Photocatalytic degradation of indigo carmine in aqueous solution by TiO$_2$-coated non-woven fibres

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Abstract

The photocatalytic degradation of indigo carmine has been investigated in aqueous solutions using TiO$_2$ coated non-woven fibres as photocatalyst. The experiments were carried out to investigate the factors influencing the photocatalytic degradation, such as the previous adsorption in the dark, initial concentration of dye solution, temperature, and pH. The experimental results show that adsorption is an important parameter controlling the apparent kinetic constant of the degradation. The photocatalytic degradation rate was favoured by a high concentration of solution in respect to Langmuir–Hinshelwood model. The degradation rate was pH and temperature dependent with a high degradation rate at high temperature.
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1. Introduction

Organic dyes constitute one of the larger groups of pollutants in wastewater released from textile and other industries. The discharge of highly coloured wastewater into the ecosystem involves environmental problems like aesthetic pollution (even a small amount of dye is clearly apparent), and perturbation of aquatic life.

Among the most useful dyes, there is indigo carmine (3,3′-dioxo-2,2′-bis-indolyden-5,5′-disulfonic acid disodium salt) or acid blue 74. Apart from its use as textile colouring agent and additive in pharmaceutical tablets and capsules as well as in confectionery items, indigo carmine is also used for medical diagnostic purposes. In conjunction with acetic acid, the dye facilitates diagnosis of Barrett's oesophagus [1]. It can also help to target biopsies, since inhomogeneously stained or unstained areas seem to correlate with intraepithelial neoplasia [2]. However, indigo carmine is not readily metabolized but is rather freely filterable by the kidneys. Giving intravenous injection of indigo carmine for intra-operative cystoscopy is a safe technique that can detect otherwise undetected intra-operative compromise

of the urinary tract [3]. It also contributes to intra-vital staining for contrasting and accentuating changed mucosal processes [4].

The indigo carmine is considered as highly toxic indigoid class of dye. Contact with it can cause skin and eye irritations. It can also cause permanent injury to cornea and conjunctiva. The consumption of the dye can also prove fatal, as it is carcinogenic and can lead to reproductive, developmental, neuron and acute toxicity [5]. It has also been established that the dye leads to tumours at the site of application [6]. When administered intravenously to determine potency of the urinary collecting system, it is also known to cause mild to severe hypertension, cardiovascular and respiratory effects in patients [7–9]. It may also cause gastrointestinal irritations with nausea, vomiting and diarrhoea [10,11]. The toxicity tests of the dye revealed long-term toxicity in mice [12] and short-term toxicity in the pig [13].

Thus, keeping the toxicity of this dye in view, various attempts have been made for the removal of indigo carmine from water and wastewater. Apart from adsorption over chitin and chitosan [14] and charcoal from extracted residue of coffee beans [15], electrochemical [16], biological [17] and photochemical [18] techniques have also been explored. Out of all this attempts, the photocatalytic treatment is a more attractive alternative for the removal of soluble organic compounds. It can give the com-

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plete mineralization of organic compounds to carbon dioxide, water and mineral acids. Contrary to physical processes, such as coagulation and adsorption, which merely transfer the pollutants from wastewater to other media and cause secondary pollution. Moreover, photocatalysis does not require expensive oxidants and can be carried out at mild temperature and pressure. However, the obligation to separate the small TiO_2 particles from the suspension after treatment limits the process development. Alternatively, the catalyst may be immobilized onto a suitable solid inert material, which eliminates the catalyst removal step [19–21], and permits the reuse of the photocatalyst several times.

The aim of this study is to analyze the feasibility of discoloration of indigo carmine dye using a new photocatalytic material, which consists on TiO_2 supported on natural and synthetic non-woven fibres. The factors that influence the dye photocatalytic removal were investigated.

2. Experimental

2.1. Materials

The immobilized photocatalyst used in this study was a commercial Titania photocatalyst from Ahlstrom firm (France). It consists in PC500 Titania by Millennium inorganic chemicals (anatase: >99%, specific surface area 350–400 $m^2 g^{-1}$, crystallites mean size = 5–10 nm). Titania PC500 was coated on non-woven fibres (natural and synthetic fibres 254 μm of thickness) using an inorganic binder. The binder was an aqueous dispersion of colloidal SiO_2 (EP1069950B1 European patent). A specific surface area extender (zeolite UOP, 2000 $m^2 g^{-1}$) was used to increase adsorption properties of the photocatalyst. The physical and chemical properties of the photocatalyst are shown in Table 1.

The indigo carmine ($C_{16}H_8N_2S_2O_8Na_2$) was obtained from Labosi (colour index: 73015) and used as received without further purification. Solutions were prepared by dissolving requisite quantity of the dye in distilled water. The pH was adjusted to a given value in the range 2–10 by addition of HCl (1N) or NaOH (1N) (analytical grades) and was measured using a Schott titroline (TE96) pH-meter.

Table 1
Chemical and physical properties of the Ahlstrom photocatalyst (Ref: 1048)

Composition	
PC500	18 g m^{-2}
SiO$_2$	20 g m^{-2}
UOP200	2 g m^{-2}
Physical properties	
Mass per unit area	75 g m^{-2}
Thickness	254 μm
Air permeability	2570 L m^{-2} s^{-1}
Tensile strength MD	1100 N m^{-1}
CD	500 N m^{-1}
Elongation MD	3%
CD	5%
Water drop	2 s

2.2. Photocatalytic reactor

Experiments were carried out using a cylindrical batch reactor opened at air, 8 cm in diameter and 12 cm in working height. The water jacket has a diameter of 5 cm contains the UV lamp and permit the water circulation. The photoreactor was recovered inside with (11 cm × 25 cm) of the photocatalyst and was exposed to a luminous source composed of a HPK 125W Philips UV-lamp (the wavelength maximum of the light source was 365 nm) placed in axial position inside the water jacket. The reactor was initially loaded with 500 cm^3 of indigo carmine aqueous solution and maintained in low continuous stirring (100 rpm) by means of a magnetic stirrer.

2.3. Procedure and analysis

The adsorption experiments were carried out by immersing 11 cm^2 of the photocatalyst in 20 cm^3 of the dye solutions for 1 h (previous study of the kinetic of adsorption showed that only 20 min are sufficient to establish the equilibrium of adsorption). The adsorption isotherms was obtained by different initial concentrations (4–20 mg dm^{-3}) at 20 °C, and the effect of temperature was obtained by varying temperature from 20 °C to 40 °C with an initial concentration of 12 mg dm^{-3}. The quantity adsorbed was calculated by measuring the concentration of the solution before and after adsorption using the following equation:

$$q_e = \frac{C_0 - C_e}{S} \tag{1}$$

where q_e (mg m^{-2}) is the quantity of indigo carmine adsorbed per unit surface of the photocatalyst at adsorption equilibrium, C_0 (mg dm^{-3}) the initial dye concentration, C_e (mg dm^{-3}) the dye concentration at equilibrium and S (m^2 dm^{-3}) is the ratio of the surface of the photocatalyst per litre of aqueous solution.

The photocatalytic degradation experiments were carried out by loading 500 cm^3 of indigo carmine solutions in the photocatalytic reactor. The effect of initial concentration was obtained with different initial concentrations (4–20 mg dm^{-3}) at 20 °C and initial pH. The effect of temperature was obtained by studying the photocatalytic degradation at different solution temperatures (20–40 °C) with an initial solution concentration of 12 mg dm^{-3}. The effect of pH was carried out by varying the initial pH of aqueous solution from 2 to 10, with an initial concentration of 12 mg dm^{-3} and at 20 °C. All photocatalytic experiments were carried out after 30 min of previous adsorption in the dark.

The dye aqueous solutions were filtered by Millipore membrane filter type 0.45 μm HA, and the concentrations were determined from UV–vis absorbance characteristic with the calibration curve method. A Jenway 6405 UV/visible spectrophotometer was used. The wavelength of the maximum of absorption (λ_{max}) was 610 nm.

3. Results and discussion

3.1. Adsorption study in the dark

It is likely that sorption of the dye is an important parameter in determining photocatalytic degradation rate. The adsorbed dye on the surface of the semiconductor particles acts as an electron donor, injecting electrons from its excited state to the conduction band of the semiconductor under UV irradiation. Adsorption tests in dark were carried out in order to evaluate the equilibrium constants of the adsorption of the dye on the photocatalyst surface. Fig. 1 shows an isotherm of L-shape according to the classification of Giles et al. [22]. The L-shape of the isotherm means that there is no strong competition between the solvent and the adsorbate to occupy the adsorbent surface sites.

The experimental data was fitted to the Langmuir equation (Eq. (2)) to describe the adsorption of indigo carmine on the surface of the photocatalyst:

$$\frac{q_e}{q_m} = \frac{KC_e}{1 + KC_e} \tag{2}$$

where q_m (mg m^{-2}) is the maximal amount of the dye adsorbed per unit surface of the photocatalyst, q_e (mg m^{-2}) the amount of the dye adsorbed per unit surface of the photocatalyst at the equilibrium, K (dm^3 mg^{-1}) Langmuir equilibrium constant and C_e (mg dm^{-3}) is the concentration of the dye in aqueous solution at the equilibrium.

The linear transformation of Eq. (2) can be expressed by the following equation:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{Kq_m}\frac{1}{C_e} \tag{3}$$

The linear transforms are given in the insert in Fig. 1, the ordinate at the origin is equal to the reciprocal of q_m, whereas K can be calculated from the slope ($1/q_m K$). From the data obtained, the maximal adsorption quantity and the Langmuir adsorption constant are respectively, 20.20 mg m^{-2} and 0.131 dm^3 mg^{-1}.
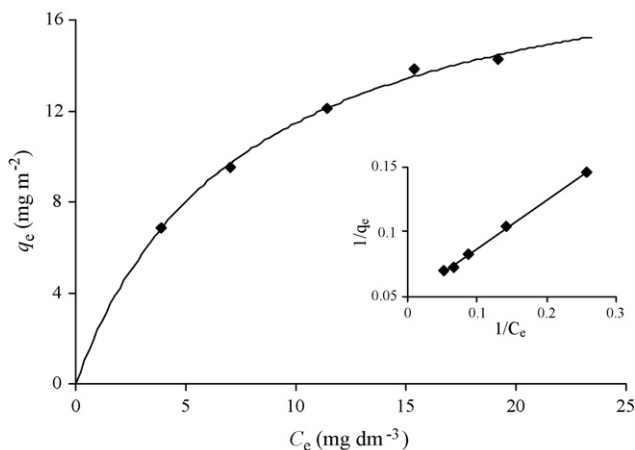

Fig. 1. Adsorption isotherm of indigo carmine on the photocatalyst. In the insert: reciprocal of the quantity adsorbed as a function of reciprocal of equilibrium concentration.
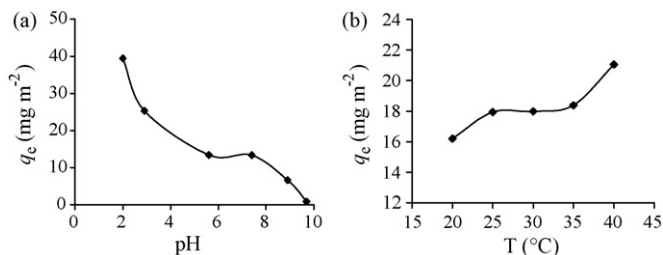

Fig. 2. Variation of indigo carmine amount adsorbed on the photocatalyst as function of pH (a) and solution temperature (b).

Since real effluents to be treated can be at different temperature (according to the seasons, the geographical sites, during the treatment itself, etc.) and at different pHs, comparative experiments were performed by varying all these parameters. Fig. 2(a) shows the variation of the amount of indigo carmine adsorbed on the photocatalyst as function of pH at 25 °C. The figure indicates that the amount of dye adsorbed is higher in acidic medium and decrease with increasing initial pH. This result may be due to the influence of the solution pH on both the surface state of TiO$_2$ and the ionization state of ionisable organic molecule of the dye.

Chun et al. [23] and Hu et al. [24] have suggested that the isoelectric point of TiO$_2$ decreases to pH 3 when the TiO$_2$ is supported on SiO$_2$. As a consequence, the TiOH$_2$$^+$ group is predominant when pH solution < 3 in the case of TiO$_2$/SiO$_2$ photocatalyst. Moreover, the dye is weak acids, it dissociates less towards an acid pH and is found consequently in neutral electrical form φ-SO$_3$H. From the figure, it can be seen that the amount of indigo carmine adsorbed on the photocatalyst material decreases for a pH higher than three, in correlation with the decrease of the amount of TiOH$_2$$^+$. It appears, therefore, that TiOH$_2$$^+$ could be responsible for the dye adsorption on photocatalyst surface, suggesting that electrostatic attraction leads to the observed adsorption [25]. On the opposite, the adsorption at basic pH is disfavoured by repulsive electrostatic forces existing between φ-SO$_3$$^-$ and TiO$^-$ which are predominant in this range of pH.

The variation of the indigo carmine adsorbed on the photocatalyst as function of solution temperature is shows in Fig. 2(b); an increase of the amount of indigo carmine adsorbed was observed when the temperature increases. From these results, the enthalpy of adsorption (ΔH) has been calculated using the linear transformation of the following equation [26].

$$q_e = (q_e)_0 \exp\left[-\left(\frac{\Delta H}{RT}\right)\right] \tag{4}$$

The linear transformation of this equation expressed by ln(q_e) as function of $1/T$ gives a straight line whose slope is equal to $-\Delta H/R$. From the data obtained, the enthalpy of adsorption calculated was 8.34 kJ mol^{-1}; the positive sign of this energy indicates that the adsorption reaction was endothermic.

3.2. Kinetic analysis as function of initial concentration

No photolytic degradation by UV light of indigo carmine has been observed in the same operating conditions, so dye
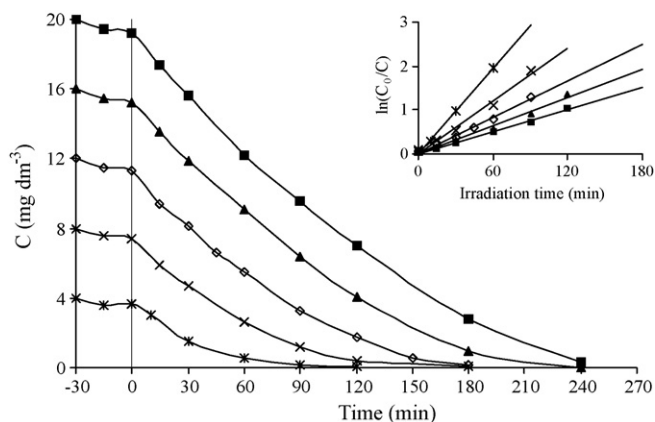
Fig. 3. Kinetics of the photocatalytic degradation of indigo at different initial concentrations. In the insert: first-order linear transforms $\ln(C_0/C) = f(t)$.
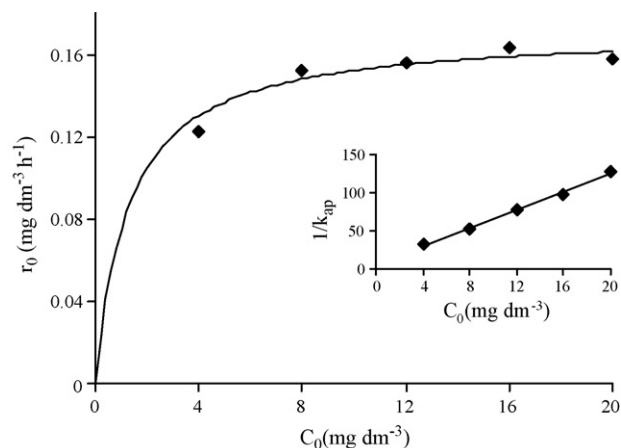

Fig. 4. Effect of initial indigo carmine concentration on the initial rate of degradation. In the insert: plot of the reciprocal of apparent rate of degradation against initial concentration.

disappearance represents exactly the photocatalytic degradation on the photocatalyst surface. The kinetics of the photocatalytic degradation of indigo carmine at different initial concentrations is represented in Fig. 3. It is evident that the photodegradation rate depends on the initial concentration of the dye. Since the lifetime of hydroxyl radicals is very short (only a few nanoseconds), they can only react at or near the location where they are formed. A high dye concentration logically enhances the probability of collision between organic mater and oxidizing species, leading to an increase in the decolouration rate.

According to numerous works [26–29], the kinetic of the photocatalytic degradation rate of most organic compounds is described by pseudo-first order kinetics.

$$-\frac{dC}{dt} = k_{ap}C \tag{5}$$

where K_{ap} (h^{-1}) is the apparent rate constant and is affected by dyestuff concentration. Integration of that equation (with the same restriction of $C = C_0$ at $t = 0$) will lead to the expected relation:

$$\ln\left(\frac{C_0}{C}\right) = k_{ap}t \tag{6}$$

The plot of $\ln(C_0/C)$ versus t with different initial concentration of indigo carmine is shown in the insert in Fig. 3. The figure shows that the photocatalytic degradation follows perfectly the pseudo-first order kinetic in the cases of initial concentrations of 4 and 8 mg dm^{-3}. However, for concentrations higher than 8 mg dm^{-3}, the photocatalytic degradation takes place in two stages; the first stage of the process follows pseudo-first order kinetic with respect to indigo carmine concentrations and a second slower stage until the end of the process of the photocatalytic degradation. The length time of the fist stage decrease with increasing the initial indigo carmine concentration. This result can be explained by the competing adsorption/degradation between indigo carmine molecules and its degradation intermediates, which could be more significant with high concentration in solution. And also by the loss of oxygen concentration in the solution during the photoreaction due to the very low solubility of oxygen in water.

The effect of initial indigo carmine concentration on the initial rate of degradation is shown in Fig. 4. The figure indicates that the rate of decolouration increases with increasing initial concentration of indigo carmine which corresponds to Langmuir–Hinshelwood adsorption model according to the following equation:

$$r_0 = k_{ap}C_0 = \frac{k_c K C_0}{1 + K C_0} \tag{7}$$

where r_0 (mg dm^{-3} h^{-1}) is the initial rate of the photocatalytic degradation, k_{ap} (h^{-1}) the apparent rate constant, K (dm^3 mg^{-1}) the adsorption equilibrium constant and k_c is the constant depending on the other factors influencing the process (UV intensity, temperature, etc.).

A linear expression can be conventionally obtained by plotting the reciprocal initial rate constant against initial concentration:

$$\frac{1}{k_{ap}} = \frac{1}{k_c}C_0 + \frac{1}{k_c K} \tag{8}$$

The plot of $1/k_{ap}$ against C_0 as shown in the insert in Fig. 4, gives linear relation ship between $1/k_{ap}$ and C_0. From the values of the slope ($1/k_c$) and the intercept ($1/k_c K$), k_c and K values for the photocatalytic degradation of indigo carmine were found to be respectively 10.45 mg dm^{-3} h^{-1} and 0.78 dm^3 mg^{-1}. The constant of adsorption calculated from the Langmuir–Hinshelwood model is different to that calculated from adsorption isotherm; this difference may be due to the fact that, there are two fractions adsorbed on the photocatalyst material: the fraction adsorbed on TiO$_2$ who underwent discoloration under UV irradiation and the fraction adsorbed on the silica binder. So the isotherm of adsorption regroups the adsorption on both TiO$_2$ and SiO$_2$ and supporting fibres, contrary to Langmuir–Hinshelwood model which represents only the adsorption of the dye on the photoactive TiO$_2$.
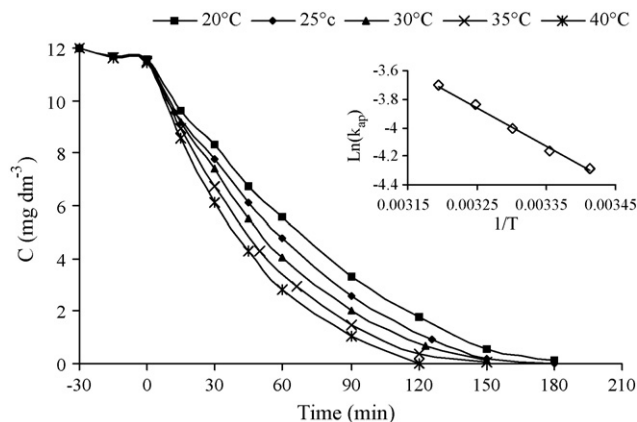
Fig. 5. Effect of temperature on the kinetic of the photocatalytic degradation of indigo carmine. In the insert: plot of $\ln(k_{ap})$ vs. $1/T$.

Fig. 6. Effect of the pH on the pseudo-first order rate constant of the photocatalytic degradation of indigo carmine.

3.3. Effect of temperature

Generally, photocatalysis is usually not very temperature dependent. However, an increase in temperature can affect the amount of adsorption and helps the reaction to complete more efficiency with $e^- \_ h^+$ recombination [30]. Experiments have been made at different working temperature in the range of 20–40 °C, the results is shown in Fig. 5. The figure indicates that, the rate of the photocatalytic degradation is temperature dependent and is favoured with the raise of solution temperature.

The apparent activation energy (E_a) has been calculated from the Arrhenius equation:

$$k_{ap} = k_{ap0} \exp\left[-\left(\frac{E_a}{RT}\right)\right] \tag{9}$$

where k_{ap} (h^{-1}) is the apparent rate constant, k_{ap0} the temperature independent factor (h^{-1}), E_a the apparent activation energy of the photocatalytic degradation (J mol^{-1}), R the gas constant (8.31 J K^{-1} mol^{-1}) and T is the solution temperature.

The linear transform $\ln(k_{ap}) = f(1/T)$, who is shown in the insert in Fig. 5, gives a straight line whose slope is equal to $-E_a/R$. from the data obtained, the apparent activation energy is 22.76 kJ mol^{-1}. This apparent energy represents the total activation energy of both adsorption and photocatalytic degradation of indigo carmine.

By considering the Langmuir–Hinshelwood model to describe the photocatalytic degradation process, the apparent rate constant can be expressed by:

$$k_{ap} = \frac{k_c K}{1 + KC} \tag{10}$$

At low concentration KC can be neglected with respect to 1 and one gets the simplified expression

$$k_{ap} = k_c K \tag{11}$$

This equation can also be expressed as a function of temperature by applying the Arrhenius's law to k_c and the Van't Hoff
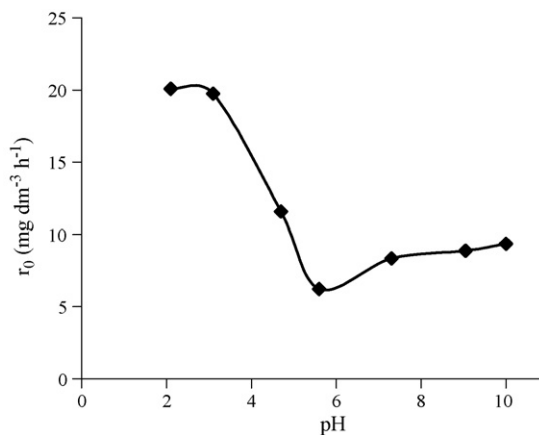
one to K:

$$k_{ap} = k_{c0} \exp\left[-\left(\frac{Et}{RT}\right)\right] K_0 \exp\left[-\left(\frac{\Delta H}{RT}\right)\right]$$
$$= k_{c0} K_0 \exp\left[-\left(\frac{Et + \Delta H}{RT}\right)\right] \tag{12}$$

thence

$$E_a = E_t + \Delta H \tag{13}$$

where E_t represents he true activation energy of the photocatalytic degradation, from this results the true activation energy is equal to 14.42 kJ mol^{-1}, this value is close to the true activation of Acid Blue 25 dye on Degussa P-25 obtained by Bouzaida et al. [26].

3.4. Effect of pH

The efficiency of the photocatalytic processes strongly depends on the pH of the reaction solution. Fig. 6 shows the variation of the variation on the apparent rate constant of the photocatalytic degradation with varying the initial pH of aqueous solution from 2 to 10. The high adsorption of the dye on the photocatalyst material leads to a fast decrease of the dye concentration in acid pH zone. These results suggest that the influence of the initial pH of the solution on kinetics of photocatalysis is due to the amount of the dye adsorbed on TiO$_2$. This hypothesis agrees with a reaction occurring at the surface of TiO$_2$ and not in the solution, close to the surface. For basic pH, a small increase of degradation rate is observed. This could be attributed to a slight increase in OH$^\bullet$ radicals whose formation is favoured by the presence of hydroxyl ions OH$^-$.

4. Conclusion

The results of our study have shown that the degradation of indigo carmine dye was successfully carried out using coated TiO$_2$ on paper fibres. A correlation between the adsorption of the dye onto photocatalyst material and the rate of degradation has been found. pH influences both the photocatalyst surface and

the dye structure. The maximum dye adsorption was achieved for pH less than 4 in relation with the p_{zc} of the pair TiO$_2$/SiO$_2$. The photocatalytic degradation was obviously affected by the initial concentration with respect to Langmuir–Hinshelwood kinetic model. The use of TiO$_2$ coated on Ahlstrom non-woven fibres is an efficient photocatalyst to degrade textile dye avoiding the tedious filtration step.

Acknowledgement

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