edge at λ 450 nm. When
 345 Ag₃PO₄, g-C₃N₄ and Fe₃O₄ were supported on sepiolite, the optical absorption range was
 346 broader, and the optical absorption intensity over the whole range of 200 -600 nm. This
 347 indicates that Ag₃PO₄, g-C₃N₄, Fe₃O₄ and sepiolite have a synergistic effect. Thus, the
 348 increase in the absorption of g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposite indicates that the
 349 nanocomposite may demonstrate a remarkable photocatalytic activity in the visible region.

350 The band gaps of three samples can be calculated according to the Kubelka-Munk formula,
 351 which is the following (Eq.2)[37, 38]:

$$352 \quad \alpha h\nu = A(h\nu - E_g)^{n/2} \quad (2)$$

353 Where α is the absorption coefficient, h is Planck's constant, ν is the frequency of light, E_g
 354 represents the band gap energy, A is a constant and n refers to the type of electron
 355 transition.**Figure. 11b** shows $(\alpha h\nu)^2$ versus energy (h ν) diagrams of the band gap energy of g-
 356 C₃N₄, Ag₃PO₄ and g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep. As illustrated by the Tauc plot in **Figure.**
 357 **11b** the band gap energies of g-C₃N₄, Ag₃PO₄ and g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep are 2.94, 2.44
 358 and 2.83 eV, respectively. So, the narrow band gap of the g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep
 359 nanocomposite due to the existence of synergistic effect between sepiolite, Ag₃PO₄, g-C₃N₄
 360 and Fe₃O₄ shows that it has a higher visible light absorption ability, which could help in the
 361 separation of electron-hole pairs.

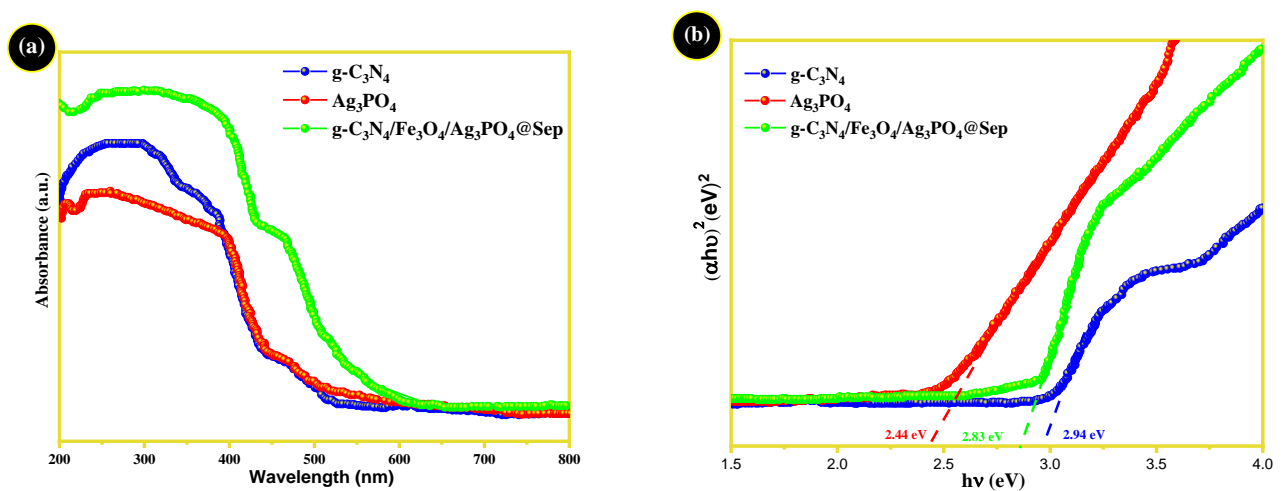


Figure. 11. (a) UV–Vis diffuse reflectance spectra and (b)Tauc plot of the prepared samples: g-C₃N₄, Ag₃PO₄ and g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep.

362

363 3.2. Photocatalytic activity of g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposite

364 The photocatalytic activities of all synthesized photocatalysts were examined by degradation
365 of MG dye under sunlight irradiation to study their potential applicability in the field of
366 environmental treatment.

367 Firstly, the photodegradation of MG without catalyst was studied for comparison (i. e. MG
368 aqueous solution irradiated with sunlight in the absence of the photocatalyst). In the absence
369 of the photocatalyst (**Figure. 12a**), the results indicate that no degradation of MG was
370 observed after 12 minutes of irradiation. This indicated that MG dye is not effectively
371 decontaminated by photolysis alone (i.e. under sunlight irradiation and in the absence of the
372 photocatalyst). In the other hand, as can be seen in **Figure. 12a**, in the absence of Sunlight
373 irradiation, the adsorption of MG from water onto the prepared catalyst surfaces, such as, g-
374 C₃N₄, g-C₃N₄/Sep, g-C₃N₄/Ag₃PO₄@Sep and g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposites,
375 were also investigated. It can be seen from **Figure. 12a** that the MG dye molecules were only
376 slightly removed from water after 60 minutes. The removal efficiencies of the MG dye, in the
377 absence of Sunlight irradiation, achieved approximately 13%, 10%, 7% and 2% for g-C₃N₄, g-
378 C₃N₄/Ag₃PO₄@Sep, g-C₃N₄/Sep and g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposite,
379 respectively. These data indicate that all the synthesized photocatalysts show low adsorption
380 activities towards the MG dye.

381 Besides, **Figure. 12b** shows the MG dye removal, under Sunlight irradiation, from aqueous
382 media onto different types of prepared photocatalysts, including g-C₃N₄, g-C₃N₄/Sep, g-
383 C₃N₄/Ag₃PO₄@Sep and g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposite during the same period.
384 The observed degradation efficiencies for MG dye are about $\approx 23.91\%$, $\approx 25.52\%$, $\approx 76.55\%$
385 and $\approx 100\%$, for the g-C₃N₄, g-C₃N₄/Sep, g-C₃N₄/Ag₃PO₄@Sep and g-
386 C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposite in the 12 min of irradiation, respectively.
387 Obviously, the order of photocatalytic activity of the prepared photocatalysts is: g-
388 C₃N₄/Fe₃O₄/Ag₃PO₄@Sep > g-C₃N₄/Ag₃PO₄@Sep > g-C₃N₄/Sep > g-C₃N₄. **Figure. 12b**
389 shows clearly that the concentration of MG dye decreases dramatically, as time increases, and
390 nearly disappears within only 16 min. So, the results obtained demonstrate that the
391 photocatalytic activity of g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposite towards MG dye, under
392 sunlight irradiation, is higher in comparison to the others photocatalysts. Such difference in
393 behaviour between g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep and the others catalysts, can be due to several

394 effects. Firstly, the magnetic nanocomposite exhibits high ability to absorb visible light.
 395 Secondly, the synergistic effect occurring between the three samples: Ag₃PO₄, g-C₃N₄ and
 396 Fe₃O₄, leading to photoactivity enhancement. Thirdly, the high electrostatic interactions
 397 occurring between the Ag₃PO₄ nanoparticles and the sepiolite negative sites, lead to the
 398 stability of Ag₃PO₄ nanoparticles caused by the strong adhesion of Ag₃PO₄ on the sepiolite
 399 surface, improve the electrons and holes separation, and prevent their recombination.
 400 Fourthly, the increase in the degradation efficiency is due to the availability of more active
 401 sites in the g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposite. Fifthly, the sepiolite was used as an
 402 excellent support by increasing the contact between Ag₃PO₄ and the solar-light photons.
 403 Finally, the Fe₃O₄ nanoparticles can be used as an efficient electron transfer compound
 404 leading to recombination reduction of the photogenerated carriers and facilitating the transfer
 405 of photogenerated electrons. Therefore, it can be concluded that the preparation of the
 406 magnetic Z-heterojunction g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep should be used as a stronger
 407 photocatalyst for the degradation of hazardous organic pollutants such as toxic dyes.
 408 Furthermore, the photocatalytic performance of the magnetic nanocomposite prepared in the
 409 present work, was evaluated and compared with other photocatalysts found in the literature
 410 (**Table 2**). Besides, the experimental kinetic data for the MG dye photodegradation in the
 411 presence of the g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposite were assessed and compared to
 412 the first-order Langmuir-Hinshelwood model. Thus, according to (**Eq. 3**) the apparent
 413 degradation rate constant of the first-order reaction, **K_{app}**, can be calculated from the plot of ln
 414 (C₀/C_t) versus t. Knowing the **K_{app}** value, the half-life **t_{1/2}** value can also be determined
 415 according to (**Eq. 4**):

$$416 \quad \ln \left(\frac{C_0}{C_t} \right) = K_{app} \times t \quad (3)$$

$$417 \quad t_{1/2} = \frac{0.693}{K_{app}} \quad (4)$$

418 where **K_{app}** (min⁻¹) is the apparent degradation rate constant of the first-order reaction, t is the
 419 irradiation time (min), C₀ (mg/L) and C_t (mg/L) are the initial and residual concentrations of
 420 MG dye.

421 The linearization of ln (C_t/C₀) as a function of irradiation time for each photocatalyst is given
 422 in **Figure. 12c**. The calculated values of **K_{app}** and half-life **t_{1/2}** were also reported in **Table 3**.

423 **Table 2.** Comparison of photocatalytic activity of g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep towards MG
 424 dye with other similar photocatalysts from literature.

Photocatalyst	Light Source	C ₀ (mg/L)	Time (min)	%	Ref
ZnO/CNT	Visible light	30	60	79 %	[39]
α -NiMoO ₄	UV– Visible	10	180	79.43 %	[40]
poly(azomethine)/Ti O ₂	Sunlight	50	300	95	[41]
rGO/CuS	Sunlight	10	90	97.6%	[42]
Fe ₃ O ₄ / SiO ₂ /TiO ₂	UV	10	150	100%	[43]
Pt-TiO ₂ /SiO ₂	UV–Vis. light	10	60	79%	[44]
RGO-Fe ₃ O ₄ /TiO ₂	UV–Visible	5.5	55	100	[45]
g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep	Sunlight	10	12	100	This work

425

426 **Table 3.** MG dye degradation parameters for different prepared photocatalysts.

	g-C ₃ N ₄	g-C ₃ N ₄ @Sep	g-C ₃ N ₄ /Ag ₃ PO ₄ @Sep	g-C ₃ N ₄ /Fe ₃ O ₄ /Ag ₃ PO ₄ @Sep
K_{app} (min⁻¹)	0.0097	0.01	0.143	0.264
t_{1/2} (min)	4.34	4.238	1.64	0.96

427

428 The obtained rate constants (K_{app}) values for the g-C₃N₄, g-C₃N₄@Sep, g-C₃N₄/Ag₃PO₄@Sep
429 and g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposites are, 0.0097, 0.01, 0.143 and 0.26 min⁻¹,
430 respectively. The use of the g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposite indicates
431 enhancement of the MG dye photocatalytic degradation, under solar irradiation, leading to a
432 higher rate constant K_{app} value, which is 27, 26 and 1.85 times higher than g-C₃N₄, g-
433 C₃N₄@Sep, g-C₃N₄/Ag₃PO₄@Sep, respectively. Therefore, the photocatalytic enhancement of

434 magnetic nanocomposite $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ to degrade organic molecules such as
 435 MG dye under solar light irradiation was attributed to the synergy effects occurring between
 436 Ag_3PO_4 supported by sepiolite clay and $g\text{-C}_3\text{N}_4$ combined with the Fe_3O_4 nanoparticles.

437

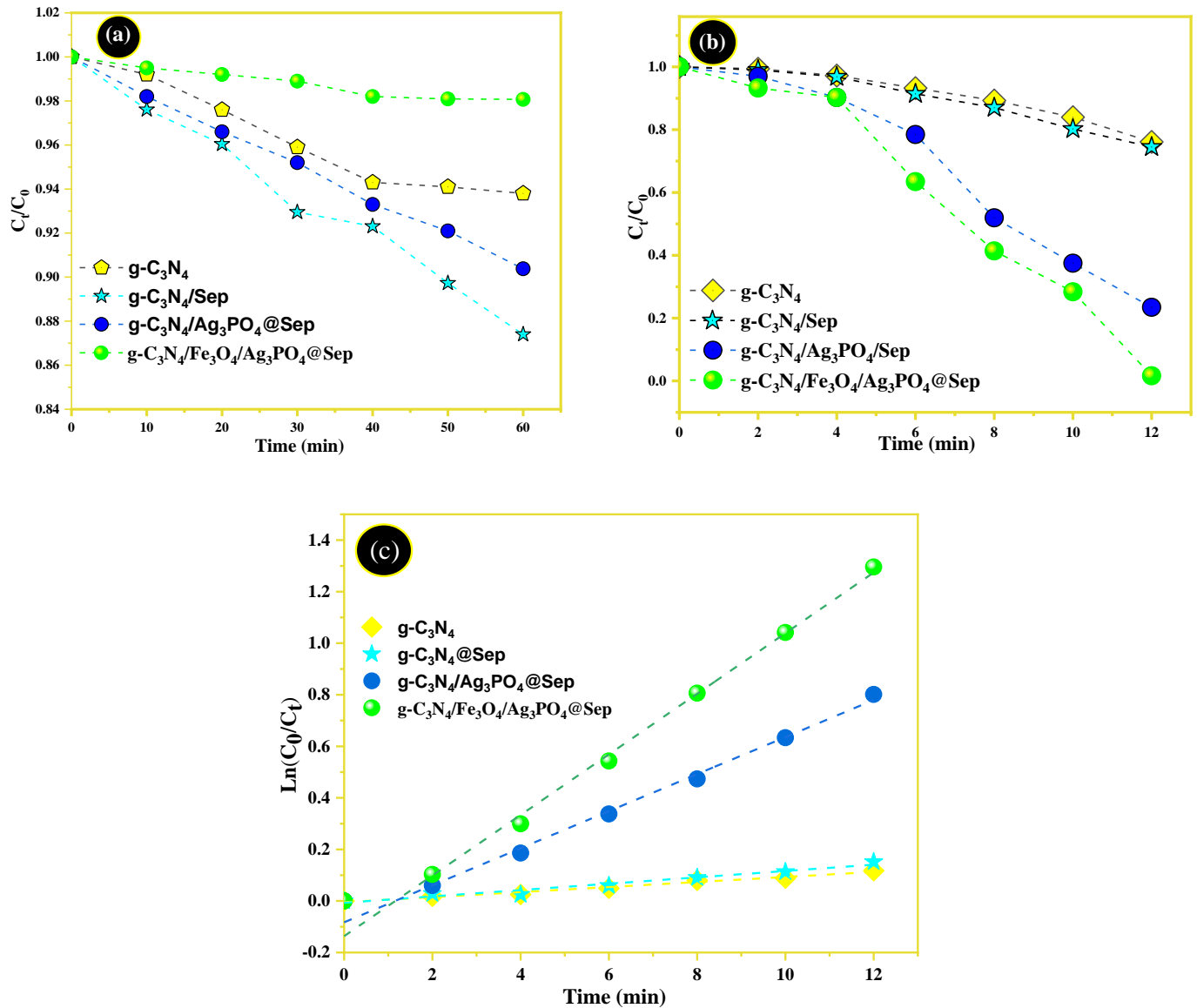


Figure.12. Irradiation of MG aqueous solution in the absence of the photocatalyst, and adsorption curves of MG dye from water onto various prepared samples, in the absence of the sunlight irradiation (a). Photocatalytic activities in the presence of various photocatalysts for MG degradation, and under sun light irradiation (b). Pseudo-first-order kinetic plot for degradation of the MG dye (c).

The pH is one of the important factors in the photocatalytic process because it affects the surface charge of the photocatalyst, degree of ionization of the target organic pollutants and dissociation of the functional groups on the active site of the photocatalyst [46]. **Figure.13** displays the influence of initial pH on the photodegradation of malachite green (10 mg. L⁻¹) catalyzed by g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep, which were performed by changing the pH in the range of 3-11 and adjusted by NaOH (0.1 M) or HCl (0.1 M). It is observed that the g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposite exhibits the greatest photocatalytic efficiency at pH = 7 (approximately 100%). However, in the acidic medium is reduced to 65.76% and 83.53% at pH = 3 and pH=5 which can be due to the fact that in acidic media, the surface of Sepiolite can be surrounded by the positive charges of H⁺, which prevents the cationic MG molecules from reaching the active site active site of Ag₃PO₄ and g-C₃N₄. Nevertheless, under a strongly alkaline solution pH =9 and pH =11, the degradation efficiency is decreased to 25.15% and 20.62%. This can be related to the instability of g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep nanocomposite in a strong alkaline solution (Ag₃PO₄ can react with NaOH to form Ag₂O, and then reduces the degradation performance). Hence, pH=7 was found to be more adequate for MG degradation.

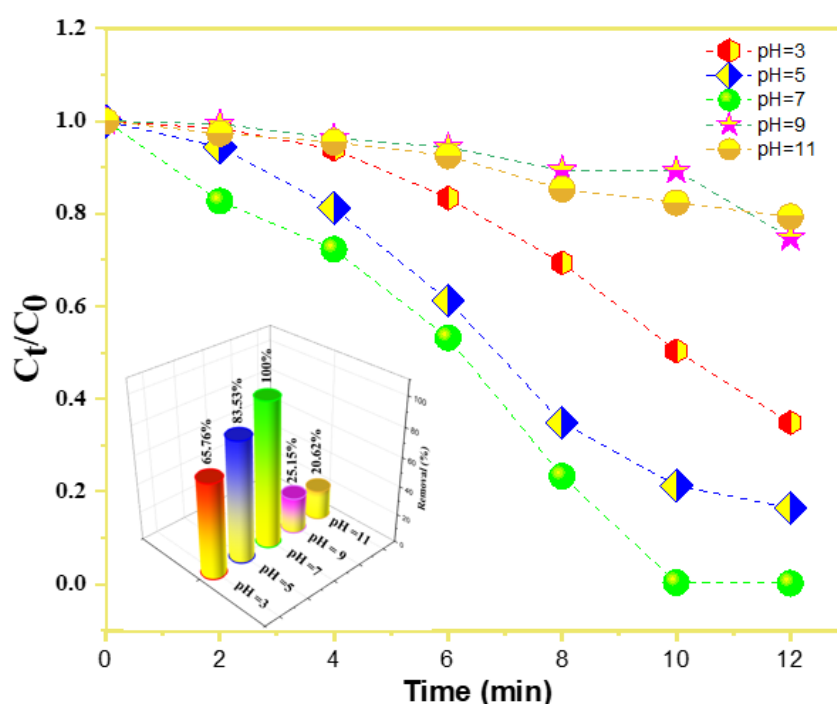


Figure. 13 Effect of pH values on MG photocatalytic degradation by g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep

439 3.3. Possible photocatalytic mechanism

440 In order further to understand the photocatalytic mechanism of $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$
441 nanocomposites in details. Several active species, like the hydroxyl radical ($\cdot\text{OH}$), the hole
442 (h^+), and the superoxide anion radical ($\cdot\text{O}_2^-$) are participate in the photodegradation processes,
443 and the function of active species generated by nanocomposite photocatalysts is evaluated
444 with different scavengers. However, the typical radical trapping tests for MG dye degradation
445 were examined in the presence of ethylenediamine tetra-acetic acid disodium (EDTA-2Na),
446 L-ascorbic acid (ASC), and Isopropanol Alcohol (IPA), which are utilized as capture agents
447 for h^+ , $\cdot\text{O}_2^-$, and $\cdot\text{OH}$, respectively [37]. It can be seen from **Figure. 14** that the removal rate
448 of MG by $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ photocatalyst was achieved up to 100 % under 12
449 minutes of visible light irradiation, without the introduction of a capture agent. Besides, the
450 decolorization activity of $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ nanocomposite towards MG dye in the
451 presence of EDTA-2Na, IPA and ASC decreased to 16.35%, 10.44% and 87.6%, respectively,
452 indicating that $\cdot\text{O}_2^-$ was not the main reactive species in the degradation photocatalytic
453 activity. Whereas the photocatalytic activity was strongly inhibited by the introduction of
454 EDTA- 2Na and IPA, which indicated that that h^+ and $\cdot\text{OH}$ are the major reactive species in
455 the photocatalytic degradation of MG. Therefore, h^+ and $\cdot\text{OH}$ radical are expected to be the
456 main reactive species for $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ nanocomposite in the photocatalytic
457 degradation process of MG under sunlight illumination. While ($\cdot\text{O}_2^-$) played a secondary role.
458 The same results were obtained in the previous study [13].

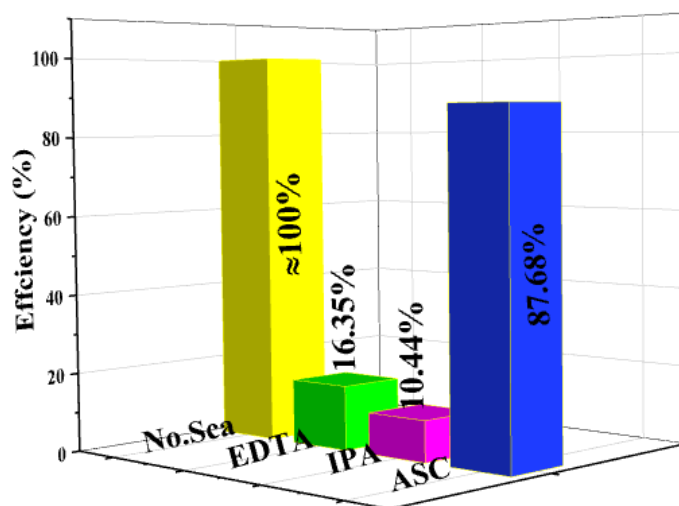


Figure. 14. Effect of scavengers on the photocatalytic degradation of MG by $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ nanocomposite.

460 The possible mechanism of the improved photocatalytic activity for g-
 461 C₃N₄/Fe₃O₄/Ag₃PO₄@Sep toward MG dye was investigated based on our previous
 462 experimental and schematically illustrated in **Figure. 15**. For two pure Ag₃PO₄ and g-C₃N₄,
 463 the electrons and holes photogenerated tend to recombine, and then only a proportion of them
 464 participated in the photocatalytic reaction. Thus, resulting in a comparatively low
 465 photocatalytic activity. However, the CB and VB positions of Ag₃PO₄ and g-C₃N₄ were
 466 determined using the empirical equations as shown below[46]:

$$467 \quad \chi(A_a B_b C_c) = [\chi(A)^a \cdot \chi(B)^b \cdot \chi(C)^c]^{\frac{1}{a+b+c}} \quad (5)$$

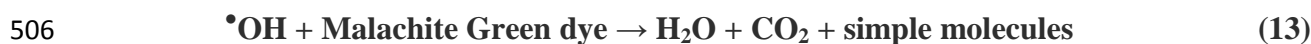
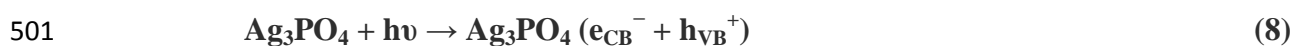
$$468 \quad E_{CB} = \chi - E_0 - \frac{E_g}{2} \quad (6)$$

$$469 \quad E_{VB} = E_{CB} + E_g \quad (7)$$

470 where χ indicates the absolute electronegativity of the semiconductor, which is defined as the
 471 geometric mean of the absolute electronegativity of the constituent atoms, E_0 is the energy of
 472 free electrons on the hydrogen scale (about 4.5 eV vs. NHE) and E_g (eV) the band gap energy
 473 of the semiconductors. The χ values for Ag₃PO₄ and g-C₃N₄ are calculated to be 5.96 and
 474 4.73, respectively. The CB and VB positions of g-C₃N₄ are determined to be -1.24 and +1.7
 475 eV, respectively, whereas those of Ag₃PO₄ are about +0.13 and +2.68 V, respectively (**Table**
 476 **4**). In this study the sepiolite clay was used as a support for the three semiconductors which
 477 helped to increase the adsorptive properties of the g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep
 478 nanocomposite surface, and to enhance its anionic active sites density, leading to removal
 479 from water of more hazardous MG dye molecules [43].

480 Due to the irradiation of sunlight, the electrons in the valence band (VB) of Ag₃PO₄ can be
 481 rapidly transferred from the conduction band (CB) leaving holes (h⁺). Besides, the g-
 482 C₃N₄ was also very activated by sunlight photons, and the generate the electrons in the
 483 conduction band (CB) and holes in the valence band (VB). At the same time, the Fe₃O₄
 484 nanoparticles were used as a solid electron mediator to link Ag₃PO₄ and g-C₃N₄ and can it
 485 enhances the electron transfer capability of photocarriers. On the other hand, the photo-
 486 generated electrons (e⁻) formed in the CB of Ag₃PO₄ were captured by the Fe₃O₄
 487 nanoparticles and transferred rapidly to VB of g-C₃N₄, because the •O₂ radicals cannot be
 488 formed in the surface of Ag₃PO₄ due to the CB potential ($E_{CB} = 0.24$ eV) is more positive
 489 than that of the O₂/•O₂ potential (-0.046 V vs NHE)[47]. Nevertheless, g-C₃N₄ can react with
 490 O₂ to produce the OH• radical species through the reduction of O₂ to H₂O₂, followed by the

491 further reduction of H₂O₂ to OH⁻ and the OH[•] radical species. This is due to the CB edge
 492 potential of g-C₃N₄ (E_{CB} = - 1.24 eV / NHE) being more lower than the standard potential of
 493 the O₂/H₂O₂ redox couple, which is 0.68 eV at the normal hydrogen electrode (NHE).
 494 Consequently, the accumulation of electrons in the CB of g-C₃N₄ and the holes in the VB of
 495 Ag₃PO₄ exhibited a high reduction and oxidation ability to mineralize MG dyes in H₂O and
 496 CO₂, respectively. In the above results, it is clear that the fabricated nanocomposite act as a
 497 Z-scheme photocatalysts and the synergistic effect between three synthesized semiconductor
 498 play a curcial role in the enhanced photoctalytic efficiency. Consequently, the
 499 photodegradation activity of g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep toward MG dye could be displayed
 500 as follows:



507

508 **Table 4.** Values of the electronegativity (χ), the bang gap energy (E_g), and the potential
 509 energy for valence band (E_{VB}) and conduction band (E_{CB}), for the g-C₃N₄ and
 510 Ag₃PO₄ catalysts.

catalyst	χ	E_g (eV)	CB (eV)	VB (eV)
g-C₃N₄	4.73	2.94	-1.24	1.7
Ag₃PO₄	5.96	2.44	0,24	2,68

511

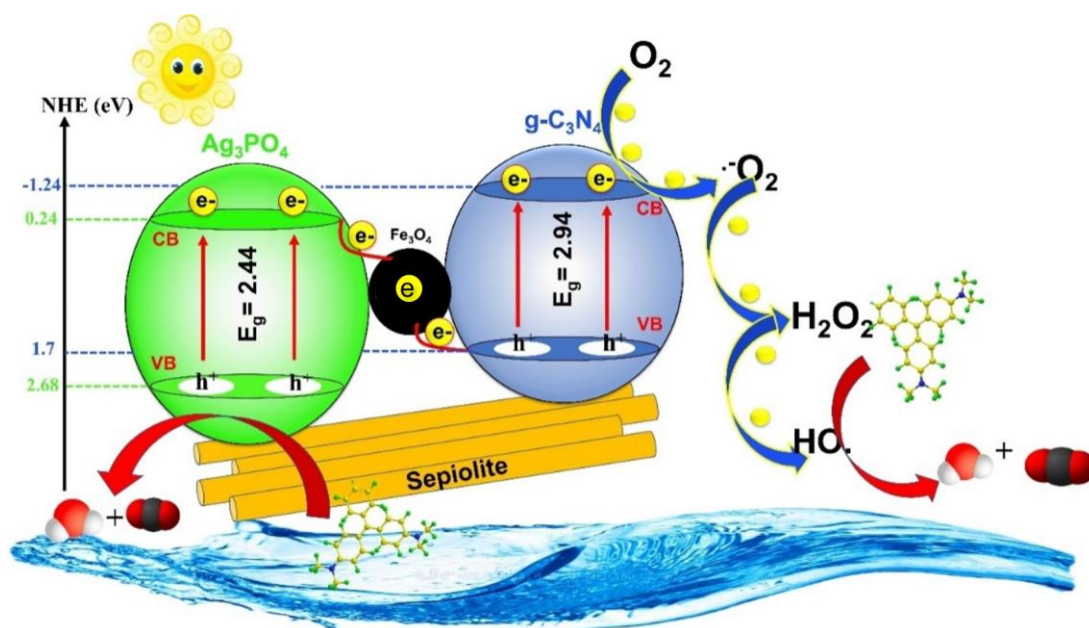


Figure. 15 : Schematic Illustration of Photocatalytic activity toward MG dye using $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ nanocomposite under sun-Light Irradiation.

512

513 3.4. Reusability and stability

514 The stability of photocatalysts is also an essential characteristic from the point of view of
 515 practical applications[49]. To investigate stability and the reusability of the $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$
 516 and Ag_3PO_4 samples, the recycle experiments for the degradation of MG dye under sunlight illumination in 12 min was studied. As illustrated in **Figure. 16**,
 517 after four cycles, the degradation of MG dye by pure Ag_3PO_4 exhibited an evident decrease
 518 (<22%) due to their high solubility in aqueous solution and the photoreduction of Ag^+ in
 519 Ag_3PO_4 to metallic Ag under sunlight illumination ($4\text{Ag}_3\text{PO}_4 + 6\text{H}_2\text{O} + 12\text{h}^+ + 12\text{e}^- \rightarrow 12\text{Ag} + 4\text{H}_3\text{PO}_4 + 3\text{O}_2$). Also, part of the pure Ag_3PO_4 may degrade to Ag_2O when Ag_3PO_4 is used. In
 520 the other hand (<13%), the photocatalytic activity of $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$
 521 nanocomposite shows a small loss, suggesting that the nanocomposite photocatalyst is
 522 comparatively stable during the photocatalytic degradation of MG dyes, which might be due
 523 to the fact that $g\text{-C}_3\text{N}_4$, Fe_3O_4 and sepiolite prevented Ag_3PO_4 from being reduced to metallic
 524 silver under sunlight irradiation. However, the color of the $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$
 525 nanocomposite slightly changed, while the pure Ag_3PO_4 changed to gray. We hypothesized
 526 that the photocorrosion phenomenon happened in the pure Ag_3PO_4 nanoparticles. Thus, the
 527 enhanced photostability of $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4@\text{Sep}$ had the potential for long-term
 528 wastewater purification.
 529
 530

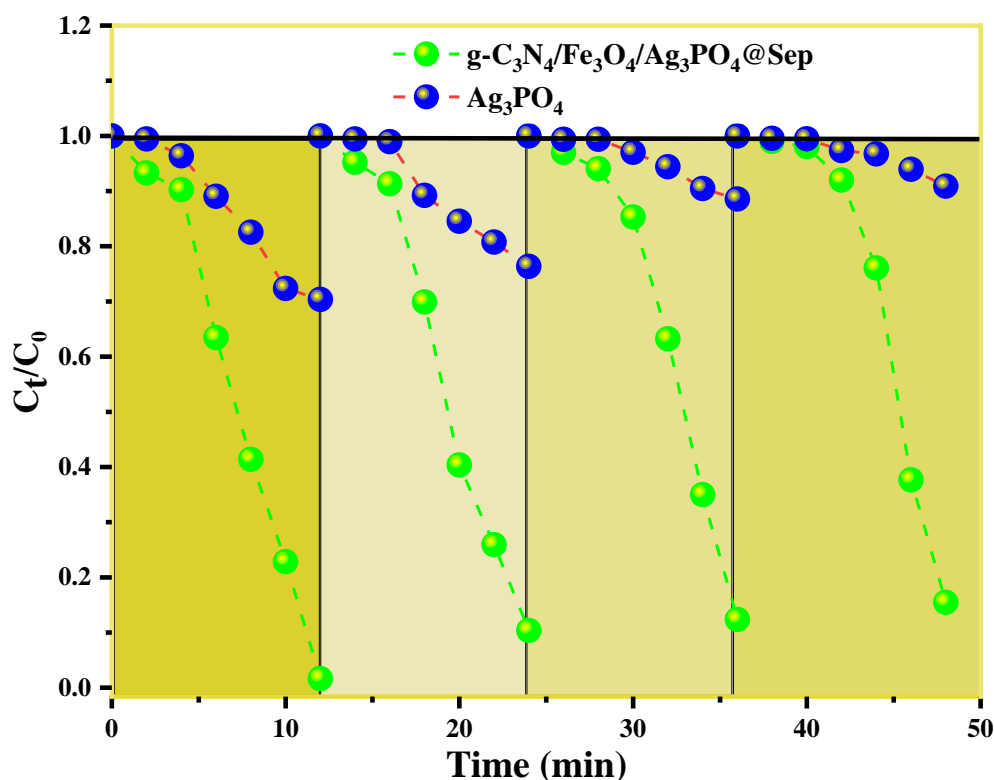


Figure. 16. Cycling runs for photocatalytic degradation of MG dye using g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep and Ag₃PO₄ under sunlight irradiation.

531

532 **3.5. The formation of nano-composite Fe₃O₄/Ag₃PO₄@Sep by Monte Carlo adsorption** 533 **locator simulation**

534 After optimization of structures by quantum calculations based on DFT-D, the adsorption
 535 performance of 6 of g-C₃N₄, Ag₃PO₄ and Fe₃O₄ molecules on Sep was occurred to make
 536 Fe₃O₄/Ag₃PO₄@Sep surface by adsorption locator module and forcefield; universal in
 537 Materials Studio 2017 software (ball-and-stick structures of nanocomposite are in **Figures**
 538 **17a-b**. The total energy of the system after the adsorption of C₃N₄, Ag₃PO₄ and Fe₃O₄ (E_{ad}) on
 539 Sep was obtained about -4.984×10^3 kcal/mol, resulting in coadsorbed g-C₃N₄, Ag₃PO₄ and
 540 Fe₃O₄ owing to the high negative value and exothermic system. In other hand, the calculated
 541 adsorption energy of this configuration was the most stable. Additionally, the top view of the
 542 Fe₃O₄ molecule vertically adsorbed on Sep are shown in **Figure.2b**. The energy of rigid
 543 adsorption, deformation, E_{ads} of Ag₃PO₄, Fe₃O₄ and C₃N₄ was obtained -439.766, -4.544×10^3 ,
 544 -11.147, -478.748 and -335.253, respectively. By analysis and comparison, adsorption energy
 545 for Fe₃O₄ and g-C₃N₄ parallel to Sep and their adsorption energies of both configurations were
 546 higher than that of Ag₃PO₄.

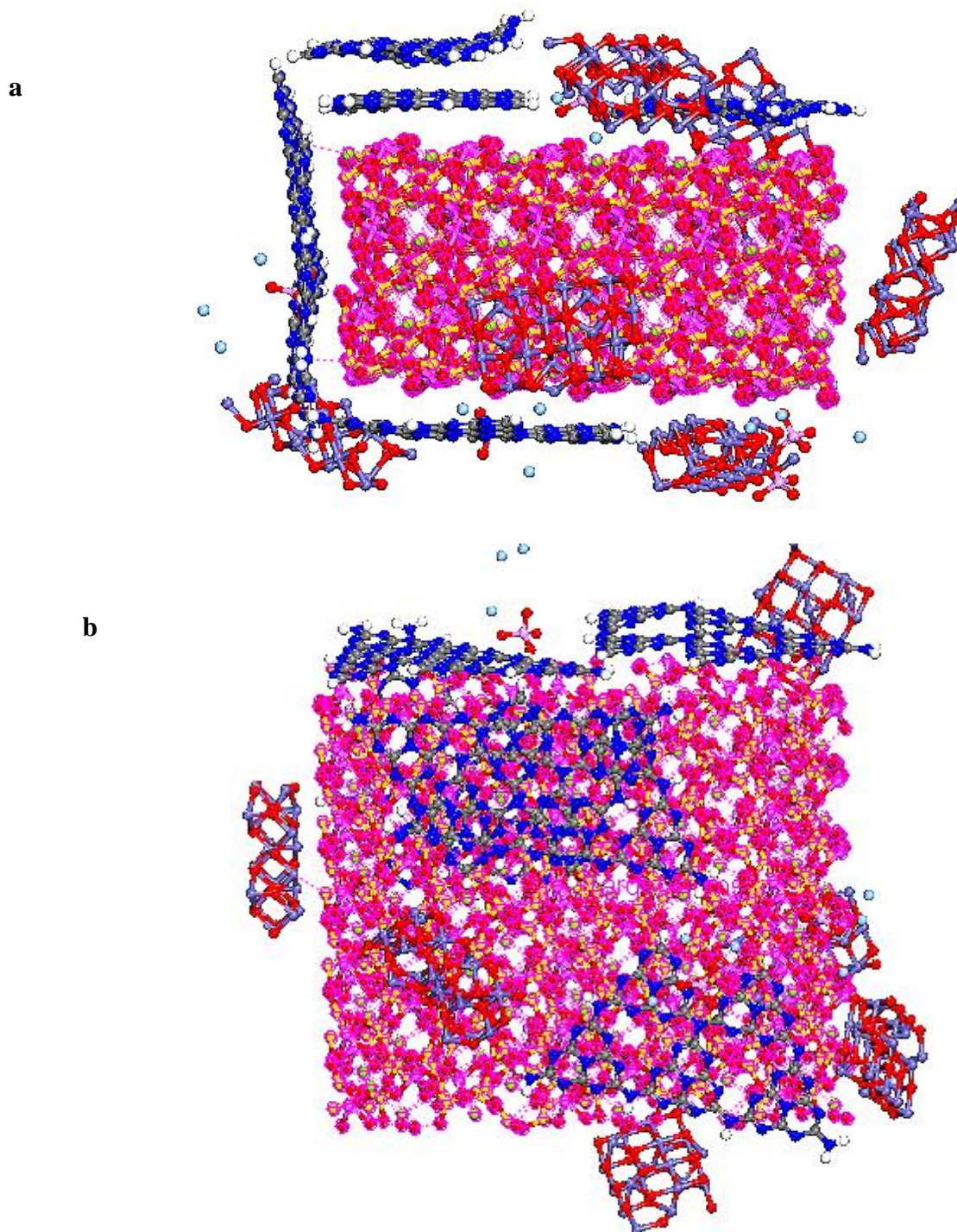


Figure. 17. (a and b); side and top views of the adsorption of 6 C_3N_4 , Ag_3PO_4 and Fe_3O_4 molecules on Sep by adsorption locator module in Materials Studio 2017 software.

547

548 **3.6. MG adsorption on $Fe_3O_4/Ag_3PO_4@Sep$ by Monte Carlo adsorption locator**
 549 **simulation**

550 In order to determine the most favorable adsorption geometry of MG on $Fe_3O_4/Ag_3PO_4@Sep$,
 551 6 MG molecules were applied to adsorb on nano-composite in the gas phase by adsorption

552 locator module and forcefield; universal in Materials Studio 2017 software (**Figures 18a-b**).
553 The total energy of the system after the adsorption of MG (E_{ad}) on adsorbent was estimated
554 about -436.229 kcal/mol as non-covalent interactions. The above adsorption energy reflected
555 the thermodynamic stability of the whole adsorption system due to the negative value[50]. In
556 other hand, the interaction was spontaneous and exothermic[51]. Based on the adsorption
557 results, MG can be transported horizontally by van der Waals and electrostatic interactions as
558 well as π - π stack between C_3N_4 and the delocalized π electron of MG, resulting dye
559 elimination. The significant adsorption of the MG can be related π - π stack interactions by g-
560 C_3N_4 [52]. The computational studies revealed that all MG molecules on nanocomposite were
561 the physisorption[53].

562

563

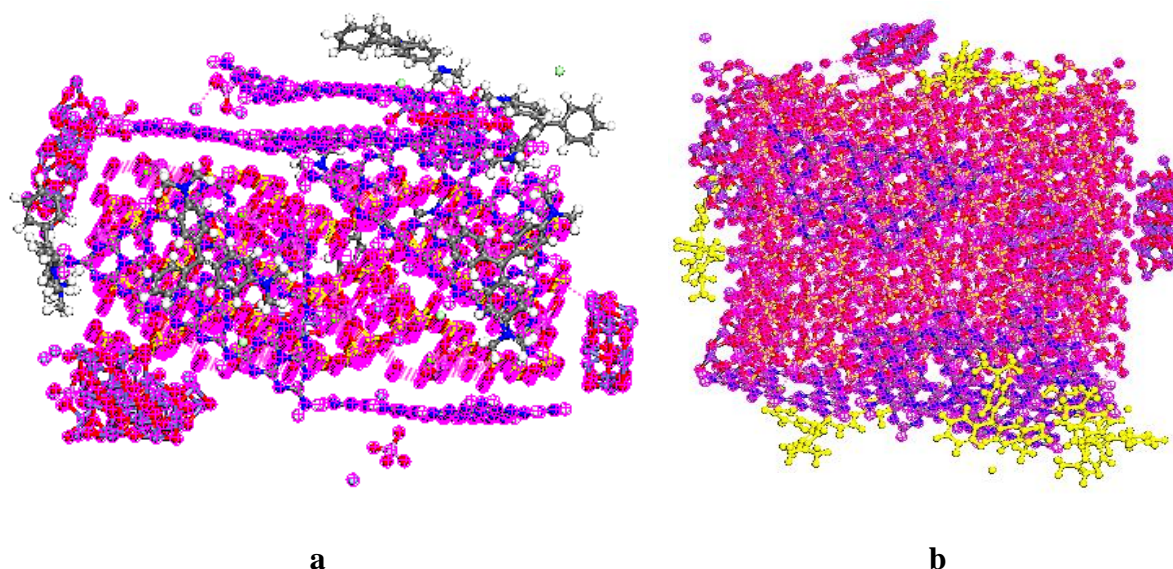


Figure. 18. (a and b); views of the adsorption of 6 MG molecules on $Fe_3O_4/Ag_3PO_4@Sep$ by adsorption locator module in Materials Studio 2017 software.

564

565 **Conclusion**

566 In brief, a simple approach synthesis was used to produce $g-C_3N_4/Fe_3O_4/Ag_3PO_4@Sep$
567 photocatalysts. The sepiolite clay was used as a support for the three semiconductors
568 investigated Ag_3PO_4 , $g-C_3N_4$ and Fe_3O_4 . Based on the characterization results, Ag_3PO_4 , $g-$
569 C_3N_4 and Fe_3O_4 particles were formed on the sepiolite clay surface with intimate interactions
570 occurring between them. The $g-C_3N_4/Fe_3O_4/Ag_3PO_4@Sep$ magnetic nanocomposite in

571 comparison to the others prepared photocatalysts, was found to be the most stable and it
572 showed the higher activities for the MG degradation under sunlight irradiation. The
573 photocatalytic enhancement of magnetic nanocomposite g-C₃N₄/Fe₃O₄/Ag₃PO₄@Sep to
574 degrade organic molecules such as MG dye under solar light irradiation was attributed to the
575 synergy effects occurring between the Ag₃PO₄, the g-C₃N₄ and the Fe₃O₄ nanoparticles,
576 supported by the. sepiolite clay. The overall data indicate that the co-precipitation method,
577 presented in this work, is a suitable approach to design and to synthesis new magnetic Z-
578 scheme nanocomposite photocatalysts with enhanced stability and activity towards MG
579 degradation. At the first, all structures were optimized by DFT-D in Material Studio 2017.
580 The next stage, adsorption locator module was applied to adsorb Fe₃O₄ and Ag₃PO₄ on Sep,
581 resulting exothermic system due to the high negative energy. Then, the adsorption mechanism
582 of MG onto Fe₃O₄/Ag₃PO₄@Sep nano-composite was computationally investigated using MD
583 through adsorption locator module. The result showed that MG was adsorbed through
584 physisorption into nano-composit by using van der Waals and electrostatic interactions as
585 well as π - π stack between C₃N₄ and MG. by MG adsorption, MG degradation can be
586 happened by nanocomposite. This DFT simulation result confirmed experimental results.

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