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Visible Light Assisted Heterogeneous Photodecouloursiation of Vat Orange 02 Textile Dye in Aqueous Solution using Calcined Ferrihydrite Modified Diatomite

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Abstract: The decolourisation of vat orange 02 textile dye was investigated as a function of pH solution ,titanium dioxide concentration and dye concentration in the study were led by UV lamp of transilluminator using the titanium dioxide TiO_2 (Degussa P25) like catalyst with a co-adsorbent, which is a rock formed primarily by frustules accumulation in diatoms called “ diatomite or kieselgührs” obtained from the Sig deposit located in the westward of Algeria. The diatomite,which will be modified by ferric oxide “the deposit of ferrihydrite on raw diatomite by $FeCl_2.4.H_2O$”. The ferrihydrite-modified diatomite was made through surface modification treatments including NaOH treatment an ferrihydrite deposition on raw diatomite, in the NaOH treatment to increase the surface area of diatomite, surface SiO_2 of diatomite was partially dissolved in the NaOH solution, then the ferrihydrite modified diatomite was calcined at 600°C at a rate of 1°C min^{-1} for 24 h . For the mixture (DMF1X6 +TiO_2) gave a better colour remove rate about 97% at pH= 4.

Keywords: Diatomite, ferrihydrite, dye, photodegradation, UV lamp, TiO_2.

Introduction

Bezathren Orange RRTS (C.I. Vat Orange 02) is a so-called vat dye, which before dyeing. it has the appearance of blue needles with metalliclustre and melting point of 470-500 °C. Traditionally both biological and chemical methods have been employed for dye removal, but these techniques have not been very successful due to the essential non-biodegradable nature of most dyes[1]. However, currently pratical application of TiO_2 –based photocatalysis is still limited, since TiO_2 has a large band gap (3.2 and 3.0 eV for anatase and rutile, respectively) and therefore only small fraction (5%) of solar light can be utilized for its photoexcitation. Hence, conciderate efforts have been devoted to TiO_2 modification in order to extend that absorption band-edge of TiO_2 into visible light region.Until now,doping with metallic species such as V,Cr,W and Fe,has been unit[2,3].Among them,Fe doped TiO_2 by substitution of Ti^{4+},introducing a new energy level within the band gap of ,TiO_2 which is responsible for the visible light photoactivity [2,3,4]. The principal phases of ferric oxide in nature are, in order of increasing crystallinity, ferrihydrite maghemite (γ-Fe_2O_3), lepidocrocite (γ-FeOOH), hematite (α-Fe_2O_3), and goethite (α-FeOOH) [5].The least crystalline ferrihydrite is a brown ferric oxide with a large surface area [6].Ferrihydrite is also known as a transient phase of ferric oxide [7].Irradiation, it was reported that impurities (eg., Si and P) of ferric oxide with a substantially lower content played an important role in this transformation [8].

An alternative to granular ferric hydroxide adsorbents consisting of iron oxide dispersed on a host matrix, which is preferably environmental friendly, cost effective and easily adaptable to column filtration process. Among these materials are diatomite ($SiO_2.nH_2O$),also known as diatomaceous earth or kieselgühr, which refer to a soft lightweight rock composed of amorphous silica microfossils of aquatic algae[9]. Jang et al.[10] have for example successfully prepared hydrous ferric oxide incorporated into diatomite .FHMD was produced through partial dissolution of diatomite in 6M NaOH followed by hydrolysis and oxidation of 1M $FeCl_2$ [11].This compound was made through diatomite surface modification treatments including NaOH treatment and ferrihydrite deposition on raw diatomite [12].This materials was calcined at 600°C in oven for 24h.On same direction, the objective of this study was to develop a simple method for preparation of calcined ferrihydrite modified diatomite which consisted mainly of crystallized hydrous ferric oxide (FeOOH) by an environmentally friendly process, the efficiency of the prepared material was evaluated in photocatalytic degradation of vat orange 02 textile dye as a function of pH ,titanium dioxide (TiO_2) concentration and dye concentration were led by UV lamp of transilluminator using the TiO_2 (Degusssa P25) like catalyst with a co-adsorbent which is a rock formed primarily by frustules accumulation of diatoms called “diatomite or kieselgühr” in the layer of Sig having the advantage of being locally available and less expensive.

Experimental

Raw diatomite DB sample (45 g) was immersed in 300 ml 6M NaOH solution at 90°C for 2h to partially dissolve Si [13].The mixture was immediately added to 300ml $FeCl_2.4H_2O$ solution of concentration (1M) and stirred and oxidized in air at room temperature (25°C) for 24 h. The mixture was centrifuged with at a of rate 12000 rpm for assorted the separation .The solid obtained through centrifugation was washed with distilled water and oxidized in air at room temeperature overnight. The mixture was centrifuged for 30 min with rate 15000 rpm for assorted the separation to remove the excess of NaOH. The solid obtained through centrifugation was washed with distilled water and oxidized in air to continue the oxidation $Fe(OH)_2$ and remove the excess of NaOH for 24 h.The mixture was dried at 105°C for 24 h.The products of this procedure was calcined at 600°C at a rate of $1°Cmin^{-1}$ for 24 h. This Product of this procedure was named DMF1X6.

The pH of vat orange 02 solution was adjusted using sodium hydroxide (NaOH) or by hydrochloric acid (HCl).The objective of this work is to optimize the operating conditions of the photodegradation using the titanium dioxide TiO_2 (Degusse P25) with different samples calcined ferrihydrite modified diatomite “DMF1X6”,.The pH of solution is an important parameter in photocatalytic process which not only plays an important role to characterize the dye but also determines the surface charge of the properties TiO_2 .Photodecolourisation of vat orange 02 textile dye using TiO_2-DMF1X6 was studied in pH range of 4-10 and fixed the concentration of titanium dioxide TiO_2 is 0.02 gL^{-1} and 0.5 gL^{-1} for DMF1X6,then thus release the textile dye (Vat orange 02) which is used as indicator of contamination at concentration of 20 mgL^{-1},0.02 gL^{-1} of TiO_2 [Degussa P25,its crystalline structure : 80% anatase + 20% rutile,which a specific surface area is 50 m^2g^{-1}: photophysics characteristic : band gap (E_g = 3.2 eV for anatase , and E_g = 3 eV for rutile with wavelength of 390 nm] [2,3]. The using materials are perepared from titanium dioxide (Degussa P25) concentration fixed at 0.02 gL^{-1}.and 0.5 gL^{-1} for DMF1X6 with different pH (4,7,and 10).They were 20 mgL^{-1},then the solutions were put in the the dark under ultraviolet irradiation of transilluminator to take 10 ml of samples every 15 min to measure the absorbance on a spectrophotometer model optizen 2120 UV micrometrics,Korea Republic.

Decolourisation (%) = $(C_0 – C) /C_0$

Here C is the absorption of vat orange 02 solution at irradiation time of “t” min, and C_0 is the initial absorption at t= 0 min.

Results and Discussion

FTIR Analysis

FTIR-ATR spectra of calcined ferrihydrite modified diatomite (DMF1X6) with help of spectrometrer using a model Bruker α Alpha H Gmbh D8 FTIR-ATR between 4000 cm^{-1} and 400 cm^{-1}, and a resolution of 4 cm^{-1}; 28 scans were performed . the sample is conditioned with the dispersion form in the powder of DMF1X6 . The result is shown in **Fig.1**.

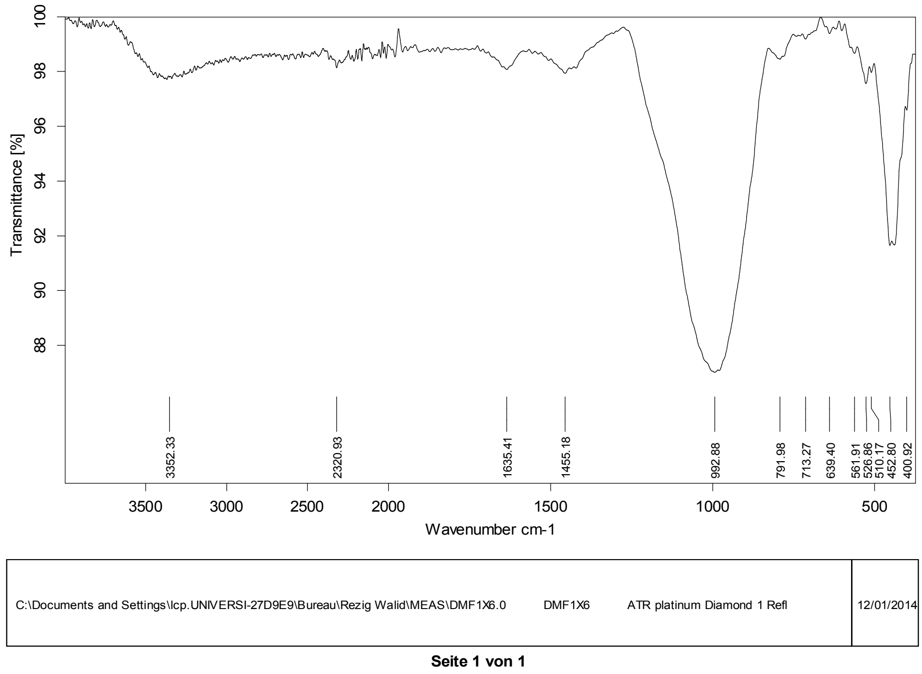

FIG.1.FTIR-ATR spectra of DMF1X6.

For the DMF1X6, the absorption band at 3352.33 cm^{-1} refers to monomeric hydrogen bonds,which are assigned in diatomite system to Fe-OH species present on surface, indected in the case of non-hydroxylated atoms. The surface irons atoms tend to complete their coordination shell by reacting with water molecular in order to form surface Fe-OH species [15],furthermore the observed shift indicates on the one hand some noticeable changes caused to frustule surface H-bonded silanols (previously identified by vibration mode at 3399.89 cm^{-1} [14] during DMF1X6 system formation and on the other hand the increase of hydrogen bonding in DMF1X6 system [73,74].The absorption band at 2320.93 cm^{-1} corresponds the vibration of Si-H [16].

Photo Catalytic Activity

Fig. 2 shows the colour removal of vat orange 02 in different pH's using the mixture (DMF1X6 + TiO_2).

At 60 min of reaction, it was verified that in pH = 4, there was a colour remove about 97 %, at pH = 7, there was a colour remove about 91 %, and at pH = 10, there was a colour remove about 84 %.It was verified that in pH = 4, there was a better colour remove about 97 % .It was observed that the vat orange 02 textile dye degradation has pH dependency ,the better result is at pH = 4.

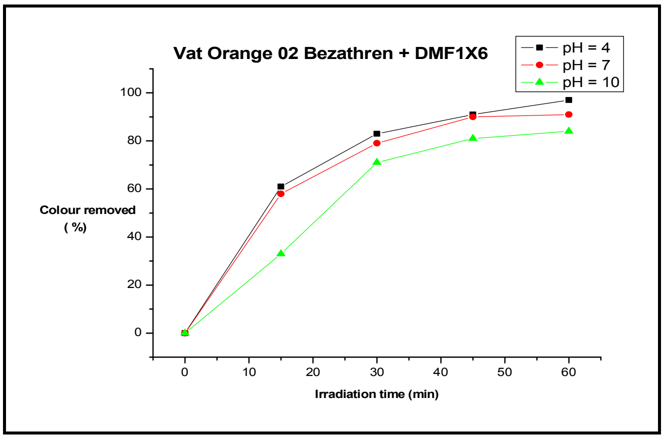

FIG.2.Colour removal of Vat Orange 02 in different pH's using the mixture (DMF1X6 + TiO_2)

Fig.3. shows the kinetics colour removal of vat orange 02 in different pH's using the mixture (DMF1X6 + TiO_2).

In all the photodecolourisation experiments, the reaction followed first order kinetics .Plots of Ln[C_0/C] versus time showed linear relationship where C is the concentration of vat orange 02 remaining in the solution at irradiation time of t, and C_0 is the initial concentration at t = 0 min in different pH's.First order rate constants were evaluated from the slopes of ln[C_0/C] versus time plots (**Fig.3**).In this work, the "k" is calculated by linear regression shown in **Fig.3.** At pH= 4, the observed rate constant for the photodecolourisation of vat orange 02 in the presence of the mixture (DMF1X6 + TiO_2) is 5.85 x 10^{-2} min^{-1}, at pH= 7 , the observed rate constant for the photodecolourisation of vat orange 02 in the presence of the mixture (DMF1X6 + TiO_2) is 5.8 x 10^{-2} min^{-1}.at pH=10, the observed rate constant for the photodecolourisation of vat orange 02 in the presence of the mixture (DMF1X6 + TiO_2) is 0 min^{-1} because linear regression does not pass on all the points of samples.As concluded about the observed rate constant ,the reaction followed first order kinetics at pH = 4,and at pH = 7, but at pH = 10, the reaction followed is not nor first order and nor pseudo-first order .

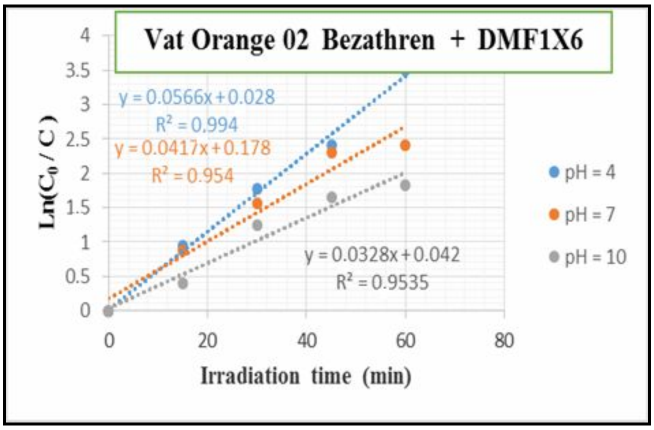

FIG.3.Effect of pH solutions on reactions kinetics order determination for photodecolourisation of vat orange 02 textile dye using the mixture (DMF1X6 + TiO_2) in function of irradiation time.

Conclusions

The result of Fourier transform infrared (FTIR-ATR) shows that the calcined ferrihydrite–modified diatomite (DMF1X6) different phases of ferric oxide are : For the mixture (DMF1X6 + TiO_2), at 60 min of reaction, it was verified that in pH = 4, there was a better colour remove about 97%, it was observed that the vat orange 02 textile dye degradation has pH dependency, the better result is as pH = 4.The goal of this work is to test the capacity and efficiency of calcined ferrihydrite–modified diatomite (DMF1X6) prepared in the laboratory to degrade the vat orange 02 textile dye from wastewater textile.As concluded about the calcined ferrihydrite-modified diatomite (DMF1X6) was doped with TiO_2 by the formation of new structure through bonding Si-O-Fe and Ti-O-Fe linkages which were responsible for its visible light photocatalytic activity for photodecolourisation of vat orange 02 textile dye.

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