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EFFICIENT SOLAR PHOTOCATALYST BASED ON TiO_2 /CORN SILK NPS COMPOSITE FOR REMOVAL OF A TEXTILE AZO-DYE FROM AQUEOUS SOLUTIONHayrunnisa Nadaroglu^{1,2*}, Asghar Lesani², Seyedeh Sara Soleimani², Aynur Babagil², Azize Alayli Gungor^{2,3}¹Ataturk University, Erzurum Vocational Training School, Department of Food Technology, Erzurum, TURKEY²Ataturk University, Faculty of Engineering, Department of Nano-Science and Nano-Engineering, Erzurum, TURKEY³Ataturk University, Erzurum Vocational Training School, Department of Chemical Technology, Erzurum, TURKEY

ABSTRACT

Background: The results of investigations on a new advanced oxidation process regarding a new embedded heterogeneous photocatalyst on corn silk/titanium dioxide nanoparticules composite are presented. **Methods:** UV-VIS-spectroscopy, Scanning electron microscopy (SEM), Fourier-transform IR spectrometry (FT-IR), and X-ray powder diffraction (XRD) were applied to characterize the effect of functionalization, structure, surface morphology and optical properties of composites and mineralization of pollutants. **Results:** The present work confirmed the role of corn silk/titanium dioxide NPs as a factor which not only activated the catalyst with UV light but also raised the adsorption of species by increasing the active surface area. A small UV-shift of band gap values regarding that of commercial photo-active TiO_2 was detected as consequence of the quantum size effect, suggesting that photocatalytic experiments should be performed under UV-radiation assistance. **Conclusion:** The synthesized corn silk/titanium dioxide (TiO_2)NPs showed good activity in the photocatalytic oxidation of Direct blue 15 (DB 15) achieving conversions higher than 90% within 30 s.

INTRODUCTION

Our world is faced with a huge problem of environmental pollution due to the rapid growth and industrialization influence results. Dyes and pigments are the most important source of water pollutants. The dyeing process as well as consume a large amount of water is an important factor polluting rivers [1]. Reactive dyes are especially used in textiles, paper, wool, cotton, silk, printing and leather industries. Because these dyes were discarded in large amounts and toxic, they cause great environmental pollution problems [2,3]. Every year, 80 000 tons of reactive dyes are produced for different industries and they are the source of environmental pollution. Reactive azodyes are generally synthetically produced and aromatic and they includes complex molecular structures such as benzene, naphthalene, anthracene comprises to luene and xylene [4]. Reactive dyes are the largest class of synthetic dyes with high ability to dissolve in water and they are usually resistant to bio degradation process [5]. The discharge of these colored compounds into the environment causes considerable non-aesthetic pollution and serious health risks [6].

Physico-chemical processes such as adsorption [7, 8], ion exchange [9] and membrane filtration [10] are expensive, insufficient, and these processes can be applied to a large amount of dye waste water. Instead of this method, the biodegradation, bio accumulation and biosorption techniques are used these methods are too weak in terms of impact [11].

Another dye removal method is enzymatic process. However, in this method, enzymes are inhibited at different pHs, temperatures and in the presence of inhibitors and they aren't effective [12]. Chemical methods such as chemical oxidation [13], electro chemical degradation [14] and ozonation [15] are quite effective methods. However, these generally used techniques are very expensive and lead to the formation of toxic byproducts. Especially as the oxidizing agent used as the hypochlorite is halides' decolorizes organic toxic substances. In addition, the pre-treatment requirements for the implementation of these methods constitutes a significant draw back [16].

Recently, nano particles hold an important place in the presence of photocatalytic degradation, due to the cheap and effective. In addition, through this process, toxic azo dyes are also converted to CO_2 , water and mineral acid. This process is performed generally in the presence of a semiconductor metal and UV light ($\lambda < 400 \text{ nm}$). TiO_2 which is widely used is a photo catalyst which is easily obtainable, inexpensive, non-toxic and stable [17]. TiO_2 nanoparticles have more photocatalytic activity in the liquid medium and collecting of them is extremely difficult from their aqueous environment. After using, TiO_2 NPs are often left in a freely into the environment, and they can easily penetrated to membranes of biological microorganisms and plants and they cause their death. For this reason, to be immobilized on a support material of TiO_2 NPs photo catalyst is a big advantage. Glass, silica, quartz, activated carbon, mesoporous clays, and polymeric materials have been used as support material for TiO_2 NPs [18]. Most materials with granule-shaped reduce the photo catalysis performance because of reducing the effect of UV photon [18]. TiO_2 is not available any research in literature related to immobilization TiO_2 NPs with corn silk. Corn silk is non-toxic, bio-degradable and a fibrous material. In this study, to be immobilized TiO_2 NPs onto corn silk fiber structure and usability of this material in degradation of DB 15 azo dye was investigated.

KEY WORDS

Corn silk, titanium dioxide NPs, textyl dye, Direct blue 15

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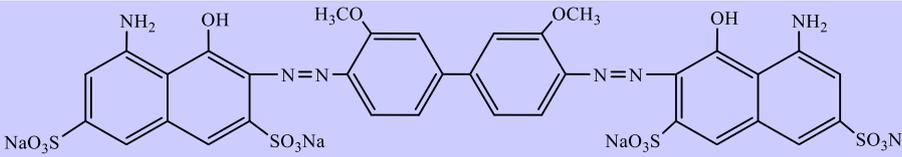
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MATERIALS AND METHODS

Chemicals

Direct blue 15 (DB15), sodium hydroxide (NaOH), hydrochloric acid (HCl), Sodium hypochlorite (NaClO), Titanium dioxide Nanoparticles (TiO_2 NPs) (<20 nm) were purchased from Sigma/Aldrich Co. The chemical characteristics and structures of DB15 were summarized in Table 1. Distilled water was used for all the tests performed (GFL 2004).

Table 1: General characteristics of Direct blue 15 dye

Direct blue 15 (DB15)	
Chemical formula	$\text{C}_{34}\text{H}_{24}\text{N}_6\text{O}_{16}\text{S}_4\text{Na}_4$
Chemical structure	
Molar mass (g mol^{-1})	992.80
λ_{max} (nm)	596

Supply and preparation for analysis of corn silk material

Corn silk (CS) is obtained from local corn seller. 25 g corn silk sample was taken and added to 250 mL, 0.5 M NaClO solution. Then, this mixture was incubated in a water bath (80 °C) for 1 hour. Corn silk then washed thoroughly with 250 ml of pure water and corn silk was incubated in the same conditions with 1 M NaOH solution. Then, corn silk was thoroughly washed with pure water and dried in oven at 60 °C for 8 hours. Dried corn silk sample was fractionated with pure water in the steel blender. Then, 0.2 g TiO_2 NPs were added to obtained mixture and incubated for 2 h in an ultrasonic bath environment at 60 °C for immobilizing TiO_2 NPs onto silk corn. Then, TiO_2 immobilized corn silk was separated from the supernatant. TiO_2 immobilized corn silk support material was washed 5 times with pure water and unbound TiO_2 NPs were removed. This obtained TiO_2 immobilized Corn silk support material was dried in the oven at 60 °C for 8 hours and it was used in all studies.

Characterization methods of the CS and TiO_2 -IML CS

The Scanning Electron Microscopy (SEM) images and chemical analysis at Energy Dispersive X-ray (EDX) of nanoparticles were recorded with a Zeiss Sigma 300 field emission SEM. The analysis was performed by mounting CS and TiO_2 -IML-CS samples onto pin type SEM stubs using carbon/platinum adhesive tabs and was coated with carbon by electro deposition under vacuum prior to analysis to enhance the surface conductivity.

X-ray diffractogram (XRD) of CS and TiO_2 -IML-CS, before and after dye treatment, was undertaken using a PANalytical Empyrean model XRD at $\text{Cu-K}\alpha$ radiation ($\lambda=1.54 \text{ \AA}$). The analysis of dried CS and TiO_2 NPs-IML-CS were carried out continuous scans from 10 to 100 ° at 2 ° scan rate at 2 θ min⁻¹ in ambient air.

FTIR analysis of DB 15 dye and TiO_2 NPs-IML-CS, before and after dye treatment, was recorded using a Vertex 80 Model FTIR Frontier spectrophotometer with attenuated total reflection (ATR) technique in the 4000-400 cm^{-1} region.

Preparation of dye solutions and UV-vis analysis

The stock solutions of DB 15 were prepared in 50 mg/L concentration and used by diluting with deionized water further experiments. Before experiments, desired pH of the solution was adjusted by Thermo scientific Orion 4 Star digital pH meter with diluted HCl or NaOH solutions. The UV-vis spectra of dye solutions were recorded from 200 to 900 nm using an Epoch Microplate Spectrophotometer equipped with a quartz cell of 1.0 cm path length. The concentrations of samples were quantified by measuring the absorption intensity at maximum wavelength.

Batch experiments

Direct blue 15 azo dyes degradation was carried out in a closed system consisting of a magnetic stirrer and UV-C lamp. For this purpose, the reaction medium was prepared by adding 25 mL (50 mg / L) DB 15 azo dye and 0.4 g of TiO_2 -NPs IML- CS sample in a 250 ml beaker. The same tests were performed for CS and TiO_2 NPs samples, respectively. Distilled water was used as a blank sample. The dye removal efficiency was calculated using the following equation:

$$\text{Removal}(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where Removal (%) was the dye removal efficiency, Co (mg/L) was the initial dye concentration, and Ct (mg/L) was the concentration of dye at t min [19].

Effect of some parameters

Degradation of DB15 azo dyes was followed by measuring absorbance at 596 nm. In order to determine the content time, degradation reaction in UV system was followed during 10 min. For this purpose, samples taken periodically from reaction medium measured against distilled water and degradation% was calculated using the equation (1).

Also, the effects of pH and stirring speed on the photo degradation of DB15 were investigated. For this purpose, the pH of DB15 azo dye was adjusted using a pH meter and 0.01 N HCl / NaOH solutions at pHs 3-10. In each pH value, absorbance changes were monitored at 596 nm by establishing the same experimental.

The effect of stirring speed

In order to monitor the effect of stirring speed; 0.4 g corn silk was added to 25 mL, DB15 azo dye at 50 mg / L concentration solution and reactions were occurred at 25 °C, and pH 3.0 and at 100, 200, and 300 rpm, respectively. Absorbance values were recorded at 596 nm against distilled water.

The effect of support material

In order to investigated of the effect of support material onto removal of DB15, different reactions were performed between 0.1 and 0.8 g TiO₂-IML-CS, respectively.

The effect of dye concentration

The effect of dye concentration on the photocatalytic degradation of DB15 azo dye was investigated following the prepared reactions in the same conditions (pH 3.0, 25 °C, 300 rpm) and at 5, 25, 50, 75, 100, 150 and 200 mg/L DB15 dye concentrations [20].

Reusability experiments for TiO₂ NPs immobilized corn silk

The removal of DB15 was performed 10 cycles to assess the potential reusability of TiO₂-IML-CS NPs at an initial concentration of 50 mg/L. Before each cycle, TiO₂-IML-CS NPs pieces were washed three times with distilled water. All tests were done in triplicates and the data referred in this paper is the mean value [21].

RESULTS AND DISCUSSION

Characterization of support material

The surface morphology of TiO₂ nanoparticles and TiO₂ nanoparticles immobilized corn silk after removal of DB15 azo dye samples are given in [Fig. 1]. Although a quantity of TiO₂ nanoparticles agglomerates in [Fig. 1A], it appears to be immobilized TiO₂ NPs on the corn silk fibrous structure very well in [Fig. 1B]. Corn silk fiber structure in the photocatalytic effect of TiO₂ NPs can be understood from [Fig. 1B] can show very easily. Thus, the TiO₂ NPs can be easily removed from the reaction medium as a way to be able to participate effectively in both the photocatalytic reaction.

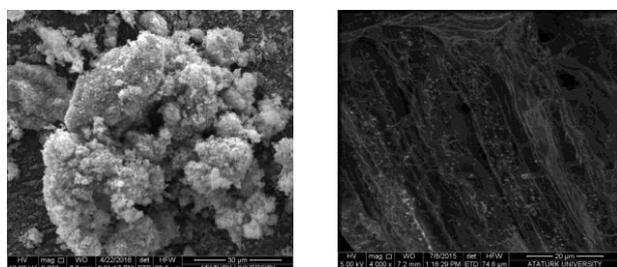


Fig. 1: SEM images of (A) TiO₂ nanoparticles and (B) TiO₂ nanoparticles immobilized corn silk after DB15 dye removal.

FTIR Spectra of the corn silk fibers [Fig. 2] showed the FTIR spectra of CS, TiO₂ NPs, TiO₂ NPs-IML-CS and TiO₂ NPs-IML-CS+DB15. In the FTIR spectrum of CS, the IR spectra had peaks at ca.1650-1700 cm⁻¹ which was attributed to the C=O stretching and 2600-3000 cm⁻¹ which correspond to the ester C=O stretching vibration and carboxylic acid O-H [22].

The peaks at 3400 and 1639.5 cm⁻¹ in the spectra are due to the stretching and bending vibration of the -OH group. In the spectrum of pure TiO₂, the peaks at 596.0 cm⁻¹ show stretching vibration of Ti-O and peaks at 1060.84 cm⁻¹ shows stretching vibrations of Ti-O-Ti [23].

The FTIR spectrum of TiO₂ NPs-IML-CS after treatment on DB15 shows the peak at 3410.13, 2920.20 and 2380.1. The band at 3410.13 shows -NH₂ group aliphatic and aromatic group, 2920.20 shows C-H, aliphatic group, 2380.1 shows C-N azo group and 1047.3 cm⁻¹ shows that OR aromatic group.

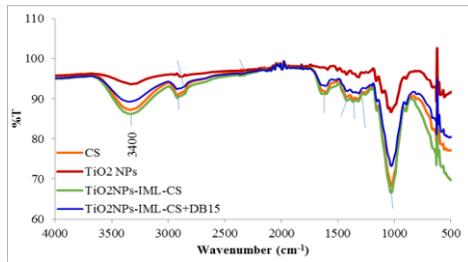


Fig. 2: FT-IR spectra of the CS; TiO₂ NPs; TiO₂ NPs-IML-CS and TiO₂ NPs-IML-CS+DB15.

When it was compared nature CS and immobilized TiO₂ NPs-IML-CS peak

According to CSPDS card with numbered 21-1272; the obtained peak at 2 theta = 25° (101) was belong to TiO₂ NPs (anatase). Also, at the 2Theta=32°, 48°, 55° and 62° peaks were approved that TiO₂ NPs were bound to CS fibers.

When the looking at the XRD diagrams of TiO₂ NPs; TiO₂ NPs-IML-CS and TiO₂ NPs-IML-CS+DB15:

It was observed that all immobilized TiO₂ NPs were reacted with DB15 azo dye during Photo reaction under UV light. Therefore, it was not seen all peaks related to TiO₂ in the TiO₂ NPs-IML-CS+DB15 and this event confirmed that the photo degradation was done [Fig.3].

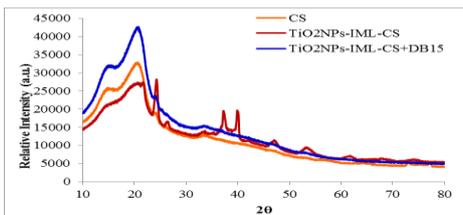


Fig. 3: XRD diagram of CS; TiO₂ NPs; TiO₂ NPs-IML-CS and TiO₂ NPs-IML-CS+DB15.

Effect of time

To confirm the photo degradation of DB 15 azo dye, the absorbance of the samples was analyzed at several time points during the reaction. As seen from [Fig. 4], the there was a 97.05% reduction in the presence of TiO₂-CS-IML when the immobilized TiO₂ onto CS fibers were allowed to degrade DB-15 dye (50 ppm) for 30 sec. When the only corn silk was used, it was achieved 2% and 5% removal of DB 15 azo dye for 30 sec 10 min, respectively. Too effectively removal of DB15 azo dye at 30 sec with TiO₂ NPs-IML-CS, it will be brought great benefits in terms of low cost, energy and time on an industrial scale [24].

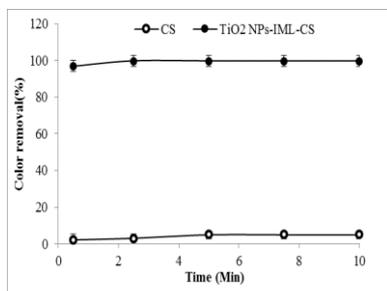


Fig. 4: The photocatalytic removal rate of DB15 at a concentration of 50 mg/L, 25°C and 300 rpm.

Effect of pH

pH is an important parameter for photo degradation reactions taking place on the surface of TiO₂ nanoparticles. pH variation can in fact influence the adsorption of dye molecules onto the TiO₂ surfaces [25]. The effect of solution pH was studied in the range of 3 to 10 for the DB 15 azo dyes under study using both CS and TiO₂-IML-CS. [Fig. 5] showed the variation on the efficiency photocatalytic degradation of DB15 at different pH values. Photo degradation was higher in acidic media (pH 3 to 5) using TiO₂-IML-CS

for 30 sec, with degradation rates of 99 and 95%, respectively. Degradation rate of DB 15 azo dye as UV catalytically using TiO₂-IML-CS for 30 sec (s) was obtained at 90.0%. Up to a pH value of 7, the dye degradation efficiency decreased to 81.12% using TiO₂-IML-CS. Above pH 7, the degradation continued to decrease to about 80.78% at pH 10 [25].

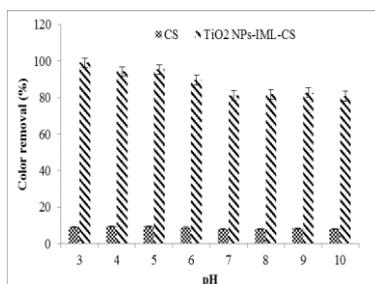


Fig. 5: The effect of pH on the photocatalytic removal rate of DB 15 azo dye (pH:3.0, 25°C, 300 rpm).

TiO₂ NPs-IML-CS surface is positively charged in acidic reaction medium (pH<7.0), whereas under alkaline conditions (pH>7.0) it is negatively charged [26]. Seeing the structure of DB 15 azodye [Fig. 6], a positive charge excess in the TiO₂ surface supports a strong interaction with four SO₃-groups of the dye [Fig. 6A]. A negative charge excess promotes there pulsing of the DB 15 azodye by the TiO₂ NPs-IML-CS surface, reducing the catalytic activity of this photo catalyst [Fig. 6B]. These results suggest that the influence of the initial pH of the solution on photo catalysis reaction kinetics is due to the amount of the dye adsorbed on TiO₂ NPs-IML-CS [25,27]. This hypothesis supports with a reaction occurring at TiO₂ NPs-IML-CS surface and not in the solution, close to the surface.

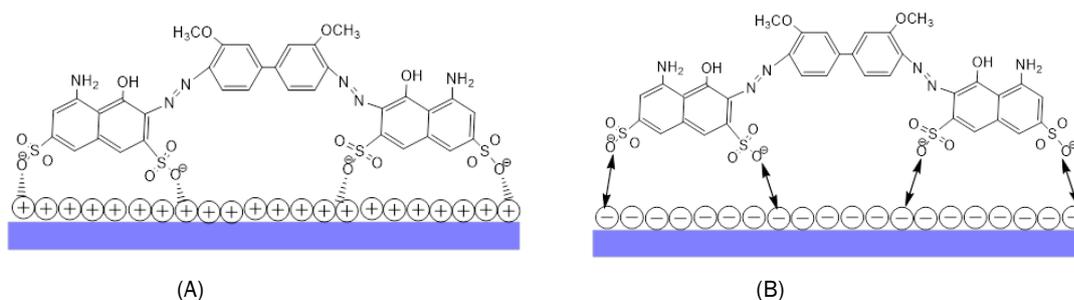


Fig. 6: Schematic reaction mechanism of DB 15 and TiO₂NPs IML CS (A) acid sites and (B) basic sites.

The effect of stirring speed

The effect of stirring speed on the photo degradation reaction of DB15 azo dye was investigated using stirring speed from 100 to 300 rpm using dye concentration of 50 mg/L, contact time 30 s, and temperature was 25°C. It was shown from [Fig. 7] that with increasing of the stirring speed photo degradation of DB 15 was increased from aqueous solution. This increase in degradation of DB15 azo dye reached a maximum at 300 rpm as 99.76% removal rate using TiO₂-IML-CS. The increase in photo degradation of DB15 may be increase the contact between the surface of TiO₂-IML-CS and DB 15 with increasing the stirring speed [28].

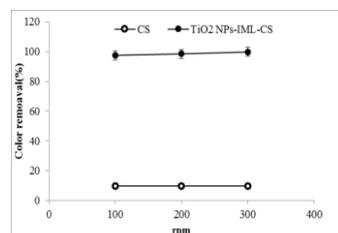


Fig. 7: The effect of stirring speed on the photocatalytic removal rate of DB 15 azo dye (pH:3.0, 25°C, 30s).

Effect of dye concentration

The effect of the initial concentration of DB 15 on the photo degradation of the dye under UV photon was determined. The obtained results are presented in [Fig. 8]. When initial dye concentration effect on the removal efficiency is also investigated, it is seen that at Fig. 8 low initial dye concentration values are effective for DB 15 dye removal. When the initial dye concentration decreases 200 to 50 mg/L the removal efficiency of DB 15 increases from 71.13% to 99.76%. The results indicate that the photo degradation in rate of DB 15 dye strongly depends on the initial dye concentration. The efficiency of photo degradation of DB 15 dye decreased with increase of the initial dye concentration [29].

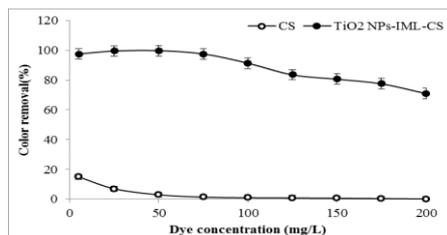


Fig. 8: The effect of dye concentration on the photocatalytic removal rate of DB 15 azo dye (pH:3.0, 25 °C, 300 rpm, 30 s).

The effect of photo catalyst amount

The effect of TiO₂ NPs-IML-CS amount was also investigated. The obtained results are presented in [Fig. 9]. The results were indicated that the TiO₂ NPs-IML-CS amount increased 0.05 to 0.75 g/ 50 mL, removal efficiency of DB 15 increases from 89.25 to 99.76%. Using CS and TiO₂ NPs-IML-CS, DB 15 with 0.4 g/50 mL of photo catalysts showed rates of degradation of 99.76 and 7%, respectively. It was observed that the efficiency of photo degradation of DB 15 azo dye decreased with increasing of the initial photo catalyst amount [30]. Therefore, photo catalyst prevented UV rays to reach the surface of the DB 15. Therefore, photo catalyst prevented the UV rays reaching the surface of DB 15 azo dye.

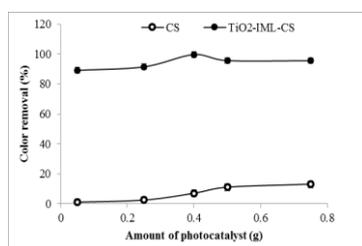


Fig. 9: The effect of photo catalyst amount on the photocatalytic removal rate of DB 15 azo dye (pH:3.0, 25 °C, 300 rpm, 30 s).

Reusability

The reusability of TiO₂ NPs-IML-CS was investigated in order to establish the stability [Fig. 10] while studying reuse of photo catalyst; all parameters including irradiation time (30 s), pH: 3.0, DB 15 concentration (50 mg/L), and amount of and photo catalyst (0.4 g) were kept constant. The photo catalyst was separated from the solution mixture through filtration. The recovered photo catalyst was washed with distilled water and reused ten times as in the previous degradation process. According to the obtained results, after using of 6 cycles, it was identified 73.32% removal of DB-15 azo dye. Results showed no significant reduction in photocatalytic performance in photodegrading DB 15 at the first six times, thus this indicated the stability of TiO₂ NPs-IML-CS as a photo catalyst [12].

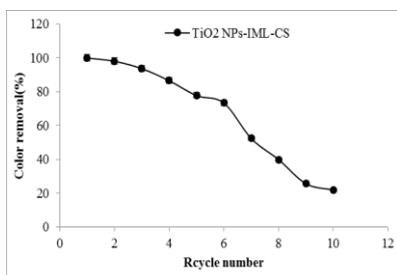
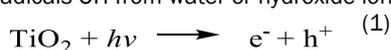
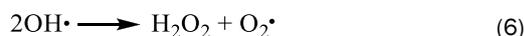
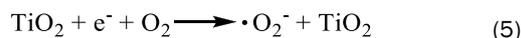
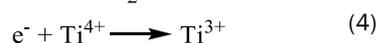


Fig. 10: The effect of reusability capability of TiO₂ NPs-IML-CS on the photocatalytic removal rate of DB 15 azo dye (pH:3.0, 25 °C, 300 rpm, 30 s).

Reaction mechanism of photo catalytic DB15 dye degradation

Hetero generous photo catalysis for the treatment of azodyes appears as an interesting technique. Indeed, titanium dioxide (TiO₂) activation under UV irradiation ($\lambda < 390$ nm) allows the generation of highly reactive free radicals OH from water or hydroxide ions as follow:





These free radicals can then react with the DB15 azo dye adsorbed on the surface of TiO_2 until DB 15 total mineralization. The photocatalytic mechanisms of TiO_2 are assumed as follow [Fig. 11A] (Birhanli and Yesilada 2006). The ambient temperature and the possible use of solar UV are the advantages of photo catalysis; moreover, TiO_2 is not toxic. The reaction mechanisms of TiO_2 photocatalytic oxidation of azodyes was similar to the bio degradation process of oxidation of azodyes with $\cdot OH$ radical. One of the reaction mechanisms of oxidation of azodyes that react with $\cdot OH$ radical was proposed as follows [Fig. 11B] [31].

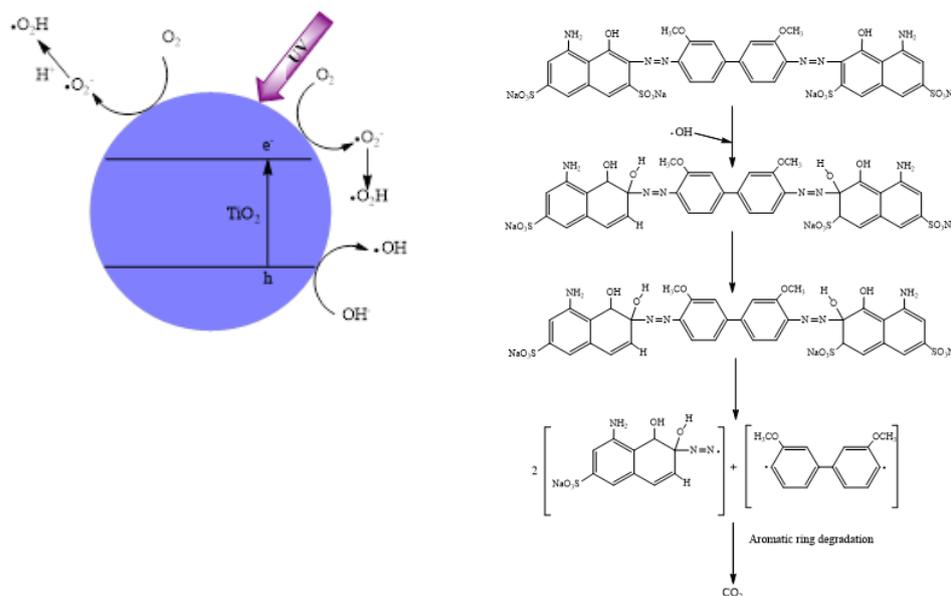


Fig. 11: Photo catalytic oxidation reaction mechanism of TiO_2 for DB 15 azodyes removal.

CONCLUSION

The photo catalytic degradation of Direct blue 15 (DB 15) azo dye mediated by TiO_2 NPs-IML-CS was successfully achieved. Before and after treatment with dye, the XRD of CS and TiO_2 NPs-IML-CS showed that modified CS with TiO_2 NPs reacted with DB 15 azo dye very high level. The results of UV-vis and FTIR spectras showed that de colorization of DB 15 was confirmed the cleavage of azo bonds of molecule. Three main steps were proposed for the de colorization mechanism using TiO_2 NPs-IML-CS (a) the cleavage of the azo bonds by reduction of DB15 dye /oxidation of TiO (b) adsorption of anionic dye on the TiO_2 NPs-IML-CS (c) When the used TiO_2 NPs-IML-CS, TiO_2 NPs could be joined the photocatalytic reaction and then easily removed from the reaction medium. In designing the dye removal experiments with low and high level of independent variables such as CS amount, initial dye concentration, temperature and pH, the amount of DB 15 azo dye removal (%) was obtained as response. According to obtained results, the best reaction medium for DB 15 removal (%) was determined as 0.4 g/50 mL TiO_2 NPs-IML-CS amount, 50.0mg/L initial dye concentration, pH 3.0 and 25.0 °C temperature. There cycling of TiO_2 NPs-IML-CS can be performed and it was observed that with the photo catalyst being able to be adequately used five times. According to best solution, the maximum DB 15 removal percent is 99.76%.

CONFLICT OF INTEREST

There is no conflict of interest.

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FINANCIAL DISCLOSURE

None

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