

# Synthesis of Iron Oxyhydroxide Modified Diatomite Innovative Material Composite and their Enhanced Photocatalytic Activity Driven by UV Light

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**Abstract**—Ferrihydrite silicide is widely used to realize contact terminals of integrated circuits and is usually formed by ex-situ heating treatments in-situ reactions during sputter deposition of a ferrihydrite with  $\text{SiO}_2$  of diatomite have been investigated in this work, by means of x-ray diffraction , x-ray fluorescence , infrared spectroscopy, , scanning electron microscopy. Diatomite which will be modified by iron “ the deposit of ferrihydrite on raw diatomite by  $\text{FeCl}_2$ , and  $\text{NaOH}$ . Comparison of XRD results proves that raw diatomite has an irregular structure but it becomes more regular at ferrihydrite modified to obtain ferric oxides different phases from crystallinities are: ferrihydrite , maghemite, magnetite, akaganeite, hematite, goethite, and schwertmannite. Kinetics photodegradation ( photocatalytic degradation) depend a pH solution Vat Green 03 textile dye. It is more important with low pH (pH= 4). Ferrihydrite modified diatomite ( DMF1) offer a great potentials for dyes eliminations and their wastewaters.

**Keywords**—Ferrihydrite, silicide, diatomite, ferric oxides, dye.

## I. INTRODUCTION

The principal phases of ferric oxide in kind are, in rule of crystallinity, ferrihydrite, maghemite, lepidocrocite, hematite, and goethite increasing [5]. The least of crystalline ferrihydrite is a brown ferric oxide with a big surface [6]. The ferrihydrite is also known like momentary ferric oxide phase [7]. The pure ferrihydrite transforms into more crystalline ferric oxides with time [7]. The ferrihydrite modified diatomite ( DMF) was produced the partial dissolution of diatomite by the solution of 6M  $\text{NaOH}$  followed by the hydrolysis and oxidized of the 1M solution of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  [8]. The inferior content of Si could

have like the consequence of more crystalline ferric oxides because the ferrihydrite transformed. The Objective of our work is to simplify the mode of water treatment of effluents in sight :

- To improve the results found by coagulation-flocculation used by the Algerian companies of the textiles;
- To apply a new method which is it proceeds by the process of advanced oxidation;
- And finally to preserve the environment of the harmful effects of the dyes remaining in the effluents like in untreated muds. Currently, the photocatalysis is always based by the dioxide of titanium ( $\text{TiO}_2$ ) for the experimental application.

The dioxide of titanium has a big space of band : 3.0 eV for rutile and 3.2 eV for anatase and thus only the small fraction ( 5 %) of a solar light can be used for its photoexcitation .Consequently, of the efforts of considerate were devoted the modified of  $\text{TiO}_2$  in order to prolong the band-edge of absorption the  $\text{TiO}_2$  in the obvious light irradiation [1,2]. Among them ,Fe doped with  $\text{TiO}_2$  was intensively studied the ions of Fe could be built in dioxide of titanium by the substitution of  $\text{Ti}^{4+}$ , presenting a new force in the space of band of  $\text{TiO}_2$  which is responsible for the photoactivity of visible light [ 1,3,4],

## II. MATERIALS AND METHODS

Before studying the photodegradation of the dyes by the diatomite, we considered to be useful to modify our material in order to improve its properties. The details of DMF prepared were previously reported and are recapitulated here [8]. The diatomite used in this study comes from the area of Sig (50 Km of the town of Oran) in Algeria. It is presented in the form of a powder of white color. The Geographical location of layer off diatomite (Kieselguhr) the area of Sig is shown in Fig.1. After crushing and sifting the size of the particles of the fraction lies between 0.4-0.6 mm. This material is of great interest and has several uses such as: purification of drinking water, absorbent of the pesticides, manufacture of antibiotics, some pharmaceutical syrups and it is qualified like friendly material with to respect the environment [9]. The choice of this material was indicated to us by the fact that :

It is very abundant; it has an adsorptive affinity towards the organic heavy metals. [10, 11] and molecules [12, 13]. The chemical composition of raw diatomite DB studied was determined by x-ray fluorescence X ( XRF) ( Philips PW 1404 ) and by electronic Micro sounder based on chemical analysis by x-ray fluorescence x ( XRF) ( Philips PW 1404 ). Raw diatomite DB is composed of 68.017 %  $\text{SiO}_2$  , 19.25 %  $\text{CaCO}_3$  , 7.575 %  $\text{Al}_2\text{O}_3$  ; 2.022 %  $\text{Fe}_2\text{O}_3$  ; 1.241 %  $\text{MgO}$  ; 1.491 %  $\text{K}_2\text{O}$  ; 0.2 %  $\text{Na}_2\text{O}$  ; 0.14 %  $\text{TiO}_2$  ; 0.038 %  $\text{MnO}$ . DB samples ( 45 g) were immersed in 300 ml 6M NaOH solution at 90 °C for 2 h to partially dissolve Si [14]. The mixture was immediately added to 300 ml of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  solutions of differing concentrations ( 1,2,3 and 4 M) and stirred and oxidized in air at room temperature (25 °C) for 24 h. The mixture was centrifuged for 30 min with the speed of 12000 rotations/min for assured the separation. The solid obtained through centrifugation was washed with distilled water and oxidized in air at room temperature overnight. The mixture was centrifuged for 30 min with the speed of 15000 rotations /min for assured the separation to remove excess NaOH. The solid obtained through centrifugation was washed with distilled water and oxidized in air to continue the oxidation  $\text{Fe}(\text{OH})_2$  and remove the excess of NaOH for 24h. The mixture was dried at 105 °C for 24h .The products of this procedure were named DMF1 as shown in Fig.1. A simplified synthetic cut was raised to facilitate the study of the layers of the diatomite and the sediments associated in the diatomite formation.



**Fig.1.** Ferrihydrite modified diatomite (DMF1 )

The Fig.1 is shown the products of modification the natural diatomite by ferrihydrite with concentration of

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (1M ).

## III. RESULTS AND DISCUSSION

### A. X-ray diffraction (XRD) studies

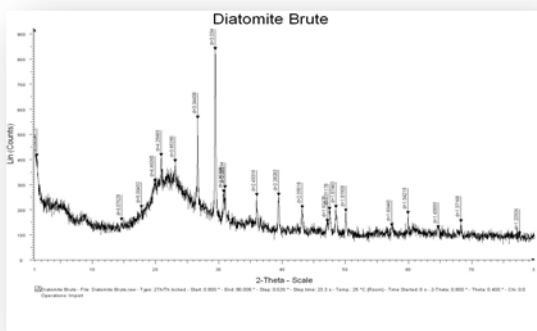
The mineralogy of (DMF1) was characterized by powder x-ray diffraction (XRD) analysis using a model PW 1729 x-ray diffraction unit (Philips, Eindhoven, Netherlands) Cu  $\text{K}\alpha$  radiation ( $\lambda = 0.1540598$  nm, 50 kV, 100 mA). As shown in Fig.4. The powder sample was coated on a plate out of glass of methanol and was dried with the room temperature, then swept  $1^\circ$  with  $80^\circ$  ( $2\theta$ ) with the size of stage of  $0.020^\circ$ .

#### 1) For the raw diatomite DB

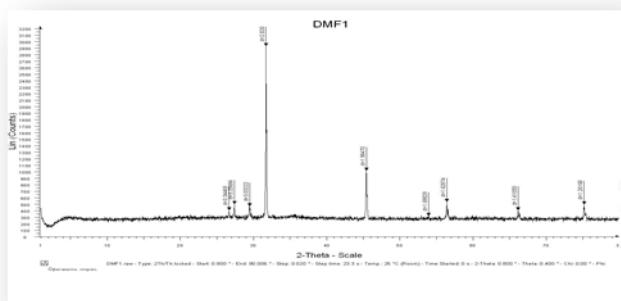
The Fig.4 represents The x-ray diffraction powder diffraction results of raw diatomite DB and Ferrihydrite modified diatomite ( DMF1,). The diffraction spectrogram indicates that the diatomite consists mainly of silica (  $\text{SiO}_2$  ) and  $\text{CaCO}_3$  with smaller amounts of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{TiO}_2$ , and  $\text{MnO}$ . The amorphous band, represented the spectrum of raw diatomite DB shown in Fig.4 is probably due to the glass formation of  $\text{SiO}_2$  as the inorganic base accompanied quartz, calcite [15]. For Quartz ( the peaks at  $2\theta = 14.5^\circ$ - $17.5^\circ$ - $19.5^\circ$ - $21^\circ$ - $23^\circ$ - $26.5^\circ$ - $36^\circ$ - $39.5^\circ$ ) and calcite ( peaks of  $2\theta = 29.5^\circ$  to  $47^\circ$ - $47.5^\circ$ - $48.5^\circ$ - $57.5^\circ$ - $60^\circ$ - $64.5^\circ$ - $68.5^\circ$ - $77.5^\circ$  ) are the characteristic peaks of the raw diatomite [16,17]. Similar spectra were found in the characterization of a Moroccan diatomite [18]. In conclusion, the diatomite has a disorganized structure (amorphous) that reported by K.Seoglu and Others [19] (Fig.2).

#### 2) For DMF1

For the Quartz (  $\text{SiO}_2$  ) : the peaks at  $2\theta = 26.5^\circ$ - $45.5^\circ$ - $56.5^\circ$ - $66^\circ$ - $75^\circ$  with the interreticular distances (  $d = 3.34$ - $1.99$ - $1.62$ - $1.41$ - $1.26$  ) [20] ( Data of ASTM 5-490). For the calcite (  $\text{CaCO}_3$  ) : the peaks at  $2\theta = 31.5^\circ$ - $45.5^\circ$ - $56.5^\circ$ - $66.75^\circ$  with the interreticulars (  $d = 2.82$ - $1.99$ - $1.69$ - $1.62$ - $1.41$ - $1.26$  ) [20]. (Data of ASTM 5-490). For the rutile (  $\text{TiO}_2$  ) : the peaks at  $54^\circ$  with the interreticular distance  $d = 1.69$  and the peak at  $2\theta = 27.5^\circ$  with the interreticular distance  $d = 3.25$  [20] (Data of ASTM 5-551). For the illite: the peak at  $2\theta = 45.5^\circ$  with  $d = 1.99$  [21] (Data of ASTM 9-343). For the Kaolinite: the peak at  $2\theta = 45.5^\circ$  with  $d = 1.99$  [21] (Data of ASTM 14-164). For the hematite: the peak at  $2\theta$  with  $d = 1.69$  [20] (Data of ASTM 8-98) (Fig.3).



**Fig. 2.** X-ray diffraction patterns of DB



**Fig.3.** X-ray diffraction patterns of DMF1

#### B. Fourier Transform Infrared spectroscopy (FT-IR)

The FT-IR spectra of raw diatomite DB and DMF1 are realized with help of spectrophotometer using a model JASCO FT /IR-4200 ( Fourier Transform Infrared Spectrometer ) between 4000  $\text{cm}^{-1}$  and 400  $\text{cm}^{-1}$  with the resolution of 4  $\text{cm}^{-1}$ . The samples are conditioned with the dispersion form in the pastille of KBr (1/200 in mass).

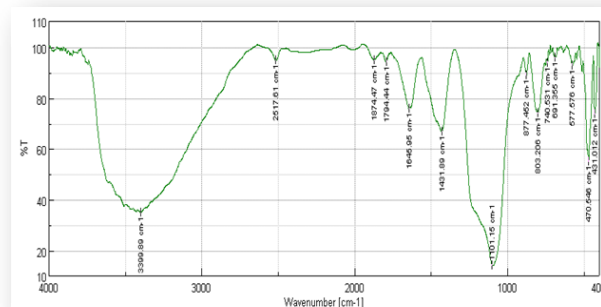
##### 1) For raw diatomite DB

The large adsorption band situated at 3399  $\text{cm}^{-1}$  and 1431.89  $\text{cm}^{-1}$  are linked with the vibrations of ( O-H ) surface and adsorbed water by the analysis of samples are proved the affinity of diatomite toward the water [22].The adsorption band at 1101.15  $\text{cm}^{-1}$  and 803.206  $\text{cm}^{-1}$  are represented the vibration of siloxane group (Si-O-Si ) [23].The absorption band at 1645.95  $\text{cm}^{-1}$  and 1101.15  $\text{cm}^{-1}$  are corresponded the vibrations of Si-O-Si [22].The adsorption band at 877.452  $\text{cm}^{-1}$  are corresponded the stained vibration of silanol group [24].The adsorption band at 803.206  $\text{cm}^{-1}$  are corresponded the vibration of ( Al-O-Si ) [25].Presence the characteristics bands of carbonates ions at ( 1431.89  $\text{cm}^{-1}$ ;740.531  $\text{cm}^{-1}$ ; 691.355  $\text{cm}^{-1}$ ;877.452  $\text{cm}^{-1}$ ; 577.576  $\text{cm}^{-1}$  ) [26].The three adsorption bands at (431.012  $\text{cm}^{-1}$ ; 470.546  $\text{cm}^{-1}$ ; and

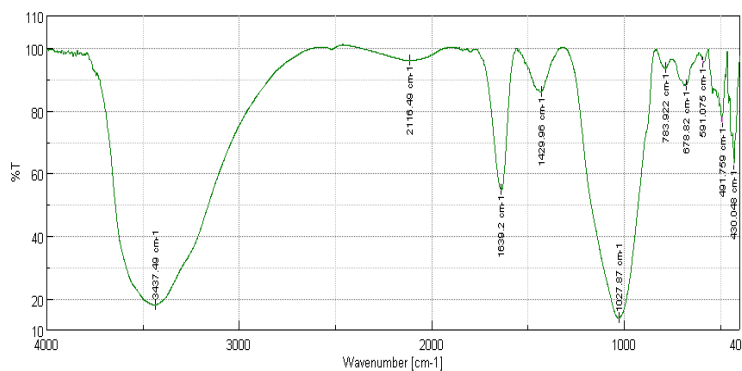
1101.15  $\text{cm}^{-1}$  ) are attributed the vibrations of Si-O-Si [24]. (Fig.4).

##### 2) For DMF1

There is a new adsorption band at 3437.49  $\text{cm}^{-1}$  corresponds the vibration of the silanol group Si-O-H [27].The infrared spectrum of raw diatomite DB. There is the disappearances of adsorption bands at (2517.61  $\text{cm}^{-1}$ ; 1874.47  $\text{cm}^{-1}$ ; 1794.44  $\text{cm}^{-1}$ ; 877.452  $\text{cm}^{-1}$ ; 803.206  $\text{cm}^{-1}$ ; 740.531  $\text{cm}^{-1}$ ; and 577.576  $\text{cm}^{-1}$  ).There is a new adsorption band 2116.49  $\text{cm}^{-1}$  corresponds the vibration of Si-H [28].The adsorption band at 1639.2  $\text{cm}^{-1}$  corresponds the vibration of Fe( OH)<sub>3</sub> [29].The adsorption band at 1429.36  $\text{cm}^{-1}$  corresponds the vibrations of CaCO<sub>3</sub> and CaFe( CO<sub>3</sub>)<sub>2</sub> [30].The adsorption band at 783.922  $\text{cm}^{-1}$  corresponds the vibration of FeOOH [31].The adsorption band at 678.82  $\text{cm}^{-1}$  corresponds the vibration of  $\alpha$ -FeOOH (goethite) [30] and FeOOH [32] and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghemite) [31].The adsorption band at 591.075  $\text{cm}^{-1}$  corresponds the vibration of maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> ) and magnetite (Fe<sub>3</sub>O<sub>4</sub>) [32].The adsorption band at 491.759  $\text{cm}^{-1}$  corresponds the vibration of Schwertmannite [32].The adsorption band at 430.048  $\text{cm}^{-1}$  corresponds the vibration of Si-O-Si [24], (Fig.5).



**Fig. 4.** FT-IR spectra of DB



**Fig.5.** FT-IR spectra of DMF1

### C. Scanning electron microscopy (SEM)

The morphologies of the mineral phases constituting the samples were investigated by scanning electron microscopy using a model ( JEOL JSM 6610 PLUS/ LA , Japan) scanning electron microscopy .The sample was first mounted flat,using carbon tape, and then coated with 30 nm of gold using a sputter coater, the working distance was set to 17 mm and then accelerating voltages of 20 kV were used.

#### 1) For raw diatomite DB

The raw diatomite DB obtained from Sig (Westerland of Algeria) mainly consists of the centric diatom particles have a diameter of approximately 0,09-0,5  $\mu\text{m}$  and the pennate diatom particles have a length of approximately 0.2-6  $\mu\text{m}$  and a width approximately 2.5-3.5  $\mu\text{m}$  , (Fig.6).

#### 2) For DMF1

The centric of DMF1 particles have a diameter of approximately 3-6  $\mu\text{m}$ ,and the pennate DMF1 particles have a length of approximately 4-9  $\mu\text{m}$ , (Fig.7).

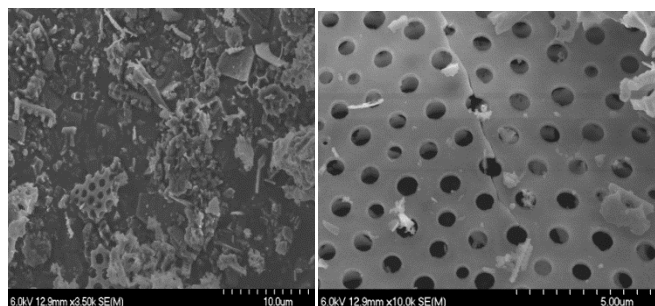


Fig.6. Typical scanning electron micrograph for DB

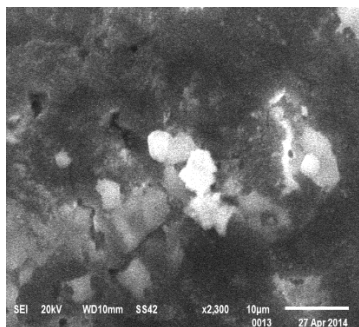


Fig.7. Typical scanning electron micrograph for DMF1

### IV. PHOTOCATALYTIC ACTIVITY

The objective for this work is to optimize the operating conditions of the photodegradation of titanium dioxide (Degussa P25) and gross diatomite and modified by ferrihydrite. For this we varied the pH of 4, 7 and 10 and fixed the concentration of titanium dioxide  $\text{TiO}_2$  is 0.1g/L, and the diatomaceous earth (DB, DMF1) ,2.5g /L and thus release industry and textile dye (Vat Green 3), which is used as indicators of contamination at a concentration of 2 mg/L .The photocatalytic activity was determined based on the pH and the absorbance of samples after each 15 min ( see Fig.7, Fig.8 et Fig.10 et Fig.11).

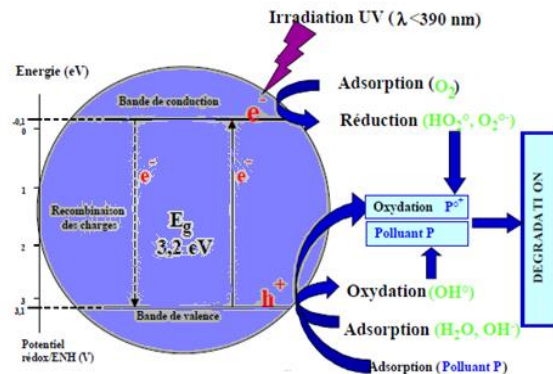
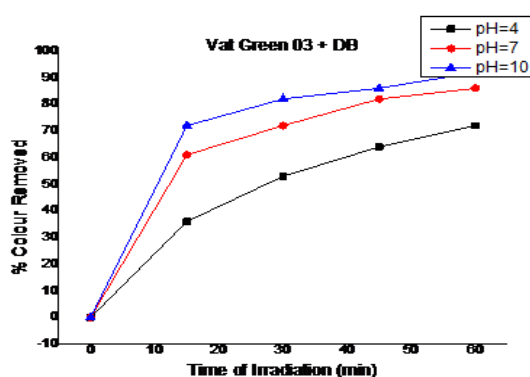


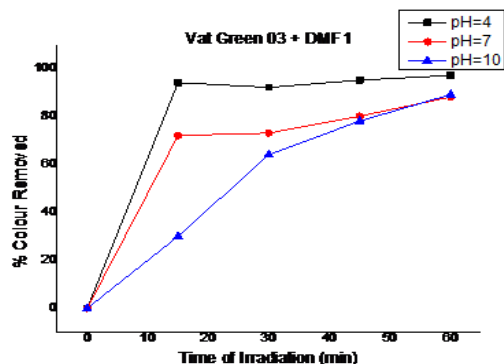
Fig.8. Heterogeneous photocatalysis principle of semiconductor



**Fig.9.** Test of photodegradation ( Vat Green 03 textile dye ) of the mixtures ( $\text{TiO}_2$  + DB ) and ( $\text{TiO}_2$  DMF1 ) in the photocatalytic reactor ( transilluminator )



**Fig.10.** Effect of pH on the photodecolourisation on Vat Green 03 textile using the mixture of (DB +  $\text{TiO}_2$ ) in function the time of irradiation.



**Fig.11.** Effect of pH on the photodecolourisation on Vat Green 03 textile using the mixture of (DMF1 +  $\text{TiO}_2$ ) in function the time of irradiation.

## V. CONCLUSION

The Comparison of the results from x-ray diffraction XRD show that the raw diatomite has an irregular structure at the modification of ferrihydrite. The photocatalytic degradation kinetic depends on the pH of the solution of Vat Green 03, it is more important at low pH (pH = 4). All these results show that The use of raw diatomite DB and ferrihydrite modified diatomite (DMF1) offer great potential for the removal of dyes. The derived photocatalysts were predominantly of anatase phase with mesoporous structure, exhibited large specific surface areas, Si-O-Fe and Ti-O-Fe linkages were evidenced in the ferrihydrite-modified diatomite doped with  $\text{TiO}_2$  photocatalysts. The presence of Fe in ferrihydrite-modified diatomite (DMF1,) could favor the formation of surface hydroxyl groups. The natural abundance of these materials low investment costs could provide a good alternative to more costly adsorbents such as activated carbon, Zeolite, alginate ... Finally, this study was designed as a major source of information processed by ferrihydrite modified diatomite.

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