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RESEARCH ARTICLE

CINETIC STUDY OF PHOTOCATALYTIC DEGRADATION BY THE (TiO_2/UV) SYSTEM OF INDIGO CARMINE DYE IN AQUEOUS SOLUTION

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Abstract

The persistence of synthetic dyes in the environment and the ineffectiveness of most conventional depollution techniques have led the scientific community to turn to advanced oxidation processes for eliminating these dyes from water. The aim of this work was to experiment with heterogeneous photocatalysis in the degradation of indigo dye in aqueous solution. The catalyst used was titanium dioxide in the anatase PC 500 form, irradiated by a polychromatic ultraviolet lamp with a wavelength λ= 365 nm. This technique proved effective, with a 77% degradation rate compared with photolysis, which removed only 17% of the indigo dye under the same conditions. Also, this work showed that low-concentration solutions were easily degraded with total decolourisation of the 12 mg/L molecule after 4 hours compared with 80% elimination of the 32 mg/L solution.The study of the influence of light intensity showed an increase in the rate of degradation of the molecule when the number of lamps placed in the reactor was increased. Total degradation was observed when 4 lamps were used for 120 minutes of irradiation.

Introduction:-

Many water-intensive industries (textiles, tanning, paper, etc.) generate large discharges of untreated wastewater into the environment. This water, which contains synthetic dyes, causes pollution characterised by wide variations in pH and high chemical oxygen demand (COD) levels in the receiving environment. Dyes are organic micropollutants that are soluble in water, and the presence of aromatic nuclei in their already complex molecular structure makes them more stable and difficult to biodegrade under aerobic conditions (Pagga and Brown, 1986). Consequently, the treatment of coloured effluents remains a major challenge, especially for developing countries which do not yet have all the opportunities to integrate the concepts of sustainable development.In Côte d'Ivoire, an agricultural country, many studies have focused on activated carbon adsorption processes based on biological materials as a means of eliminating dyes from water, due to the high availability and accessibility of agricultural biomass (Kouadio et al., 2019 ; Akessé et al., 2022; Kouadio et al., 2022). However, adsorption on activated carbon, like other conventional treatments (membrane processes, coagulation-flocculation, chemical oxidation, etc.) has the disadvantage of transferring pollution from one aqueous phase to a new phase, and in most cases leads to the formation of concentrated sludge, creating a problem of secondary waste or regeneration of materials that is often very

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expensive.It is therefore imperative to turn to alternative technologies that are part of a sustainable development perspective. Photocatalysis, which is an advanced oxidation process (AOP), is one of the new, effective and less expensive techniques that can lead to partial or total mineralisation of the pollutant. In this work, heterogeneous photocatalysis, based on the excitation of a semiconductor acting as a catalyst by absorption of high-energy photons, was tested. The catalyst used is titanium dioxide (TiO_2), which appears to be the most suitable for environmental applications because it is biologically and chemically inert, inexpensive and can withstand chemical and photochemical corrosion (Parra Cardona, 2001).

The aim of this study is therefore to highlight the effectiveness of phototocalypsis using the (TiO_2/UV) system for eliminating the Indigo carmine dye in aqueous solution.

Materials and Methods:-

Products used

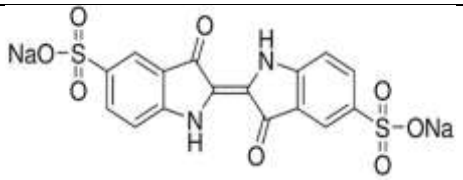
Reagents and solvents used

All the chemicals used (Indigo carmine, ammonium acetate, methanol) and marketed by Sigma Aldrich, Carlo Ebra or Fluka-Riedel-deHaën are all over 98% pure.

The water used is obtained from water purified by a Millipore MilliQ system. It has a resistivity of 18 MΩ.cm-1 and a dissolved organic carbon content of less than 0.1 mg/L-1.

The dye used, under the trade name Indigo carmine, has the gross formula C16H8N2Na2O8S2 and a molecular weight of 466.35 g/mol. Its chemical name according to the International Union of Pure and Applied Chemistry (IUPAC) is indigo 5,5-disulphonic acid. It is a standard for HPLC analysis supplied by Sigma Aldrich (CAS Number 860-22-0). Table 1 gives some characteristics of the dye and its chemical structure

Table 1:- Characteristics and chemical structure of indigo carmine.

Chemical name	Solubility	Chemical class	λ_{max} (nm)	Chemical structure
Indigo Carmine	10 g/L	colorant indigoïde	610	

Photocatalyst

The semi-conductor used is titanium dioxide (TiO_2) in the crystalline form of anatase PC 500, of purity greater than 99% and manufactured by Laboratoires Eisen-Golden.

Experimental equipment

Photochemical reactor

The photocatalytic reactor is a cylinder surrounded by several lamps. The photoreactor used is made of borosilicate glass and has a double wall surrounded by a black plastic film. The useful volume of this reactor is 500 mL. The reactor is kept under continuous stirring for a certain time before irradiating the dye solutions.

Light source

The polychromatic light source (λ >285 nm) used is a PHILIPS HPK 125 lamp whose spectrum reproduces the solar spectrum fairly closely between 290 and 800 nm.

High Performance Liquid Chromatograph (HPLC)

The HPLC used was a WATERS liquid chromatograph coupled to an iodine rod detector. A C18 column (HS-5HCODS, 5µm), 25 cm long and with an internal diameter of 3.2 mm, was used. The mobile phase consisted of a binary mixture of (A) 25 mM ammonium acetate (pH 6.9) and (B) methanol, depending on the molecule sought. The injection volume is 25 mL at a flow rate of 1mL/min.

Experimental protocols

Preparation of aqueous dye solutions

Different quantities of the powdered indigo carmine dye were weighed and diluted with distilled water in a volumetric flask to a concentration of 250 mg/L. The mixture was homogenised in the dark on a magnetic stirring plate. The daughter solutions to be used in the analysis were obtained by successive dilutions of the stock dye solutions to the desired concentrations. Dye calibration curves were established to determine the residual concentrations for the different experimental techniques.

Protocol for photocatalysis experiments (UV/TiO2 process)

200 mL of a coloured solution of a given concentration was prepared from a highly concentrated stock solution and introduced into the photochemical reactor, in the presence of 1 g/L of the semiconductor. After one (1) minute of stirring at medium speed, without illumination or instantaneously, the photocatalysis reaction is triggered by switching on the lamp. Samples of 3 mL are taken at regular intervals (15 minutes or 30 minutes) and then filtered through Millipore membrane filters (pore size, 0.2 µm) to retain residual TiO_2 particles. The decolourisation of the solution is monitored by HPLC at a wavelength corresponding to the absorption maximum of the dye, and the corresponding spectrum is given by the SAFFAS 190 DES spectrophotometer.

Results:-

Efficacy of photocatalysis in decolourising indigo carmine solution

Two tests were carried out: the first in which the dye solution was brought into contact with the light source at 365 nm, in the absence of the semiconductor. A second test in which the same dye solution was irradiated in contact with TiO2. Figure 1 shows a comparison of the degradation kinetics obtained in the presence and then in the absence of the semiconductor under the effect of irradiation at 365 nm. The negative part of the graph for direct photolysis reveals the degradation that takes place instantaneously on contact with the light approximately 1 min before the reaction is even triggered in the reactor containing the TiO_2

This figure shows that dye decolourisation is much faster with the TiO_2/UV system than with direct UV photolysis for the reaction time of 300 minutes. In fact, the rate of indigo carmine degradation reached 77% with the TiO2 catalyst compared with around 17% without TiO2 after 6 hours of irradiation.

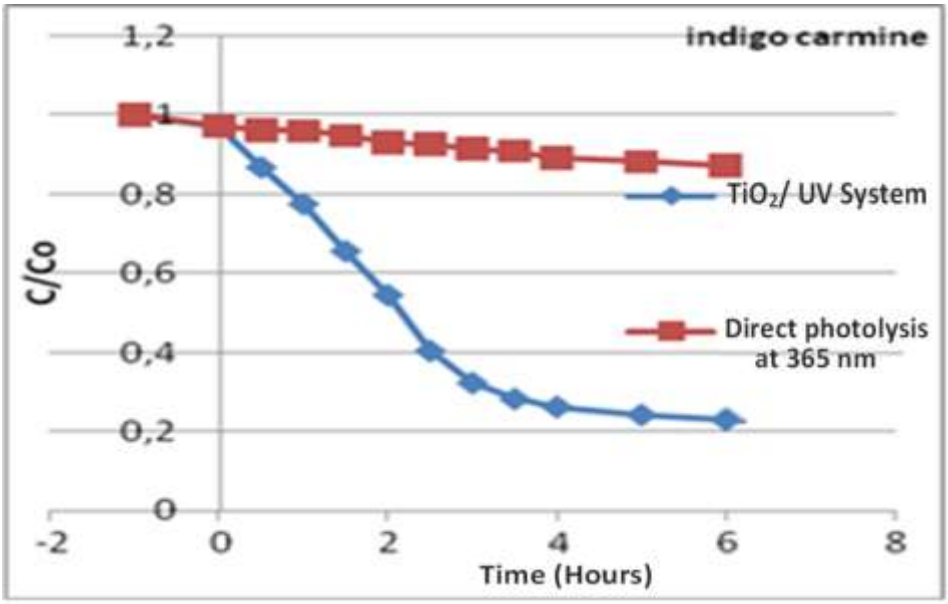


Figure 1:-Degradation kinetics of indigo carmine by direct photolysis (365 nm) and by photocatalysis in the TiO2/ UV system ([TiO2] = 1 g/L, λ= 365 nm).

Effect of irradiation on the decolourisation of indigo carmine solution

In this section, we carried out a comparative study of the adsorption of direct dyes 106 blue and indigo carmine at a concentration of 32 mg/L in the absence of light and under the effect of irradiation (Figure 2). This figure shows a significant difference between UV irradiation at 365 nm and adsorption without dye irradiation. This difference,

observed during 3 hours of contact between the indigo carmine solution and the semiconductor (TiO_2), resulted in an adsorption rate of 19.5% of the dye on the TiO_2 in the absence of light, compared with a degradation rate of 63% for the same coloured solution under UV irradiation.

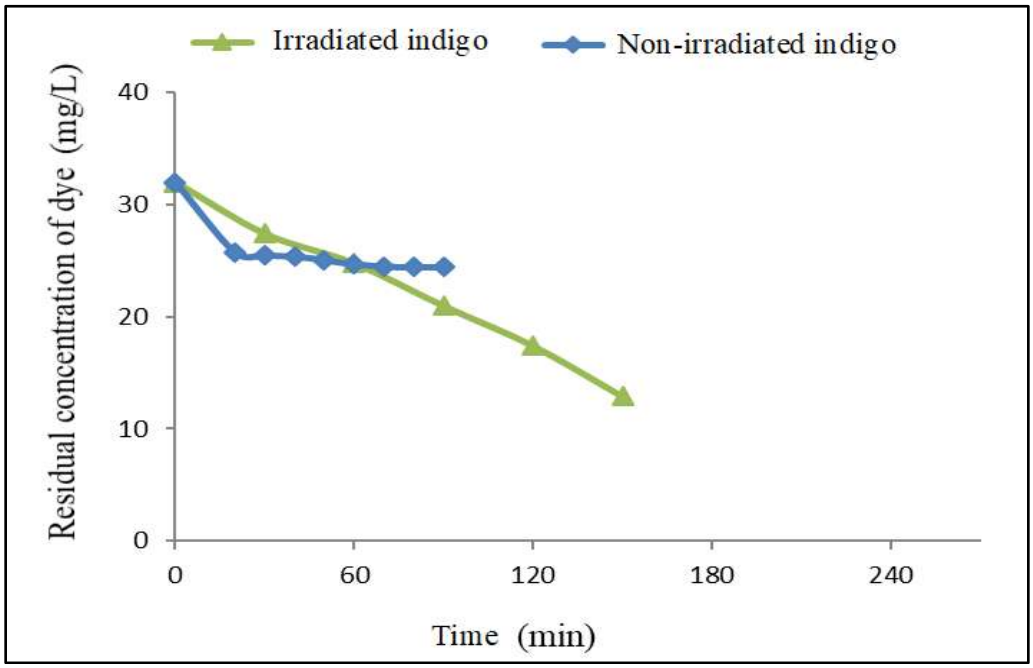


Figure 2:-Comparison of degradation kinetics in contact with TiO_2 of the dye studied in the presence and absence of UV light.

Influence of the light source

To assess the influence of light source intensity on photodegradation, four levels of light intensity were applied to the 12 mg/L indigo solution, the lowest of the concentrations studied. These light sources consisted of one lamp, two lamps, three lamps and four lamps. The lamps used were all of the same wattage (6 watts). Their different combinations give four light sources of different intensities. In this experiment, the light source and the catalyst were introduced into the system at the same time. Figure 3 shows the results of this experiment.

The results show that the degradation rate for a four-lamp light source is greater than for a three-lamp light source, and so on Table 2. The combination of these four lamps resulted in total degradation of the molecule after 120 min under the radiation. However, at the same time, the degradation rate was 98% for three lamps, 96% for two lamps and 92% for one lamp. This rate therefore decreases with decreasing light intensity.

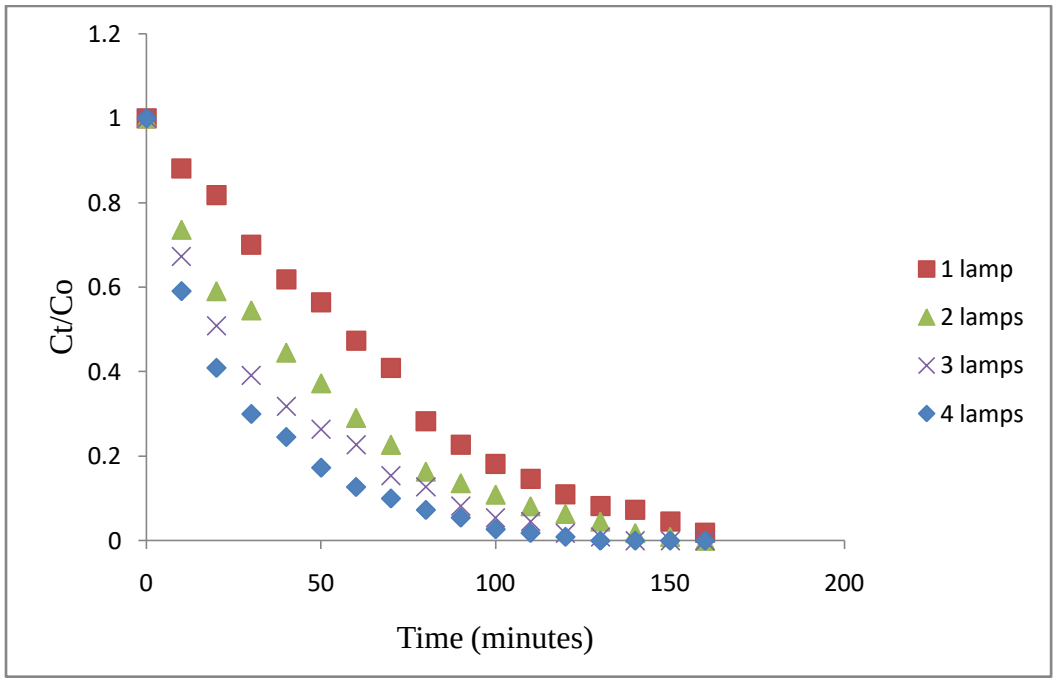


Figure 3:- Degradation of the indigo solution in the presence of different light sources.

	Kapp (s^{-1})	**Half-life (min)**
One-lamp light source	$5{,}30\times10^{-6}$	2177,42
Two-lamp light source	$6{,}92\times10^{-6}$	1670,23
Three-lamp light source	$8{,}36\times10^{-6}$	1381,68
Four-lamp light source	$9{,}83\times10^{-6}$	1174,82

Table2:-Degradation constants and half-lives for indigo under irradiation from different light sources

Influence of initial concentration on dye degradation

The kinetics of the photocatalytic reaction of the indigo carmine dye were studied with the TiO2/UV system by varying the initial concentrations of this dye. Three (3) solutions with concentrations of 12 mg/L, 16 mg/L and 32 mg/L were used.

Figure 4, which presents the degradation kinetics of indigo carmine at different concentrations, shows that the initial dye concentration has a real influence on decolourisation. For the lowest dye concentration of 12 mg/L, total elimination from the aqueous medium was achieved after 4 hours of exposure. On the other hand, it took 6 hours for the total disappearance of the dye from the 16 mg/L solution, whereas for the same exposure time, 80% of the indigo at a concentration of 32 mg/L was degraded.

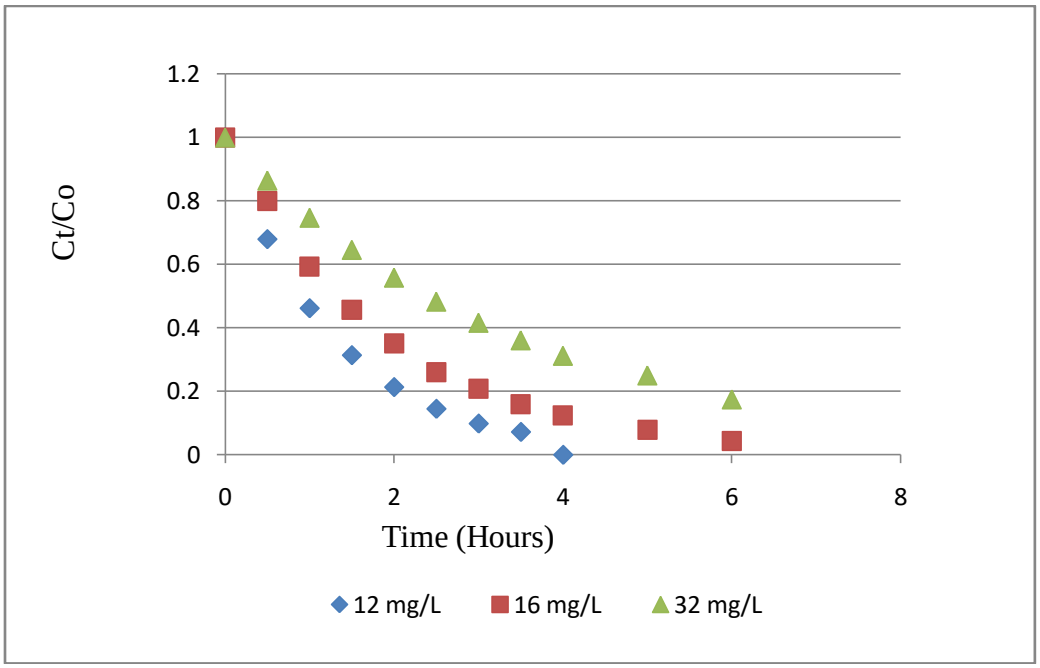


Figure4:-Kinetics of indigo carmine degradation at different concentrations.

Kinetic order of photocatalytic degradation of dyes

Figure 5 shows, in semi-logarithmic coordinates, the degradation kinetics of the indigo carmine molecule at different concentrations. The graphs obtained show very clearly that the degradation kinetics of the indigo carmine molecule at different concentrations follow the kinetic law of apparent order 1. The kinetic constants and half-lives of the molecules at the different concentrations studied are given in Table 3.

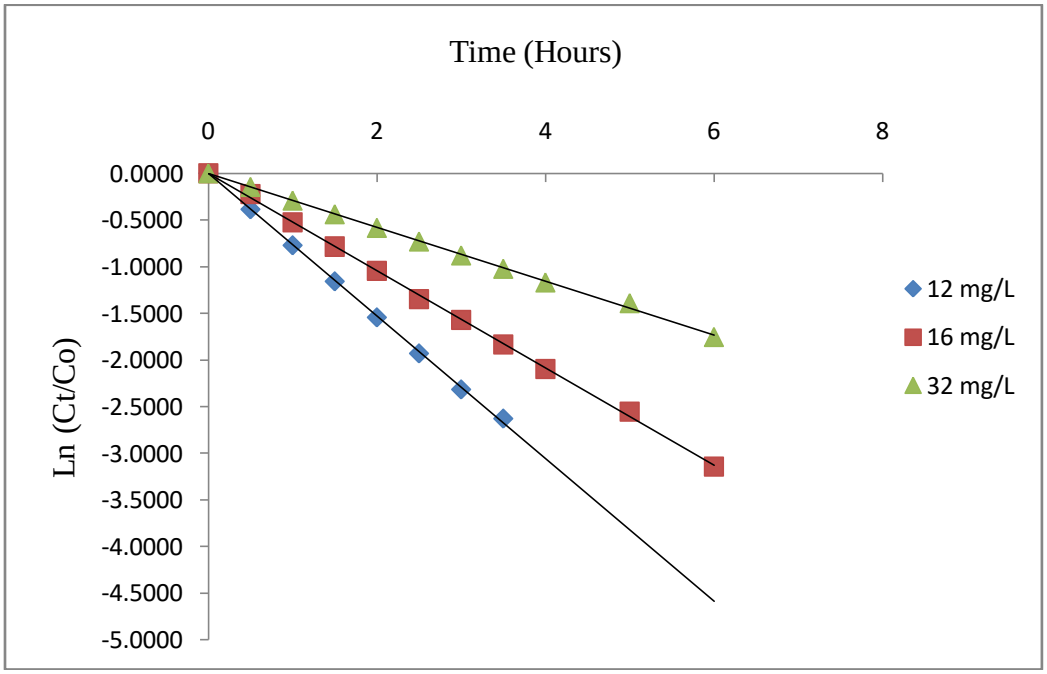


Figure 5:-Semi-logarithmic representations of the kinetics of indigo carmine at different concentrations.

Table 3:-Kinetic parameters for the degradation of indigo carmine.

	Concentration (mg/L)	K_{app} (s^{-1})	Half-life (min)
Indigo Carmine	12 mg/L	$2{,}12 \times 10^{-4}$	54,37
	16 mg/L	$1{,}45 \times 10^{-4}$	79,8
	32 mg/L	$8{,}02 \times 10^{-5}$	144

Discussion:-

The comparison of the results of the degradation kinetics of indigo carmine in photocatalysis with those of direct photolysis clearly shows that the degradation of the molecule studied is adapted to photocatalysis. This could be justified by the fact that indigo carmine absorbs weakly at the wavelength of 365 nm emitted by the UV lamp used, making it difficult to degrade this molecule by direct photolysis. The use of TiO_2 as a semiconductor catalyst accelerates the degradation of the coloured solution. Heterogeneous photocatalysis is based on the generation of highly reactive species, hydroxyl radicals ($HO^{\bullet}$) on the surface of the semiconductor (TiO_2) irradiated by high-energy photons (Bianco et al., 1999 ; Edelahi, 2004).These particles will then react with the dye molecules, causing them to degrade, unlike direct photolysis.

The irradiation therefore has an influence on the generation of radical species. Although this molecule absorbs with difficulty at 365 nm, according to Wang et al. (2004), irradiation of TiO_2 by UV lamps with wavelengths of less than 380 nm causes its activation and the ultimate production of hydroxyl radicals ($HO^{\bullet}$) with very high oxidising power, capable of breaking a large number of chemical bonds. In other words, excitation of the semiconductor by UV rays (λ= 365 nm) causes the creation of electron donor and attractor sites (e-/h+ sites). These electron-hole pairs will, as a result of oxidation-reduction reaction mechanisms (Edelahi, 2004 ; Lapertot, 2006), lead to the formation of $HO^{\bullet}$ radical species capable of more easily degrading these coloured waters compared with the adsorption process, in the absence of light, on TiO_2.

In addition, this work has shown that the rate of degradation decreases as the initial dye concentration increases. This could be explained by the fact that at high concentrations, the dye molecules can absorb a significant amount of light instead of the catalyst, thus reducing the production of h+/e- pairs (Habibi et al., 2005 ; Konstantinou and Albanis, 2004). A high concentration of dye creates a shielding effect that prevents radiation from penetrating the aqueous suspension and reaching the entire semiconductor (Liu et al., 2006). Thus, the absorption of a significant amount of UV by the dye molecules rather than by the TiO_2 surface reduces the intensity of the radiation absorbed at the catalyst, thereby reducing the efficiency of the photocatalytic reaction. Similar results were reported by Muruganandham and Swaminathan (2006) and Sobana and Swaminathan (2007) in photocatalytic oxidation studies of Reactive Orange 4 and Direct Blue 53 dyes respectively.

The influence of the power of the lamp intensity was demonstrated by Djouder et al (2012) during the degradation of salicylic acid. Using a 400 watt lamp, these researchers degraded the initial concentration of this molecule by 96%. However, using an 18-watt lamp, the degradation rate was only 43%. However, studies have shown that as the light intensity increases, the rate of degradation is independent of this intensity and stabilises at a threshold value, the limiting stage in this case being the transfer of the pollutant to the surface of the TiO2 (Brosillon et al., 2008 ; Kim and Choi, 2002). According to these authors, for low values of light intensity, the speed is proportional to the intensity because the electron/hole pairs (e-/h+) are consumed more quickly by the chemical reaction than by the recombination reactions. But beyond a certain intensity limit, the rate of recombination of (e-/h+) pairs becomes too great, limiting charge transfer.

Conclusion:-

This study showed that photocatalysis using the (TiO_2/UV) system is more suitable for eliminating the indigo carmine dye in aqueous solution. Irradiation of the coloured solution in contact with the anatase PC 500 semiconductor at a wavelength of 365 nm resulted in the degradation of 77% of the dye, compared with 17% by direct photolysis. However, this degradation, which follows the kinetic law of apparent order 1, showed its effectiveness with low-concentration solutions, since total elimination of the molecule was achieved with the least concentrated solution of 12 mg/L after four (4) hours, compared with 80% degradation with the most concentrated solution of 32 mg/L, 6 hours later. The experiments also showed that degradation accelerated as light intensity increased.

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