Photocatalytic Degradation of Methylene Blue Dye Using TiO₂ and Fe₃O₄/SiO₂/TiO₂ as Photocatalysts

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Abstract. This paper is focused on obtained two catalysts such as TiO₂ nanoparticles and Fe₂O₃/SiO₂/TiO₂ nanocomposite for adsorption and photocatalytic degradation of methylene blue (MB) dyes from aqueous solution. The morphology, structure and chemical proprieties of synthesized materials were investigated by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), N₂ adsorption-desorption isotherms and Zeta potential. The photocatalytic degradation of methylene blue under UV light in the presence of different synthesized catalysts was analyzed with spectrometer UV-Vis. The photocatalytic degradation of methylene blue was studied by focusing of photoactivity performance of Fe₂O₃/SiO₂/TiO₂ in comparison with TiO₂. An attempt has been made to study the effect of process parameters through amount of the catalysts and initial concentrations of methylene blue. In all cases was found that the kinetics of the MB photocatalytic degradation under UV light was fitted to the Langmuir–Hinshelwood. Even if the photocatalytic degradation study revealed that Fe₂O₃/SiO₂/TiO₂ and TiO₂ degraded about 90 % of methylene blue within 60 min, the magnetic nanocomposite Fe₂O₃/SiO₂/TiO₂ serves as better catalyst compared with TiO₂ nanoparticles. An important role in the photocatalytic degradation of MB is adsorption characteristic of TiO₂ and Fe₂O₃/SiO₂/TiO₂ surface. The photocatalytic performance of Fe₂O₃/SiO₂/TiO₂ remained greater than TiO₂ after 4 cycles of use.

1. Introduction
The accelerated growth of the different branches of consumption has developed the appearance of some pollutants that by their effect become more and more a threat to the quality of life. Nowadays there are several pollutants carcinogenic, inert and non-biodegradable such as rhodamine B, congo red, methylene blue, basic yellow 28 which can be remove using the conventional methods [1-4]. The disadvantages of the conventional methods involve low performance regarding color removal, consumption of high energy and high quantity of wastes [5]. For this reason, the researchers have developed new advanced materials with nanostructures architecture integrated as nano-catalysts in advanced oxidation processes [6]. These catalysts offer an easy and reliable way to degradation the carcinogenic and persistent pollutants. In this way, the new technologies combined with the production of materials, generate in the last decade another series of advanced materials with unique physical-chemical properties, addressed to different applications. Thus, in the field of advanced oxidation process, titanium dioxide (TiO₂) and its derivatives offer solutions in the field of...
environmental problems due to the specific and well defined catalytic and structural properties [7]. For such applications, the size, morphology, photocatalytic properties and specific surface disclose important characteristic of materials. Compared to the bulk material, the materials with nanostructures prove with unique chemical and physical properties. Depending on the synthesis method used these properties differ [8]. TiO$_2$ is well known as a catalyst having the best catalytic characteristics, chemically stable, good oxidation resistance, non-toxic and low cost of use [9]. The most used forms are the rutile (stable phase) and anatase (metastable phase). Although the anatase form has a bandwidth (E$_g$ ~ 3.2eV) larger than the rutile (~ 3.0eV), the photocatalytic activity between the two phases highlighted the performances of the anatase phase [10]. The use of TiO$_2$ nanoparticles for adsorption and photocatalytic degradation of dyes in industrial waters can be considered a viable alternative based on the combination of optical, chemical and electrical properties. In most cases, in the photocatalytic applications TiO$_2$ is used in the form of suspension obtained by various methods such as co-precipitation method, sol-gel method, hydrothermal method etc [11]. Although it is noted by its properties that are well known, there are certain restrictive features such as band gap and difficult separation and recovery of nanoparticles [12].

To implement the advanced oxidation process in practical water treatment applications, the overall cost of the process should be kept to a minimum, so the study focused on improving the removal of material from the system and its reuse. The strategy approached in order to improve the efficiency of the recovery of the used material was highlighted by obtained a nanocomposite with magnetic core of Fe$_3$O$_4$/SiO$_2$/TiO$_2$. The advantage of Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite as photocatalyst is very efficient because it can be recovered with a magnetic from the suspension system [13, 14]. Another challenge arises when iron oxide (Fe$_3$O$_4$) interacts directly with titanium dioxide (TiO$_2$), a phenomenon that will occur due to the interaction of forbidden darkness and reduce photocatalytic activity [15, 16]. The silica coating between the core of Fe$_3$O$_4$ and TiO$_2$ to bond the two layers. Thus, the nanocomposites formed of metal oxide material incorporated in an amorphous matrix have more interesting properties [17]. These properties depend significantly on the particle size and distribution, as well as on morphology and porosity. Silica dioxide was chosen to serve as a barrier in separating the magnetic core from the TiO$_2$ catalyst, due to its compatibility with both oxide materials as well as to prevent the oxidation of the iron oxide core by titanium dioxide reducing its magnetism [18]. The role of silica is not only to act as a bond, but also to ensure a larger surface area, improving the photocatalytic performance and also helping to separate and recovery the catalyst. The presence of a layer of silica also increases the lifetime of generating orifices which in turn increase the photoreactivity of the magnetic core [19].

In the present paper, TiO$_2$ nanoparticles and Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite were synthesized and characterized by advanced techniques such as X-ray diffractions (XRD), scanning electron microscope (SEM), zeta potential and N$_2$ isotherm. Furthermore, a study of the adsorption and photocatalytic degradation of a cationic dye, methylene blue (MB), under dark adsorption and under irradiation with UV light was performed to support the validity of the Langmuir–Hinshelwood model.

2. Experimental section

2.1. Synthesis of TiO$_2$ nanoparticles

TiO$_2$ nanoparticles was obtained using a sol-gel method, by the alkoxide route, as was described in our previous work [20]. All reagents were analytical grade.

The chemical reaction is carried out for 30 minutes under magnetic stirring using titanium isopropoxide (C$_{12}$H$_{25}$O$_4$Ti) in a mixture of acetic acid and ethyl alcohol. To obtain amorphous titanium dioxide, the mixture was treated with aqueous ammonia (NaOH) until the pH reached 10. In the end, the suspension was dried and heated at 600°C. A white power of TiO$_2$ was obtained.

This material was subjected of XRD, SEM, Zeta potential and adsorption-desorption isotherm investigation in order to prove the crystalline phase, size, stability of nanoparticles and the specific surface.
2.2. Synthesis of Fe₃O₄/SiO₂/TiO₂ as nanocomposite

Fe₃O₄/SiO₂/TiO₂ nanocomposite was obtained in three steps as was presented in our previous work [19]. In the first stage, Fe₃O₄ nanoparticles were obtained by the method of co-precipitation by mixing of FeCl₂ (1M) and FeCl₃ (2M) in alkaline solution of NaOH (0.7 M). Then, the magnetic nanoparticles encapsulation was performed using a mixture of aqueous ammonia solution and tetraethylortosilicate (TEOS). Fe₃O₄/SiO₂ nanocomposite was put into contact with diethylenetriamine (EDTA), isopropanol and titanium isopropoxide (C₁₂H₂₈O₄Ti) and treated in an autoclave at 200°C. In the end, the suspension was dried and heated at 600°C. A gray nanocomposite of TiO₂ was obtained. This material was subjected of XRD, SEM, Zeta potential and adsorption-desorption isotherm investigation in order to prove the crystalline phase, size, stability of nanoparticles and the specific surface.

2.3. Photocatalytic degradation

Photocatalytic degradation and adsorption experiments of MB using TiO₂ nanoparticles and Fe₃O₄/SiO₂/TiO₂ nanocomposite were performed at the laboratory scale, at room temperature, 50 mL reaction volume and unadjusted pH conditions. In the context of ensuring a good reaction and to improve the dissolved oxygen concentration in the solution, the suspension was subjected to a compressed air filter. Prior to the irradiation, the suspensions were shaken in the dark for 30 minutes to achieve the adsorption equilibrium of MB on the catalysts surface. In the case of the photocatalytic degradation experiments, a UV lamp equipped with 4 tubes of 15W each Philips (UV-C, λmax = 365 nm) was used as the light source. The samples were taken at set time intervals, filtered through a 0.45 µm membrane and subsequently analyzed by UV-Vis spectrometer. The absorbances were measured at the wavelength specific to MB respectively 665 nm. The percentage of MB removal was calculated using the equation:

$$\eta = \frac{C_0 - C}{C_0} \cdot 100 \text{ [%]}$$

where: \(C_0\) is the initial concentration [mg/L] and \(C\) is the concentration at time \(t\), [mg/L].

The amount of MB adsorbed at equilibrium was calculated using the following equation

$$q_e = \frac{(C_0 - C)V}{w}$$

where: \(C_0\) is the initial concentration [mg/L], \(C\) is the concentration at time \(t\) [mg/L], \(V\) is the volume of the solution [mL] and \(w\) represents the amount of catalyst used [g].

3. Results

3.1. Characterization of TiO₂ nanoparticles and Fe₃O₄/SiO₂/TiO₂ nanocomposite

The crystalline phases of the obtained TiO₂ based nanoparticles and nanocomposites as well as the size of the crystallites were analyzed by a Panalytical X’Pert PRO MPD X-ray diffractometer with Cu-Kα radiation (wavelength of 1.54 Å). The average size of the crystallites was calculated using the Debye-Scherrer (3) equation:

$$D = \frac{K\lambda_{Cu-K\alpha}}{\cos \theta \cdot FWHM}$$

where: \(D\) is the average crystallite size, \(K\) is a coefficient (0.89), \(\lambda_{Cu-K\alpha}\) is the wavelength of the radiation from the diffraction tube, FWHM is the full width at half maximum of diffraction and \(\theta\) is the diffraction Bragg angle.
To establish a comparison between TiO$_2$ nanoparticles and Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite a diffraction analysis was done as it is presented in Figure 1. The characteristic peaks of TiO$_2$ nanoparticles indicated a mixture of phases, anatase (PDF no. 01-085-5943) and rutile (PDF no. 03-065-0191), the predominant phase being anatase while the characteristic peaks of Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite indicate anatase phase. XRD pattern indicated higher intensities for the peaks attributed to Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite which denotes a more crystalline material compare with TiO$_2$ nanoparticles. The crystallite size of particles could be evaluated as 20 nm for Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite and 9 nm for TiO$_2$ nanoparticles.

![Figure 1. XRD of Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite and TiO$_2$ nanoparticles.](image1)

The morphology and structure of TiO$_2$ nanoparticles and Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite obtained were evaluated by Quanta 450 FEG scanning electron microscopy equipped with a field emission gun and an X-ray scattering spectrometer as shown in Figure 2. It can be seen that the appearance of nanomaterials based on TiO$_2$ have the same smooth structure. The difference is visible in terms of nanoparticle size in the case of Fe$_3$O$_4$/SiO$_2$/TiO$_2$ is increased due to multilayers up to a diameter of about 120 nm. In contrast, in the case of TiO$_2$ nanoparticles, the particle size is estimated to be 45 nm, the result is consistent with the XRD result.

![Figure 2. SEM image of Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite and TiO$_2$ nanoparticles.](image2)
The specific surface of TiO$_2$ nanoparticles and Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposites were investigated by using the adsorption-desorption isotherm of nitrogen at the liquid nitrogen temperature 77 K, as shown in Figure 3. Adsorption curve - N$_2$ desorption for the obtained nanomaterials suggests as a type IV isotherm, which is characteristic of mesoporous material due to high pressure values P/P$_0$ > 0.8. Under these conditions both materials obtained present the same type IV isotherm characteristic of a mesoporous material. The pore size was calculated from the desorption branch of the isotherm using the Barrett Joyner Halenda (BJH) method [21]. These results indicate that materials obtained with such physical properties, high specific surface area and high crystallinity make them good candidates for photocatalytic activity. In this context, the specific surface of TiO$_2$ nanoparticles is 79.219 cm$^2$/g with a pore volume of 0.1505 cm$^3$/g while the specific surface of Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite is 62.183 cm$^2$/g with a pore volume of 0.1241 cm$^3$/g.

Figure 3. Adsorption-desorption isotherm of Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite and TiO$_2$ nanoparticles.

Zeta potential values of solutions were measured by a Zetasizer Nano ZSP type equipment (Malvern) equipped with a glass electrode, being calibrated with different buffer solutions. After the suspensions were allowed to equilibrate for 120 sec, the pH values of the final solutions were represented according to the initial pH values. In the case of the Zeta potential for both materials, there is a tendency for agglomeration, because the Zeta potential does not greatly exceed the range of -30 mV to 30 mV. Fe$_3$O$_4$/SiO$_2$/TiO$_2$ composite shows a brief pass beyond this range, at pH values from 8.2 to 11 and 3 to 4, which corresponds to an increased stability of the material.

According to Figure 4, the value of the isoelectric point of TiO$_2$ nanoparticles is 6.4, being in agreement with other studies reported by K. Suttiponparnit, while the value of the isoelectric point Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite is 4.6. This decrease of the value of the isoelectric point in the case of the Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite occurs due to the increase of the particle size, result which is in accordance with the study reported by K. Suttiponparnit [22]. In this context, TiO$_2$ based nanomaterials are strongly positively charged under acidic conditions (below 6.4, respectively 4.6) compared to the hydroxylated surface (over 6.4, respectively 4.6) where the surface is strongly negatively charged. Therefore, under basic conditions the catalyst absorbs the positively charged molecules based on the electrostatic attraction while in acidic conditions the catalyst will have the effect of repulsion against the molecules with positive charge.
3.2. Photolysis, adsorption and photocatalytic degradation of MB

The preliminary studies performed to determine the effect of UV radiation on the photocatalytic degradation process are presented in Figure 5. Before beginning the process of photocatalytic degradation (in the presence of catalyst and UV radiation), it is useful to study the effect of the following processes (which may affect the removal of pollutants), such as adsorption in the dark (in the presence of the catalyst without UV light) and photolysis (in the presence of UV radiation, without catalyst) under the following conditions: 50 mg of each catalyst (TiO$_2$ and Fe$_3$O$_4$/SiO$_2$/TiO$_2$), 4 mg/L methylene blue (MB) as pollutant, pH 5, 25°C and 765 mmHg. According to Figure 5 the results indicated that the photolysis was very slow with a rate of MB efficiency by 23% and 43% respectively for the TiO$_2$ nanoparticles and the Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite after 60 min.

![Figure 4. Zeta potential for Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite and TiO$_2$ nanoparticles.](image)

![Figure 5. Comparative study of the efficiency of MB degradation using TiO$_2$ and Fe$_3$O$_4$/SiO$_2$/TiO$_2$ in photolysis, adsorption and photocatalytic degradation processes.](image)
The efficiency of MB was significantly improved when the TiO$_2$ nanoparticles and Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite were used in the presence of UV light, showing the importance of UV light for the photocatalytic degradation process. Therefore, the photocatalytic degradation of the MB in the presence of UV light was about 97% using Fe$_3$O$_4$/SiO$_2$/TiO$_2$ and 92% using TiO$_2$.

In this context, in the heterogeneous catalytic processes, the reaction take place on the surface of catalyst following the preliminary adsorption of MB.

### 3.3. Photocatalytic degradation of methylene blue

The photocatalytic degradation of MB has been investigated using TiO$_2$ nanoparticles and Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite at constant volume and catalysts dosage, but varying the concentrations of MB in the range 1-15 mg/L. The optimum dosage of each catalyst was 50 mg as found in our previous investigations [20].

The photocatalytic degradation of MB can be described by the pseudo-first-order kinetics [23].

\[
\frac{dc}{dt} = -k_{obs}C
\]

the integration of this equation will lead to the expected relationship:

\[
\ln\left(\frac{C_0}{C}\right) = k_{obs}t
\]

where $k_{obs}$ is the apparent first-order rate constant, $C$ is the concentration of MB time $t$, $C_0$ is initial concentration of MB.

![Figure 6](image6.png)

**Figure 6.** Linear variation of Ln (C0/C) versus time for MB degradation, using TiO2 nanoparticles and Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite.

According to Figure 6, the photocatalytic degradation of MB strongly depends on the initial MB concentrations. The kinetic parameters obtained directly from the regression analysis of the linear curves together with the regression coefficients are listed in Table 1.

In this context, in both cases the apparent first-order rates constant was found to decrease with increasing initial MB concentration while the values of $v_0$ obtained by using the equation $v_0 = k_{obs}C_0$ increased according to Figure 7.
### Table 1. Pseudo-first order constant values for the different concentration of MB.

| Catalyst Concentrations mg/L | TiO$_2$ | Fe$_3$O$_4$/SiO$_2$/TiO$_2$ |
|------------------------------|---------|-----------------------------|
|                              | Experimental results | Pseudo-first-order | Experimental results | Pseudo-first-order |
|                              | η (%) | η' (%) | $k_{obs}$ | $R^2$ | η (%) | η' (%) | $k_{obs}$ | $R^2$ |
| 1                            | 23    | 92    | 0.0361 | 0.98 | 41    | 97    | 0.0474 | 0.98 |
| 2                            | 18    | 91    | 0.0364 | 0.98 | 35    | 93    | 0.0371 | 0.97 |
| 4                            | 13    | 83    | 0.026  | 0.97 | 25    | 89    | 0.0331 | 0.98 |
| 8                            | 11    | 78    | 0.0221 | 0.96 | 20    | 82    | 0.0233 | 0.94 |
| 10                           | 8     | 67    | 0.0163 | 0.95 | 16    | 73    | 0.0207 | 0.96 |
| 15                           | 6     | 56    | 0.012  | 0.94 | 11    | 66    | 0.0172 | 0.97 |

η (%) - adsorption efficiency  
η' (%) – photocatalytic degradation efficiency

This can be explained as Ashok V. Borhade suggests that at low concentrations, the molecules are adsorbed on the active surface of the catalyst and reacts with the photogenerated holes and the hydroxyl radicals on the surface of the catalyst. In contrast, at high concentrations, the passage of UV radiation through the solution would lead to the weak interaction with the catalyst and, finally, a failure will generate electron-hole pairs [24]. This causes an insufficient hydroxyl radical to remove a high concentration of dye.

Figure 7. The variation of $v_0$ of MB degradation versus different initial concentrations.

The influence of the initial concentration of MB on the photocatalytic degradation rate is usually rationalized employing a Langmuir– Hinshelwood type model.

$$r = -\frac{dc}{dt} = k_r \frac{C_0}{1 + K_{LH}C_0}$$ \hspace{1cm} (6)

where $k_r$ is the rate constant of surface reaction (L mg$^{-1}$) and $K_{LH}$ the L-H adsorption equilibrium constant (L mg$^{-1}$) [25, 26]. Inserting eq. 4 and 6 with C=C$_0$ at t=0.

$$v_0 = k_{obs}C_0 = k_r \frac{K_{LH}C_0}{1 + K_{LH}C_0}$$ \hspace{1cm} (7)
rearranging the equation results.

\[
\frac{1}{k_{\text{obs}}} = \frac{1}{k_r K_{LH}} - \frac{C_0}{k_r}
\]  

(8)

thus the parameters \( k_r \) and \( K_{LH} \) were obtained from the slope and the interception of the graph \( 1/k_{\text{obs}} \) vs \( C_0 \). (Figure 8).

![Figure 8](image)

**Figure 8.** The variation of reciprocal of constant rate versus different initial MB concentrations.

When \( k_{\text{obs}}C << 1 \), mathematically the relationship can be written like this:

\[
k_r \frac{K_{LH}C_0}{1 + K_{LH}C_0} = k_rK_{LH}C_0.
\]

According to this condition the Langmuir–Hinshelwood type model (6) can be approximated by the pseudo-first-order kinetics as it is given in (4).

The linearization of the graphs in Figure 8 over the chosen concentrations range describes a linear behavior especially using Fe₃O₄/ SiO₂/TiO₂ having the regression coefficient \( R^2 = 0.98 \). The kinetic parameters \( k_r \) and \( K_{LH} \) for TiO₂ nanoparticles and Fe₃O₄/ SiO₂/TiO₂ nanocomposite obtained from this graph are given in Table 2.

**Table 2.** Langmuir–Hinshelwood fitting parameters.

| Catalyst | TiO₂ | Fe₃O₄/ SiO₂/TiO₂ |
|----------|------|-----------------|
| \( k_r \) mg L⁻¹ | 0.25 | 0.38 |
| \( K_{LH} \) L mg⁻¹ | 0.19 | 0.12 |
| \( R^2 \) | 0.96 | 0.98 |

3.4. Adsorption isotherm

From the beginning, according to preliminary studies it has been observed that the adsorption process is important for initiating the photocatalytic degradation reaction. Because the adsorption is an important process in the evolution of the photocatalytic degradation process, the adsorption isotherms have been investigated at optimum catalyst dosage 50 mg varying the initial MB concentrations. Langmuir - Hinshelwood model used in the process of photocatalytic degradation, is based on the idea that the absorption of MB can be described by the Langmuir adsorption isotherm (Figure 9).

\[
q_e = q_m \frac{K_L C_0}{1 + K_L C_0}
\]  

(9)
where $q_m$ is the maximum adsorption capacity and $K_L$ is the equilibrium constant for adsorption. Rearrangement of (9) yields:

$$
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}
$$

(10)

thus the parameters $q_m$ and $K_L$ were obtained from the slope and the interception of the graph $C_e$ versus $C_e/q_e$ Figure 9.

![Figure 9. Adsorption isotherm of MB onto TiO2 nanoparticles and Fe3O4/SiO2/TiO2 nanocomposite Experimental conditions $C_0$ (1-15 mg/L), Catalyst dosage 50 mg, V = 50 mL.](image)

According to Alkaim A, the constant $K_L$ represents the affinity between adsorbate and adsorbent [27]. The values of $K_L$ obtained can concluded that the adsorption was higher using Fe3O4/SiO2/TiO2 nanocomposite (0.44 L mg⁻¹) compare to TiO2 nanoparticles (0.29 L mg⁻¹). Comparing the values $K_L$ with the values $K_{LH}$ (Table 1) indicate that the Langmuir isotherm is a faster process compared to the Langmuir Hinshelwood model. As a result, the process can be described by two successive reactions: adsorption followed by photocatalytic degradation in which the slow step is the rate determination step.

The difference between the maximum capacities of MB adsorption between onto TiO2 nanoparticles (1.15 mg g⁻¹) and Fe3O4/SiO2/TiO2 nanocomposite (1.93 mg g⁻¹) can be explained by the nature of MB (cationic dye), the nature of the catalysts and the pH of the solutions. It is known that the surface charge of the catalyst is mainly affected by the value of its zero charge point (pH_pzc). This is due to the fact that TiO2 has an amphoteric character and the photocatalytic activity depends on the pH of the solution, the zero pH_pzc loading point of the super phase and the dye structure as we discussed above. Under these conditions, the photocatalytic degradation of MB is higher using Fe3O4/SiO2/TiO2 nanocomposite compared to TiO2 nanoparticles, a result which is due to the fact that the surface of Fe3O4/SiO2/TiO2 nanocomposite is negatively charged at values higher than 4.6 and as the pH of the solutions is 5, the positive structure of MB represents the key to the degradation of this dye.

According to the analysis of adsorption-desorption isotherm of nitrogen even if the total pore volume and the surface area are high for TiO2 nanoparticles, Fe3O4/SiO2/TiO2 nanocomposite showed higher photocatalytic activity indicating that the photocatalytic surface is only an index that
Characterizes the physical-chemical properties, not the decisive index to ensure the photocatalytic activity.

3.5. Reuse studies
To evaluate the performances of the TiO$_2$ based nanostructures used, their stability tests were also performed in case of reuse in several photocatalytic cycles. The reuse tests were performed under the following conditions: 1 mg/L MB, natural pH, volume of solution 50 mL, 50 mg dosage, irradiation time 60 min. After each experiment, both TiO$_2$ nanoparticles and Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite were centrifuged, washed and dried at 60°C.

![Figure 10. Adsorption isotherm of MB onto TiO$_2$ nanoparticles and Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite.](image)

Experimental conditions $C_0$ (1-15 mg/L), Catalyst dosage 50 mg, $V = 50$ mL.

From the result presented in Figure 10 after the 4 cycles of reuse, it observed a different behavior regarding the cycles of reuse of these two materials for the photocatalytic degradation of MB. In the case of the Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite, the efficiency ranged between 97% and 77% while for the TiO$_2$ nanoparticles, the efficiency varied between 92% and 54%. This decreasing tendency can be explained by the deposition of organic species on the active sites of the photocatalysts while the TiO$_2$ nanoparticles are lost in the filtration process.

According to these data, it seems that the Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite has a good stability of the photocatalytic properties, at least 4 times used repeatedly. This is also stated in the reports of M. Fanun stating that the maximum efficiency of the use of the catalyst is 4 uses [28].

4. Conclusion and perspectives
In the current context of the implementation of heterogeneous photocatalysis in practical water treatment applications, the strategy approached to improve the recovery efficiency of the material used was highlighted by obtaining a nanocomposite with Fe$_3$O$_4$/SiO$_2$/TiO$_2$ magnetic core. To highlight the performance of Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite, the results were compared with the performance of TiO$_2$ nanoparticles. MB adsorption was better described by Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite due to the regression coefficient ($R^2 = 0.99$). The rate of photocatalytic degradation of MB in the presence of the two TiO$_2$-based materials proved to be high in the case of Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanocomposite. The photocatalytic degradation decrease in MB concentrations during irradiation can be described by first-order kinetics. Under the experimental conditions of this study the rate of the adsorption of MB in the dark were found to be always higher than the rate of the photocatalytic reactions. In other words, the
process can be described by two successive reactions: adsorption followed by photocatalytic degradation in which the slow step is the rate determination step. Although the photocatalytic degradation efficiencies of MB showed values of over 90% for both TiO₂-based materials in the first cycle, Fe₃O₄/SiO₂/TiO₂ nanocomposite was distinguished by obtaining high values of photocatalytic degradation efficiency after 4 consecutive cycles of reuse. Under these conditions, Fe₃O₄/SiO₂/TiO₂ nanocomposite compared to TiO₂ nanoparticles is a better catalyst which is distinguished by its excellent performance as a viable alternative in water treatment processes.

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