

UV Lamp Assisted Decomposition of Dyes over Iron-Modified Diatomite in the Presence of TiO₂

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Abstract

The present study deals with the photodegradation (photocatalytic degradation) in the environment of a textile industrial dye the Vat Green 03 Indanthrene according to pH levels , titanium dioxide TiO₂ (Degussa P25) and Vat Green 03 Indanthrene dye concentration irradiated under UV transilluminator lamp. The Vat Green 03 Indanthrene has a chemical formula C₃₁H₁₅NO₃. The titanium dioxide TiO₂ (Degussa P25) was used as a catalyst with a co-adsorbent, which was essentially a rock formed by accumulation of diatoms frustules called « diatomite or Kieselgüher » from the a deposit in Sig region in the North-West of Algeria, which was advantageous as it was locally available and less expensive. The diatomite raw material of Sig which was to be modified by a Ferrihydrite of the raw diatomite (DB) by adding iron (II) chloride tetrahydrate in various concentrations leading to an increase of the specific surface area through the treatment with Sodium Hydroxide (NaOH) of the raw diatomite (DB) which partially dissolved in the NaOH solution. The resulting element was (DMF1) and the characterisations were carried out through x-rays fluorescence (XRF), X-ray diffraction (XRD) and Fourier's transformed infrared attenuated total reflection spectroscopy, IR-ATR). The diatomite modified by Ferrihydrite without and with calcination at 600°C contained iron (III) oxide in different phases which are: Ferrihydrite, hematite, maghemite, lepidocrocite, goethite, schwertmannite, ferroxhyte, akaganeite, ferroxide and magnetite. The sample examined by scanning electron microscope (SEM) showed: Raw diatomite (DB): centric particles of 0.09-0.5 µm diameter length and pinnate particles of 2.5-3.5 µm length. Diatomite modified by Ferrihydrite (DMF1): centric particles of 3-6 µm diameter and the pennate particles of 4-9 µm length. The absorbance measurement of Vat Green 03 Indanthrene was carried out by UV-Visible spectrophotometry. For the mixture (DMF1+TiO₂), the irradiation in 60 min time of photocatalytic reaction was at a better colour remove level of about 93 % at pH = 4, pH = 7 and pH = 10 it was verified that, it was verified that in pH = 4, pH = 7 and pH = 10 at kinetics rates constants k_{ap} were : $7,37 \times 10^{-2} \text{ min}^{-1}$, $8,13 \times 10^{-2} \text{ min}^{-1}$ and $6,8 \times 10^{-2} \text{ min}^{-1}$ respectively.

Keywords: Photodegradation ; Dye; UV lamp ; Diatomite ; Ferrihydrite .

I. Introduction

The water is the most important resource in the planet, for the human beings, the animals, the plants and the micro-organisms. Practically all the vital phenomena of the biosphere are related to the availability of water. The water pollution which affects the rivers, the seas, the ground water and the lakes, is mainly the consequence of not or insufficiently treated wastewaters, causing a degradation of the ecosystem. The problem is even more serious in the case of the industrial effluents which present a much more marked toxic character. For instance the dyes and additives used by textile industries which are the main concern of the present study, may constitute a serious threat for the environment because their presence in water, even at very small quantities, may be very harmful. Consequently, their presence in the water systems reduced the penetration of the light and delays the photosynthetic activity. They also have a tendency to complex the metal ions by producing toxicity for fauna and other organizations. Consequently, the depollution of the water contaminated by these chemical compounds is more than necessary for environmental protection and also for a possible re-use of this not-conventional water, minimizing then water losses by means of this recycling. Current research is then focusing on water treatment processes of low costs by using materials like clays and bentonites and other diatoms materials which can be a good alternative for the desorption of the dyes and the organic additives. These materials were already used in the developed countries where they proved reliable since they present good retention properties. The current problem of the treatment wastewater of any nature is mainly the management of the effluent generated in the purification plants. Indeed, the processes used, that they are chemical, biological or electrochemical produce all of the considerable quantities of muds which do not find outlets and whose management has problems.

Indeed, a not controlled spreading on arable lands is regarded as very harmful to agriculture. It is thought that while using the processes by co-precipitation with diatoms materials, one can manage to regulate the problem of organic pollution in the textile industrial wastes, since the used materials are natural and do not transmit pollution. The control of the water pollution is presented in the form of a one of the major fields of the scientific activity. The engaged activities are done by a total management of

the effluents by privileging the actions of reduction of pollution, in particular by the installation of techniques such as discoloration for example. And, although the colored organic compounds constitute only one minor fraction of the organic load of wastewater, their color makes them esthetically unacceptable. In addition, this strong coloring of water is harmful since it causes an eutrophication of water and thus an asphyxiation of the micro-organisms.

The objective of this 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 based on the advanced oxidation process;
- 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 on the dioxide of titanium (TiO_2) for the experimental application. The dioxide of titanium has a large space of band: 3.0 eV for rutile and 3.2 eV for anatase and thus only a small fraction (5 %) of a solar light can be used for its photo excitation. Consequently, efforts were made for the consideration of the modified of TiO_2 in order to extend the band-edge of absorption the TiO_2 in the obvious light irradiation [1, 2]. TiO_2 doped Fe was intensively studied and the Fe ions could be built in titanium dioxide by substitution of Ti^{4+} , presenting a new force in the band space of TiO_2 which is responsible for the photoactivity of visible light [1, 3, 4]. The principal phases of ferric, according to increasing cristallinity, are Ferrihydrite, Maghemite, Lepidocrocite, Hematite, and Goethite [5]. The least of crystalline Ferrihydrite is a brown ferric oxide with a large 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 by the partial dissolution of diatomite by the solution of 6M 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 due to because the transformed Ferrihydrite

II. Materials and Methods

Before studying the photodegradation of the dyes by the diatomite, we considered as useful the modification of our material in order to improve its properties. The details of the preparation of DMF were previously reported and are recapitulated here [8]. The origin of the diatomite used in this study was from the area of Sig (north-west of Algeria) the geographical location of which is shown in the map of Figure 1.

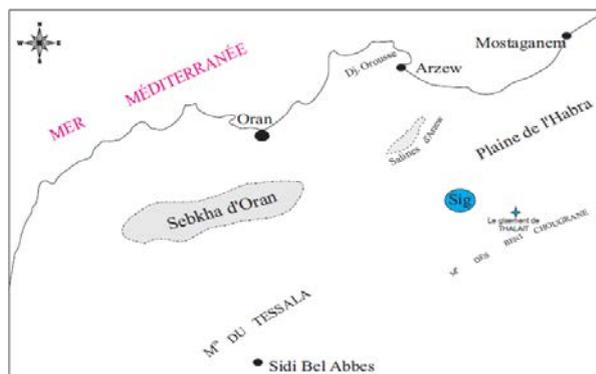


Figure 1: Geographical location of diatomite (Kieselguhr) source

A simplified synthetic cut was raised to facilitate the study of the layers of the diatomite and the sediments associated in the diatomite formation. It was presented in the form of a white powder.

After crushing and sifting, the size of the particles of the fraction was 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, respecting the environment [9]. The choice of this material was guided by various factors such as its abundance, its 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. Raw diatomite DB is composed of 68.017 % SiO_2 , 19.25 % CaCO_3 , 7.575 % Al_2O_3 ; 2.022 % Fe_2O_3 ; 1.241 % MgO ; 1.491 % K_2O ; 0.2 % Na_2O ; 0.14 % TiO_2 ; 0.038 % MnO . DB samples (45g) were immersed into 300 ml 6M NaOH solution at 90 °C for 2 h to partially dissolve Si [11]. The mixture was immediately added to 300 ml of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ solutions of 1 M concentration 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 rpm to ensure 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 rpm to ensure separation and removal of excess NaOH. The solid obtained through centrifugation was washed with distilled water and oxidized in air to continue the oxidation to $\text{Fe}(\text{OH})_2$ and remove the excess of NaOH for 24h. The mixture was dried at 105 °C for 24h. The product of this procedure was known as DMF1.

Figure 2 shows the considered local raw diatomite DB in powder (Kieselguhr).



Figure 2: The local raw diatomite DB in powder (Kieselguhr).

Figure 3 shows the products of modification the natural diatomite by Ferrihydrite with different concentrations of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1 M).



Figure 3: Ferrihydrite modified diatomite (DMF1)

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 Figure 4. The powder sample was coated on a plate out of glass of methanol and was dried with the room temperature, then swept 1° with 80° (2θ) with the

size of stage of 0.020° as previously shown in Figure 2.

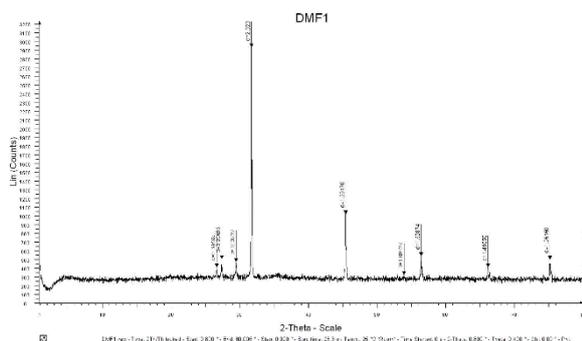


Figure 4: X-ray diffraction patterns of DMF1

For DMF1 : For the Quartz (SiO_2) : the peaks at 2 theta = 26.5° - 45.5° - 56.5° - 66° - 75° with the interreticular distances ($d = 3.34$ - 1.99 - 1.62 - 1.41 - 1.26) (Data of ASTM 5-490). For the calcite (CaCO_3) : the peaks at 2 theta = 31.5° - 45.5° - 56.5° - 66.75° with the interreticulars ($d = 2.82$ - 1.99 - 1.69 - 1.62 - 1.41 - 1.26). (Data of ASTM 5-490). For the rutile (TiO_2) : the peaks at 54° with the interreticular distance $d = 1.69$ and the peak at 2 theta = 27.5° with the interreticular distance $d = 3.25$ (Data of ASTM 5-551). For the illite: the peak at 2 theta = 45.5° with $d = 1.99$ (Data of ASTM 9-343). For the Kaolinite: the peak at 2 theta = 45.5° with $d = 1.99$ (Data of ASTM 14-164). For the hematite: the peak at 2 theta with $d = 1.69$ (Data of ASTM 8-98).

B. Fourier Transform Infrared spectroscopy (FT-IR)

The FT-IR spectra of raw diatomite DMF1 is realized with help of spectrophotometer using a model JASCO FT /IR-4200 (Fourier Transform Infrared Spectrometer) between 4000 cm^{-1} and 400 cm^{-1} with the resolution of 4 cm^{-1} . The samples are conditioned with the dispersion form in the pastille of KBr (1/200 in mass) and the summarized results are shown in Figure 5.

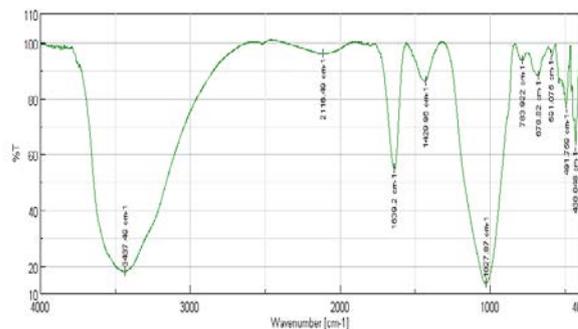


Figure 5 : FT-IR spectra of DMF1

For DMF1: There is a new absorption band at 3437.49 cm^{-1} corresponds the vibration of the silanol group Si-O-H. The infrared spectrum of raw diatomite DB. There is the disappearances of adsorption bands at (2517.61 cm^{-1} ; 1874.47 cm^{-1} ; 1794.44 cm^{-1} ; 877.452 cm^{-1} ; 803.206 cm^{-1} ; 740.531 cm^{-1} ; and 577.576 cm^{-1}). There is a new adsorption band 2116.49 cm^{-1} corresponds the vibration of Si-H. The absorption band at 1639.2 cm^{-1} corresponds the vibration of $\text{Fe}(\text{OH})_3$. The adsorption band at 1429.36 cm^{-1} corresponds the vibrations of CaCO_3 and café (CO_3)₂. The absorption band at 783.922 cm^{-1} corresponds the vibration of FeOOH. The adsorption band at 678.82 cm^{-1} corresponds the vibration of α -FeOOH (goethite) and FeOOH [32] and γ - Fe_2O_3 (maghemite). The adsorption band at 591.075 cm^{-1} corresponds the vibration of maghemite (γ - Fe_2O_3) and magnetite (Fe_3O_4). The absorption band at 491.759 cm^{-1} corresponds the vibration of Schwertmannite. The absorption band at 430.048 cm^{-1} corresponds the vibration of Si-O-Si.

C. Scanning Electron Microscopy (SEM)

The diatomite was a modified surface by the NaOH treatment and the deposit of Ferrihydrite. The SEM was used to determine the outside of structure between the raw diatomite DB and the modified diatomite by Ferrihydrite (DMF1). The modified diatomite by Ferrihydrite (DMF1) was analyzed with the scanning electron microscope of analysis the model (JEOL JSM 6610 La, Japan). Figure 6 were exposure the raw diatomite DB by an electronic micrograph, there are two principal types in the diatoms: (1) central, with veins radiating of a ring; (2) pennate, with veins being prolonged outside on the two sides of a longitudinal element. It can be seen that the raw diatomite obtained starting from the considered layer mainly includes the central and a little pennate particles of diatom. The central particles of diatom have a diameter of approximately 5-20 micrometers and the thickness of several microns. The pennate particles of diatom have a

length of approximately 12 micrometers. The micrograph confirms that the diatomite has a porous structure and has a great void volume. It can be seen from the micrograph of SEM shown in Figure 6 that the high porosity is mainly caused by many skeletal pores in particles of diatom and the interparticles pores between the particles of diatoms. The micrograph of SEM of raw diatomite DB and Ferrihydrite modified diatomite (DMF1) indicates that the raw diatomite DB has a frustules modified surface and the original geometry of the pores was destroyed by the treatment of NaOH and the deposit of Ferrihydrite (Figure 6). At the beginning, the colloidal of Ferrihydrite was 2-5 nanometers in size and the micropore was deposited (> 50 nanometers) and the larger of mesopores was (> 7 nanometers) of diatomite. After being entirely deposited in the pores of diatomite, the additional Ferrihydrite aggregates on the surface of the diatomite particles (Figure 6).

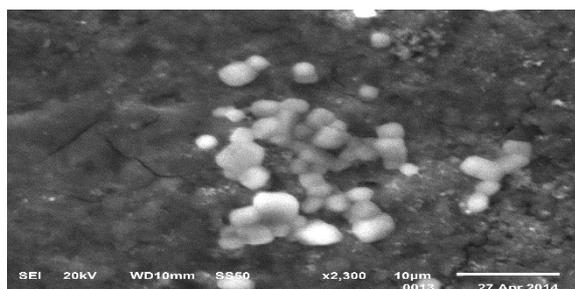


Figure 6 : Typical scanning electron micrographs for Ferrihydrite modified diatomite DMF1

IV. Photocatalytic Activity

The Indanthrene Olive Green B (C. I. Vat Green 3 ; C.I.69500) VG3 dye of textile was obtained from an industrial textile treatment Essenia « SOTEXHAM » in Oran in the West of Algeria. 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 pH of 4, 7 and 10 and fixed concentration of titanium dioxide TiO_2 is 0.1g/L, and the diatomaceous earth 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 experimental base mixtures (TiO_2 and diatomite) protocol:

A. Pollutants studied

The present study considered the Vat Green 3 of industrial textile dye that is soluble in alkaline media

to synthetic design dyeing cellulose fibers and proteins, as well as for printing cotton. It was provided to us by a local textile company. The aqueous solution of Vat Green 3 was prepared from a stock solution of 1 g/L and the discharge is diluted to 2 mg/L, since it is very concentrated and contains other additives (caustic soda NaOH, sodium hydrosulfite $\text{Na}_2\text{S}_2\text{O}_4$). All manipulations of the photodegradation of Vat Green 3 were conducted in a beaker of 250 mL with stirring at room temperature [20-25°C]. The materials used are prepared from titanium concentration fixed at 0.1 g/L titanium dioxide and 2.5 g/L of Ferrihydrite-modified diatomite (DMF1) at three different pH medium (4, 7 and 10) were introduced into the beaker. A volume of 200 mL of the dye (Vat Green 3) at concentration of 20 mg/L and 0.02 g of titanium dioxide TiO_2 [Degussa P25 its crystalline structure: 80 % anatase + 20 % rutile with a specific surface area of 50 m^2/g ; photophysics characteristic; band gap ($E_g = 3.2$ eV for anatase and $E_g = 3.0$ eV for rutile and for wavelength 390 nm)] and 0.5g of Ferrihydrite-modified diatomite (DMF1) and with an adjusted pH at 4, 7, and 10 were mixed in solutions at dark under UV irradiation ultraviolet. Samples of 10 mL were withdrawn every 15 minutes to measure the pH. The sample was centrifuged (15000 rpm) for one-half hour to finally measure the absorbance on a spectrophotometer model Optizen Micrometrics. The Photo 4 represents the manipulation of photodegradation between (Vat Green 3 dye textile) and the mixture using the titanium dioxide using Ferrihydrite modified diatomite (DMF1), respectively. The agitator speed was 300 rpm in the photocatalytic reactor but the transilluminator was changed with the length equal to 365 nm wave, the width of the lamp was 15 cm and a length of 30 cm and the energy elimination was 45 Watt (Figure 7).



Figure 7: Test of photodegradation (Vat Green 3 textile) of titanium dioxide + P25 Degussa (DMF1) in the photocatalytic reactor (transilluminator).

B. Photodegradation kinetics

Figure 8 shows the degradation kinetics of Vat Green 3 textile under the UV lamp, using the mixture of (TiO_2 + DMF1) according to the different pH values.

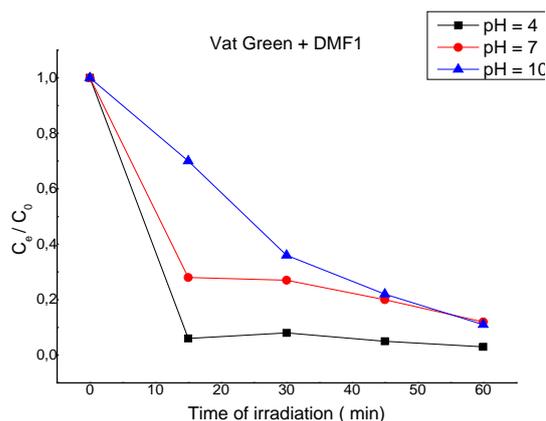


Figure 8: the degradation kinetics of Vat Green 3 textile using the DMF1 – TiO₂ mixed.

The kinetics of degradation of Vat Green 3 pennies lamp UV shows that the photoactivity of the mixture of (TiO₂ +DMF1) was favorable for a pH equal to 4 compared to the other pH values.

V. Conclusions

This work aims to test the capacity and efficiency of Ferrihydrite modified diatomite (DMF1) prepared in the laboratory, towards the industrial degradation of dyes in effluents from textile industry. In order to better understand these materials and clearly identify its morphology, the first part of the experimental work was devoted to their characterizations, particularly of diatomite by various analytical techniques. This showed that diatomite was composed mainly of amorphous silica (68.017 %) and carbonates which contaminate the surface of the mask material and part of the porosity. Porous diatomite particles are heterogeneous and Ferrihydrite-modified diatomite led to a significant improvement in average pore diatomite. This was attributed to the possible total elimination of carbonates and impurities. The specific surface area increased with the average pore diameter of the raw diatomite DB, improving adsorption. The experimental results showed that: the SiO₂ was the manufactured from the blank body diatomite with CaO and Al₂O₃ as the main impurities of the order of 19 % at 17 %, respectively.

Comparison of the results from XRD showed that the diatomite had a rough irregular structure at the modification of Ferrihydrite. The adsorption rate depended on the pH of the solution and it was more important at low pH (pH = 4). All these results showed that the use of Ferrihydrite modified diatomite (DMF1) offer great potential for the removal of dyes. The natural abundance of these materials and the low investment costs could provide a good alternative to more costly adsorbents such as activated carbon, zeolites, alginates, etc.

Acknowledgments

The authors would like to thank and express their gratitude to the laboratory team LSTGP for their help and encouragements throughout completion of the article. Sincere thanks also go to all our lecturers and colleagues of Chemistry faculty (USTO -MB).

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