Original Research Article

Optimization of Photocatalytic Degradation of Reactive Blue Dye Using Zinc Oxide Catalyst

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ABSTRACT

In this study, parameters for photocatalytic oxidation of reactive blue dye with zinc oxide as photo catalyst was optimized. Dye solution (10 mg/l) was used to contact with the zinc oxide catalyst under UV light at various reaction conditions viz; contact time; pH; and catalyst dose. The degradation of the dye was followed by measurement of absorbance of the solution using a UV Spectrophotometer adjusted at a maximum wavelength (λ_{max}) of 629 nm with distilled water as the blank. The optimum conditions established for degradation were; catalyst dose of 5.0 g/l, a neutral pH of solution at 7.0, and contact time of 180 minutes (3.0 hours).

Keywords: photocatalytic, oxidation, photocatalyst, degradation, reactive blue dye.

1. INTRODUCTION

Dyes are substances that are used in textiles, paper pulp, plastics, leather, cosmetics and food industries. Reactive dyes are considered one of the best innovations of the 20th century. [1] They are used for dyeing cellulosic fibers such as cotton, rayon, silk, wool, nylon and leather. The dyes are generally water soluble. [2] They mainly include; azo, anthraquinone, triphenodioxazine or copper phtalocyanine chromophores. Reactive azo dyes have one or more azo groups (R1–N=N–R2) and aromatic rings mostly substituted by sulfonate groups. It is this complex structure that is responsible for their intensive color, high water solubility; resist fading on exposure to sweat, soap, water and light. [3]

The most significant property of reactive dyes is their formation of a covalent bond with hydroxyl or amino groups present on the fiber. [4] Their fixation to fiber is hindered by the competitive reactions consisting on the dye hydrolysis. The unfixed dye due to hydrolysis during fixation is responsible for the intense color of rivers. [1] Effluents from dye-houses consist of high levels of pollutants largely as a result of the unfixed dye and their discharges from textile mills poses certain hazards and environmental problems since the dyes are carcinogenic and are stable compounds that are difficult to biodegrade. [5] If these effluents are improperly treated, they pose a serious threat to all aquatic species because the hydrolysis of the

pollutants in waste water can produce a great deal of toxic products. [6]

Dye degradation is the breakdown of the organic compounds in the dye stuff into harmless substances. The complete degradation of these non-biodegradable organic compounds is rear by conventional biological treatment processes, so there has been a lot of interest in the application of advanced oxidation processes (AOP's) for the removal of such organic compounds. Many processes such as photolysis, photocatalytic oxidation, ozonation, fenton oxidation, wet air oxidation and membrane separation have been proposed for the degradation of these compounds even at low concentrations. [7] Other conventional methods include flocculation, coagulation, precipitation, adsorption, aerobic biological treatment among others. [8] But these methods do not completely degrade the dye contaminant. [9]

The oxidative degradation dye in waste water can be achieved through photocatalysis. Photocatalysis is the reaction which uses light to activate a substance which modifies the rate of a chemical reaction. It is a new, fast, convenient and less expensive method for the degradation of dye under the advanced oxidation processes. [10] With photocatalysis, TiO_2 and ZnO are the important photocatalysts because of their effectiveness due to high band gap, safety, inexpensiveness, stability to photo-corrosion, and maximum removal of the dyes. [11] Zinc Oxide has a band gap of 3.17 eV while TiO_2 has 3.2 eV and ZnO also adsorbs more UV light than any other photocatalyst. When the UV is absorbed by these photocatalysts, there is generation of electrons (e-) and holes (h+) which are considered as the main species involved in photo-degradation process.

This study aimed at establishing the optimum process parameters for maximum photo-degradation of reactive blue dye in dye-house effluents using ZnO photocatalyst.

2. MATERIALS AND METHODS

From earlier studies, the approximate concentration of reactive dye in waste waters from dye houses was established at 10 mg/l. This is the concentration which was used in making dye solutions for all the experiments.

2.1 Materials

A reactive blue dye (19, C.I.61200) was purchased from a local shop in Kikubo, Kampala, Uganda for the study. ZnO photocatalyst was obtained from Chemistry Laboratory of Makerere University along with the other auxiliary chemicals such as the acid, distilled water, sodium hydroxide among others. Analytical balance was used for taking sample weights. UV-Visible spectrophotometer of UV-1700 series was used for absorbance measurements.

2.2 Preparation of solutions

The reactive blue dye powder (10.0 g) was accurately weight out and put in a volumetric flask (1000 cm^3) and dissolved in distilled water and made to the mark to form a dye solution. The dye solution (1.0 cm^3) was transferred to another volumetric flask (1000 cm^3) and made to the mark with distilled water to form a dye solution of (10 mg/l). Dilute solutions of hydrochloric acid (0.1 M, 200 cm^3) and sodium hydroxide (0.05 M, 200 cm^3) were prepared from conc. HCl and NaOH pellets respectively.

2.3 Degradation of dye at various pH values

The ZnO photocatalyst samples (0.5 g) were separately added to seven samples of dye solution (100 cm^3). By drop wise additions of HCl (0.1 M) and NaOH (0.05 M) solutions, the pH values of each sample of catalyst dye mixtures were separately adjusted to 4, 5, 6, 7, 8, 9 and 10. Each set was exposed to UV light for 120 minutes (arbitral time) with continuous stirring. The

absorbance of each sample was determined after the 120 minutes of contact.

2.4 Optimization of catalyst dose

Six samples of the dye solution (200 cm^3) were transferred to different conical flasks. To the solutions, samples of ZnO powder (0.4, 0.6, 0.8, 1.0, 1.2, 1.4 g) were separately added. The mixtures were contacted with continuous stirring for 120 minutes (arbitral time) at a neutral pH 7 (determined in experiment 2.3). The absorbance of each sample was determined after the contact time of 120 minutes.

2.5 Optimization of contact time

A portion of dye solution (200 cm^3) was transferred to a conical flask (450 cm^3). To the sample, ZnO powder catalyst (1.0 g, determined in experiment 2.4) was added. The mixture was contacted with continuous stirring for 180 minutes at a neutral pH 7 (all determined in experiments 2.2 and 2.3). The absorbance of the mixture was determined at intervals of 30 minutes from 30 to 240 minutes.

3. RESULTS AND DISCUSSIONS

3.1 The pH for optimum degradation

At pH values below 4.0, no significant change in absorbance was recorded. The ZnO powder was fully dissolved into solution. At high acid concentrations i.e. lower pH values, the photo-catalyst reacts to form a solution of Zinc chloride salt. This follows the chemical equation of reaction (1) below.

$$ZnO_{(S)} + \rightarrow ZnCl_{2\,(aq)} + H_2O_{(aq)} \dots \dots \dots (1)$$
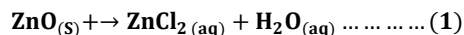
This reaction creates a loss of the solid phase hence preventing the photocatalytic reaction. Photocatalysis takes place on the solid liquid interphase which is absent or minimum at lower pH values due to salvation of ZnO. At higher pH values, the above reaction is partial and the solid-liquid phase exists giving some degree of degradation reflected by a reduced absorbance with the increase in pH. A maximum degradation was noted at a pH of 7 (neutral). At higher pH, the degree of degradation reduced as can be noted by a steady increase in absorbance as graphically illustrated in **Fig. 1.**
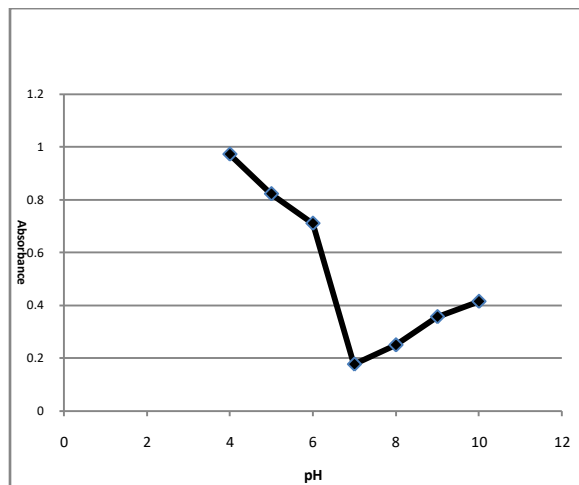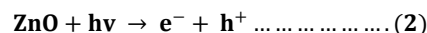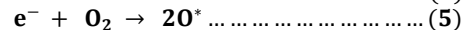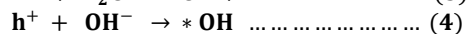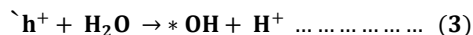

Figure1. A graph of Absorbance versus pH

During the photocatalysis, UV light excites the photocatalyst generating electron-hole pairs as shown in equation (2) below.

$$ZnO + hv \rightarrow e^- + h^+ \dots \dots \dots \dots \dots \dots (2)$$

The electron hole pairs generate the hydroxyl radicals which oxidize the dye compounds. The hydroxyl radicals are generated by chemical reactions represented by equations (3), (4) and (5); [10]

$$`h^+ + H_2O \rightarrow *OH + H^+ \dots \dots \dots \dots \dots \dots (3)$$
$$h^+ + OH^- \rightarrow *OH \dots \dots \dots \dots \dots \dots \dots (4)$$
$$e^- + O_2 \rightarrow 2O^* \dots \dots \dots \dots \dots \dots \dots \dots \dots (5)$$

In an alkaline condition at high pH, there is high concentration of hydroxyl ions. The hydroxyl ions reduce the photocatalyst to Zinc hydroxide and oxygen as in chemical equation (6) below;

$$2ZnO_{(S)} + 4OH^-_{(aq)} \rightarrow 2Zn(OH)_{2(aq)} + O_{2(g)} \dots \dots \dots \dots \dots \dots (6)$$
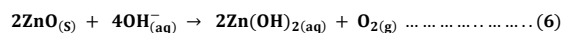
The absence of the solid phase of ZnO limits the photocatalysis whose mechanism is mentioned above and this is reflected in the decrease in dye degradation as shown by increase in absorbance of solutions with increasing pH values above 7.

3.2 Optimization of catalyst dose

Various catalyst dosages were used in quantities of 2 g/l to 7 g/l with a unit increase. As can be noticed in Fig. 2 below, absorbance decreased gradually from samples with catalyst dose of (2.0 g/l) to (5.0 g/). From catalyst dose of (5.0 g/l) to dose of (7.0 g/l) there was no observable change in absorbance of the samples. This therefore means that beyond the catalyst dosage of 5 g/l there was no further increase in degradation with additional quantity of catalyst. If we keep all the other factors constant, a catalyst dose of 5 g/l would be an optimum dose rate for maximum degradation as additional catalyst would increase cost without additional benefit. The increased catalyst dose without further increase in degradation could be a limitation due to kinetic factors like temperature and the surface area of catalyst exposed to UV light. If the catalyst surface exposed for excitation to UV light is limited then the quantity of electron hole pairs generated will be limited hence the degradation rate.
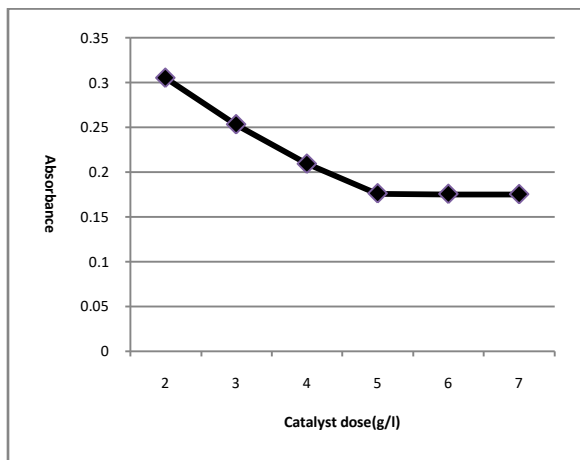

Figure 2. A graph of absorbance versus catalyst dose

3.3 Contact time for optimum degradation

The contact time was studied at a pH 7 with a catalyst dose of 5 g/l and exposed to UV light for a period of 240 minutes. The absorbance was determined from 30 minutes with incremental intervals of 30 minutes up to the 240 minutes. As can be noted in Fig. 3, the equilibrium time was found to be 180 minutes since after that time, the absorbance of the mixture remained nearly constant. The dye degradation increased with time until the equilibrium time was reached and no further degradation was observed.

As this is a study preferred for effluent treatment, and effluent leaves textile mills for treatment near room temperature, the study did not look at the effect of temperature variations. These parameters were optimized at ordinary room temperature.
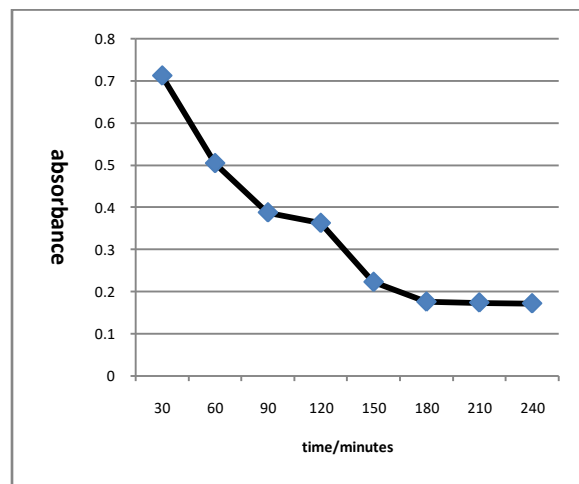

Figure 3. The variation of absorbance with times

4. CONCLUSION

Using photocatalytic degradation under UV light, a convincing discoloration of reactive blue dye in a favorable time frame was achieved. The following degradation parameters were optimized *viz*: a neutral pH of 7; catalyst dose of 5.0 g/l; contact time of 180 minutes (3 hours). Therefore, in the treatment of waste water

containing reactive blue dye, the waste treatment vessel (photocatalytic reactor) should be designed such that the retention/contact time is 180 minutes and with close adherence to the optimized parameters of catalyst dose and pH. The ZnO photocatalyst can be singly used for an effective degradation of effluents containing reactive blue dye.

5. ACKNOWLEDGEMENT

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