Investıgatıon of Removal of Dye from Aqueous Solutıon by Advanced Treatment

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Abstract

The textile dyeing and finishing industry use a significant amount of water and produce water pollution. Conventional biological treatment processes have some difficulties for degradation of nonbiodegradable compounds. Dye-bearing wastewaters have high COD and colour. In this study, a photo reactor process was used to remove color from aqueous solution.Effects of pH on Reactive Red 4 and cationic dye removal using 1g/L TiO_2, as catalyst were studied at constant inital dye concentration (25 mg/l). Cationic dye removal efficiency is better than Reactive dye removal efficiency for photocatalytic oxidation in this study.

Keywords: Dye, color, photo reactor,wastewater,advanced treatment

Introduction

The textile industry wastewater contains high concentrations of organic and inorganic chemicals and is characterized by strong color and high total organic carbon (TOC) and chemical oxygen demand (COD) values. Treatment of such wastewater by conventional treatment systems is hard and advanced technologies are required. Treatment of textile dye industry wastewater is highly complex due to the presence of color, toxicity, BOD, COD, turbidity, TDS, TSS, etc. Physical and/or chemical processes (coagulation/ flocculation, adsorption, membrane processes and so on)
are employed for the treatment of dye-bearing wastewater. But these processes have some drawbacks. Alternatively, advanced oxidation processes have received great attention in recent years for its efficiency and inexpensive.

Textile wastewaters have complex mixtures such as COD, color, salt, toxicity and other chemical compounds. One solution to the disposal problem is on-site advanced oxidation process of such wastewaters, using different systems such as fenton, photo fenton, UV, TiO_2 catalyse with UV (photocatalytic) so on. Advanced oxidation processes (AOPs) have been

used as emerging wastewater treatment technologies for various hazardous organic compounds (Reddy et al., 2016).The photocatalytic decolorization of municipal wastewater contaminated with textile dyes is one of the advanced oxidation process (Souzaa et al., 2016). The TiO_2/UV process has been known to have many important advantages, in particular: a large number of organic compounds dissolved or dispersed in water can be completely mineralized; the reaction is relatively high if large surface areas of the photocatalyst are available; TiO_2 is inexpensive and can be recycled on a technical scale (Farouk et al., 2016).

The aim of the study is to remove color and COD from textile wastewater using lab scale photo reactor with addition of catalyst (TiO_2) as advanced treatment.

Materials and methods

Experimental method

Photocatalytic experiments were carried out with working volume of 400 ml aqueous solutions. The catalyst was added to the dye solution. Then, UV lamps were run and a sample was taken with interval 30 minutes during 180 minutes working time. Catalysts were separated from the sample using a 0,45 micron filters. The sample was analyzed for color, COD and turbidity. COD analyzes were carried out by closed reflux titrimetric method according to APHA standard methods (APHA, 1995). The solution's pH was adjusted initially by adding 0.01N NaOH or 0.01N H_2SO_4. The color values of the samples were measured by spectrophotometer. According to the measured values, the color removal efficiency is calculated with Equation 1.

$$\text{Efficiency} = \frac{C_0 - C}{C_0} \quad (1)$$

C_0 is the initial dyestuff concentration, C is the dyestuff concentration of the sample.

The kinetics of photocatalytic reactions are compatible with 1st degree reactions. The 1 st degree velocity constant was determined using the Equation 2.

$$\ln C = \ln C_0 - k * t \quad (2)$$

k:velocity constant and t:time

Materials: Dyes and catalyst

Methylene Blue (MM) and Reactive Red 4 (RR4) dyestuffs were used in the study. The chemical structures of the dyes are given in Fig.1 and Fig. 2.

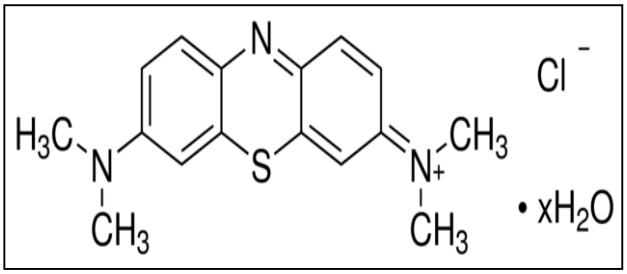

Fig. 2: Chemical structure of Methylene Blue dye (Sairoglu and Atay, 2006)

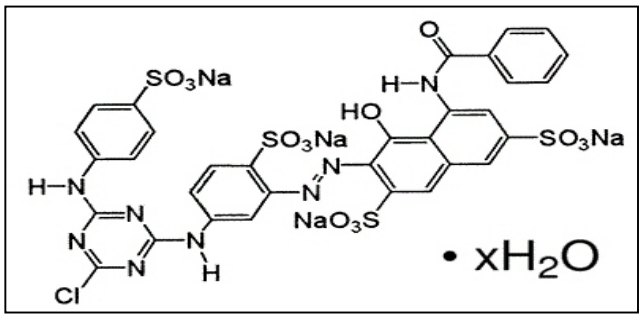

Fig. 2:Chemical structure of Reactive Red 4 dye (Url.1, 2017)

Methylene blue is a cationic dyestuff, the chemical formula is "$C_{16}H_{18}N_3SCl$", the molecular weight is 373,9 $gmol^{-1}$. It is used for coloring in textile industry and also for preventing fungus reproduction in fish breeding farms. The spectrum of the wavelength scanning in the spectrophotometer is given in Fig. 3. The λ_{max} value according to this scan is 663 nm.

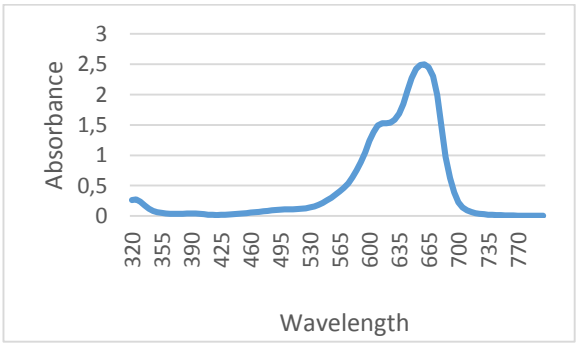

Fig.3: Wavelength scanning of Methylene Blue.

Reactive Red 4 is an anionic group of dyes. The chemical formula is "$C_{32}H_{19}ClN_8Na_4O_{14}S_4$", the molecular weight is 1000,25 $gmol^{-1}$. It is a dye used in textile industry. The spectrum of the wavelength scanning in the spectrophotometer is given in Fig. 4. The λ_{max} value is 500 nm.

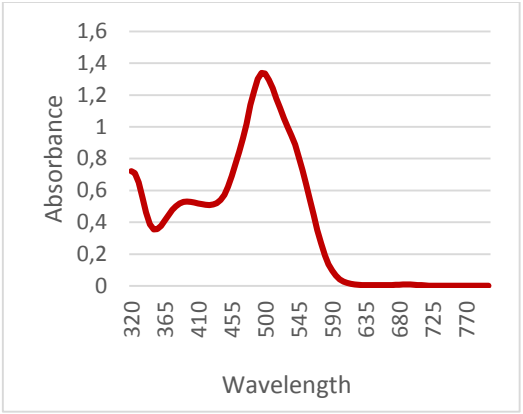

Fig. 4: Wavelength scanning of Reaktif Red 4.

The anatase TiO_2 was used as catalyst. Table 1 gives features of TiO_2.

Table 1 ***Features of TiO_2***

Average Primary Particle Size	163,723 nm
Specific Surface Area (BET)	16,00 m^2/g
Pore Volume	0,1847 cc/g
Molecular Weight	79,87 g/mol

Photocatalytic Reactor

. Batch reactor type was used in experimental studies (Fig. 5). The reactor was cylindrical and covered with black material to inhibite light. Six UV-C lamps were placed on the reactor. 8 W fluorescent type UV-C lamps with a wavelength of 254 nm were used. The lamps were placed at equally spaced reactors. A quartz tube was used in the reactor. A magnetic stirrer was used to disperse the powder catalyst in the solution homogeneously.

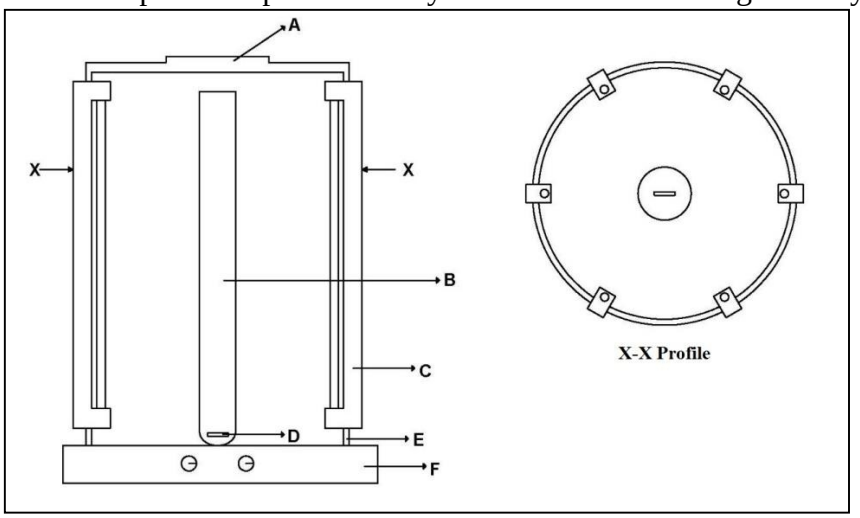

Fig. 5 Schematic representation of the photocatalytic reactor. A: Cap, B: Quartz tube, C: UV-C lamp and socket, D: Magnetic fish, E: Cylinder reactor, F: Magnetic mixer.

Results and discussion

Removal of MM

Surface charge of catalyst is essential because of occurence of OH radicals on surface (Souzaa et al., 2016).

Optimum pH was determined for studied pHs (2,5, 5,5, 7 and 9) within the 180 min. In this study 1g/L of catalyst, 3 UV-C lamb, 25mg/L of MM dye was kept constant. Fig 6 and Fig 7 show effect of pH on color removal efficiency and first order reaction rate line, respectively. As shown from the Fig.6, maximum removal efficiency was found to be 99,88% for pH 2,5. Kinetic study confirms optimum pH value. If the pH under the isoelectric point of TiO_2 (6,8), surface of catalyst is charged positive (eq.3) and positive charged surface is covered with OH^- ions . So production of OH radical increase. If the pH above the isoelectric point of TiO_2 (6,8),OH radical density decrease and so OH production decrease. (eq. 4).

$TiOH + H^+ \rightarrow TiOH^{+2}$ $(pH < pH_{iep})$ [3]

$TiOH + OH^- \rightarrow TiO^- + H_2O$ $(pH > pH_{iep})$ [4]

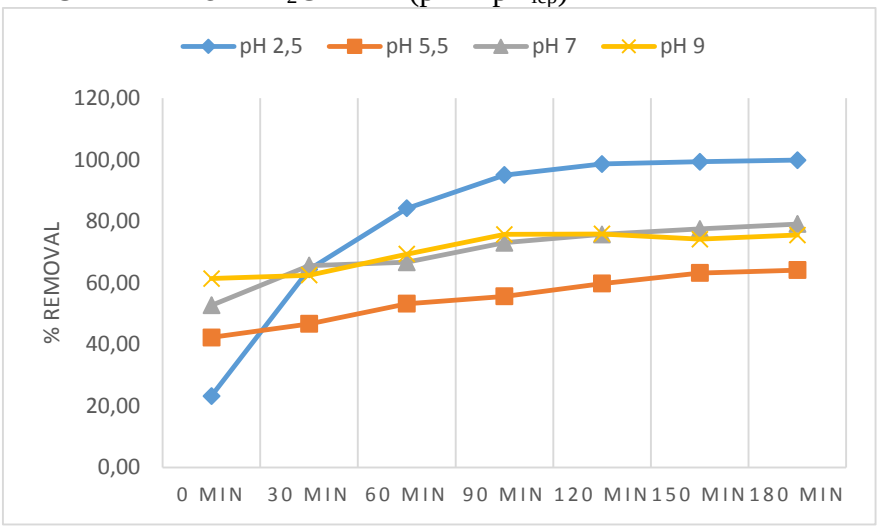

Fig 6. Effects of pH on to color removal

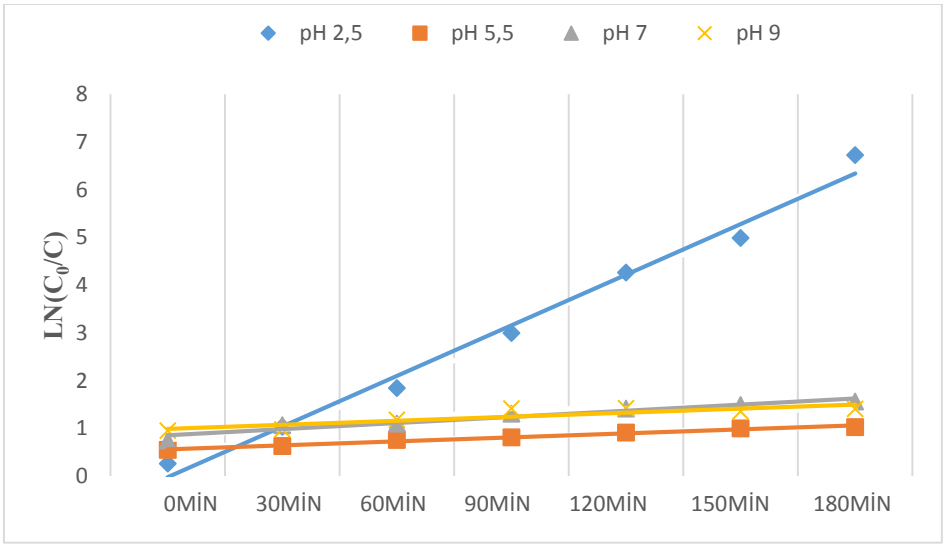

Fig 7 First order reaction rate for different pHs

Removal of Reactive Dye

Reactive Red 4 (RR4) removal study was performed at 25mg/L of RR4, 1g/L of TiO_2, 3 UV-C lamb for pH 2,5 and pH 9s. Fig 8 illustrates color removal efficiencies for studied pHs.

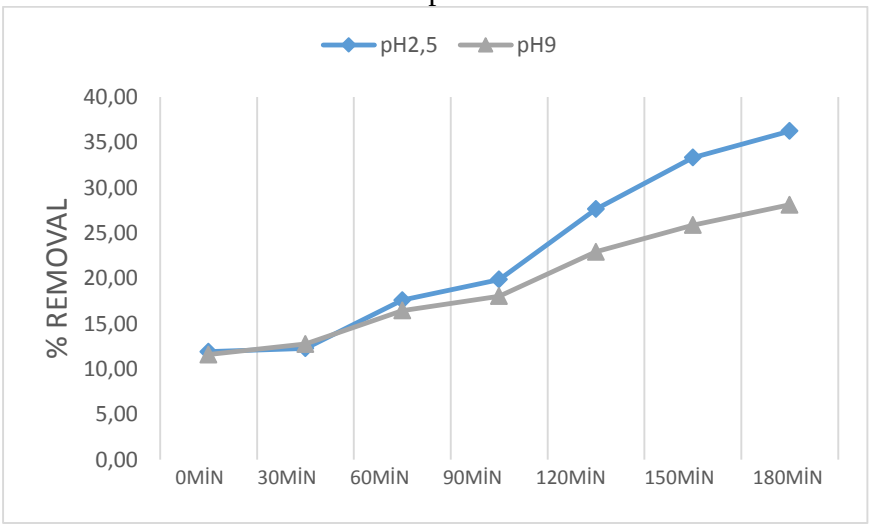

Fig.8 Color removal **(**25mg/L RR4)

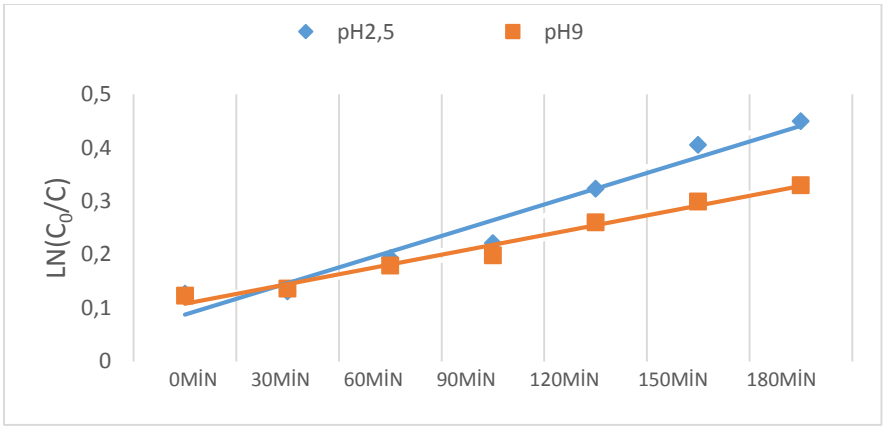

Fig. 9 First order reaction rate for RR4

RR4 dye removal efficiency was found to be 36,24 % for pH 2,5 and 28,14% for pH 9. This value is lower than cationic dye.removal efficiency. . Cationic dye removal efficiency was better than anionic dye removal efficiency. Turbidity of RR4 solution was observed as high. Increasing turbidity affected the removal efficiency of RR4.

Conclusion

In this study, a photo reactor process was used to remove color from aqueous solution. Effects of pH on Reactive red 4 and cationic dye removal usıng 1g/L TiO_2, as catalyst were studied at constant inital dye concentration (25 mg/l). Cationic dye removal efficiency is better than reactive dye removal efficiency for photocatalytic oxidation in this study.

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