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Optimization Of Process Parameters On Removal Of Azo Dye (Congo Red) By Various Fenton & Photo Fenton Process.

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ABSTRACT

Today there is a great focus on reusing the effluent water in the dyeing process. Hence there is an urgent need to develop an economical treatment system for the treatment of wastewater, which can meet the strict quality standards. Untreated disposal of textile effluent into the water bodies cause damage to aquatic life and also to human beings by mutagenic or carcinogenic effect. Thus, the removal of dyes from colored wastewaters, particularly from textile effluent is one of the major environmental concerns. Advanced oxidation processes represent a powerful treatment for pollutants present in textile wastewaters. The present investigation is focused on using Fenton and Photo Fenton process. The decolorization rate was influenced by factors such as initial hydrogen peroxide concentrations, initial iron concentrations, pH, current density and initial dye concentration. Efficiency of all the three systems was compared to select the best one for treating textile effluent. Parameters like dye concentration, temperature and ion concentration were optimized for the maximum decolorization.

Keywords: Dye, Fenton, decolorization, Advance oxidation process, Optimization.

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INTRODUCTION

Human Development Report cites over 1 billion people without access to clean water and 1.8 million children died each year by preventable water-borne diseases [1]. Textile industry which uses massive amounts of water in the production process, the excessive abstraction of ground water by the industry result in depletion of fresh water sources is further complicated by the appalling pace of untreated “colored water” polluting the soil, underground water and also surface waters which result groundwater available in these regions is no longer suited for irrigation [2]. Increasing public concern about environmental issues has led to closure of several small-scale industries. Due to usage of dyes and chemicals, effluents are dark in color, which increases the turbidity of water body. Almost 10% of the dye is lost during dyeing process of fabric and thus comes in environment through wastewater discharges [3]. Presence of the dyes in aqueous ecosystems reduces the photosynthetic rate by decreasing the ratio of light penetrating into deeper layers of waters and thus negatively affecting the water quality which in turn have toxic effects on the flora and fauna of the ecosystem. Water reclamation is a process by which waste water from industries was processed by physio-chemical, biological or a combination of these treatments so that the water can be reclaimed or returned to the environment safely.

Fenton’s reagent is very suitable for such wastewaters to remove dissolved dyes from effluents. This process involves chemical or photochemical or electrochemical techniques to bring about chemical decolorization of organic pollutants [4]. The ferrous ion initiates the decomposition of H_2O_2, resulting in the production of hydroxyl radicals. Hydroxyl radicals are capable of attacking organic substrates and causing chemical decomposition of these compounds [5]. The objective of this work is to find the feasibility of decolorization and mineralization of Congo red by Fenton and Photo Fenton process [6]. The influence of process parameters (source and intensity of light, pH and H_2O_2, Fe^{2+} and dye concentration) that affect the efficiency of decolourisation of the dye are studied.

MATERIALS AND METHODS

Chemical And Reagents

The Azo dye, Congo red and the chemicals NaOH, H_2O_2, $FeSO_4.7H_2O$ were of reagent grade. The chemicals and reagent used was of AR grade and of high purity. All the solutions were prepared by dissolving requisite quantity of dye in deionised water from a Aandavar Distilled water supplier, Chennai.

Decolourization Procedure

For Fenton process a desired concentration of dye from the stock solution, Fe^{2+}, H_2O_2 solution was freshly prepared from $FeSO_4.7H_2O$, H_2O_2. The main process variables affecting the rate of Fenton’s reaction are the molar concentrations of the oxidant and catalyst [7-9]. Increasing the H_2O_2 concentration is important to obtain high oxidation efficiencies, while elevating the Fe^{2+} concentration directly enhances the oxidation rate. The process was carried out at 1:5 molar ratio of Fe^{2+}: H_2O_2. The required amount of Fe^{2+} was added into the dye solution. Desired volume of H_2O_2 was added simultaneously into the dye solution and mixed by means of a magnetic stirrer. In Photo Fenton process the reaction time was recorded when the UV/ Visible lamp was turned on. Samples of dye solution were withdrawn at periodic intervals, centrifuged at 5000 rpm for 10 min and analyzed in a UV/Vis double-beam spectrophotometer [10]. The color of dye solution in the reaction mixture was obtained by the measure of the absorbance at maximum wavelength (530 nm) and the percentage decolorization was calculated from the initial and final absorbance values. The sludge obtained from all the the processes was analyzed by Energy-dispersive X-ray spectroscopy (EDAX) for elemental composition determination.

RESULTS AND DISCUSSION

Absorbance of the supernatant withdrawn at different time intervals was measured at the maximum wavelength for the dye ($\lambda_{max} = 530$ nm) in the visible region on a Schimadzu UV-Visible spectrophotometer (UV 1800). The percentage of decolourisation was calculated from the difference between initial and final values of absorbance.

$$\text{Percentage decolourisation} = \frac{A_i - A_f}{A_f} \times 100$$

Where A_i and A_f are the initial and final level of absorbance.

Effect of Concentration

In Fenton process significant decolorization was observed due to the use of a powerful oxidant hydrogen peroxide. Fig. 1 shows the changes of color removal efficiency in the synthetic effluent. The effectiveness of color removal was increased rapidly upto 60% within the first 30 minutes. After that, color removal efficiency gradually increased to 90% and then slowly saturated within 120 minutes. The 90% – 93% color removal was achieved for various concentration of dye. As the concentration increased from 500 to 1000mg/L the percentage decolourisation was increased further raise in concentration the colour removal efficiency was more or less same after 60min. So the optimum concentration was taken 1000 mg/L for further studies.

Effect of Source of light

Comparing processes results shows that the decolorization capacity of the UV radiation was better than visible light and solar radiation [11]. After adding H_2O_2 to processes it is clear that the decolorization capacity increases significantly for UV processes upto 88% within 30min, and completed the reaction in 45 min with the 91% of colour removal (Fig. 2). Result shows that artificial UV light has better colour removing capacity compared to solar and visible light.

Effect of Temperature

Temperature is the major factor influencing the catalytic oxidation rates in Fenton process. Fig. 3 shows the effect of temperature on the decolorization efficiency. It was observed that the decolorization increases with increase in temperature up to 60°C. Most probably the generation rate of hydroxyl ion is enhanced at a high temperature but when the temperature approaches 70°C, hydrogen peroxide undergoes self-accelerating decomposition. Thus reduces the concentration of hydroxyl ion results in less percentage decolourisation [12].

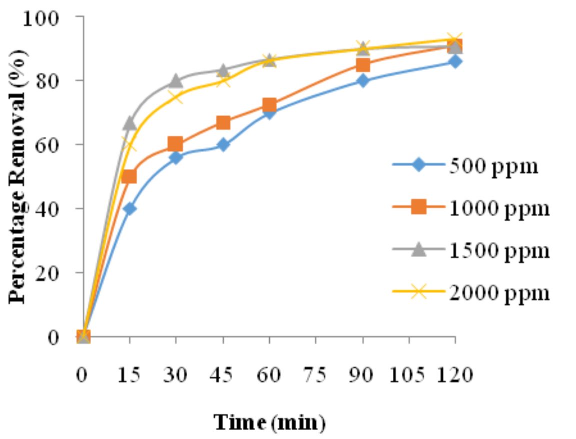


Fig 1: Effect of concentration on decolourisation

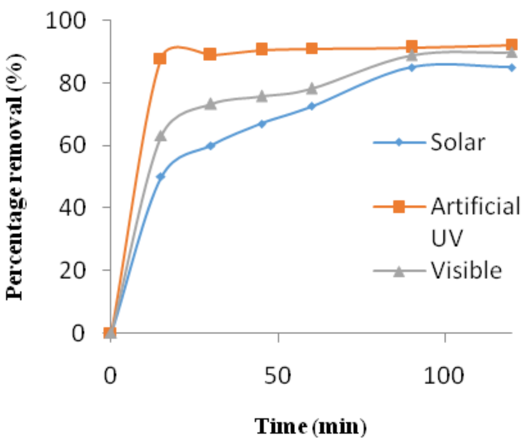
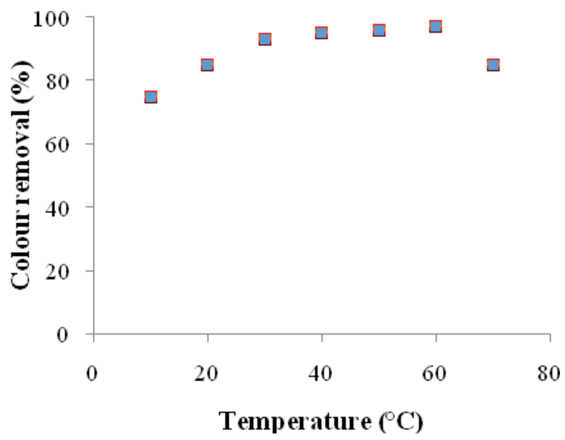


Fig2: Effect of source of light on decolourisation



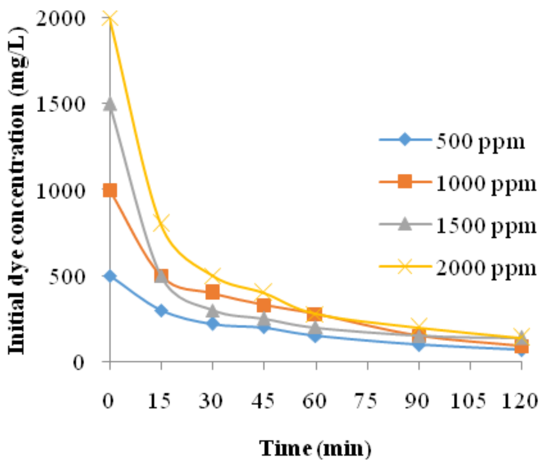


Fig 3: Effect of temperature on decolourisation **Fig 4: Effect of concentration**

Effect of pH

pH is the important factor for Fenton's oxidation [13]. Studies at different pH from 2 – 5 for degradation of dye, Fenton's oxidation optimum initial pH reported an optimum pH of between 2 to 3.

Kinetic Study

The rate of degradation of dye was calculated by testing the kinetic data with first-order model.

$$-r_A = \frac{-dC_A}{dt} = k\,C_A$$

Integrating the above rate equation between the limits 0 to t from C_{A0} to C_A, the above kinetic expression becomes

$$\int_{C_{A0}}^{C_A} \frac{(-dC_A)}{C_A} = k \int_0^t dt$$

$$\ln C_A = \ln C_{A0} - kt$$

where, C_A is the concentration of dye at time t and k (h^{-1}) is the first-order rate constant [14]. From the plot of ln C_A versus t, it was observed that this model fits the data well. The k value was found to be 0.01725 min^{-1} (Fig. 4, 5).

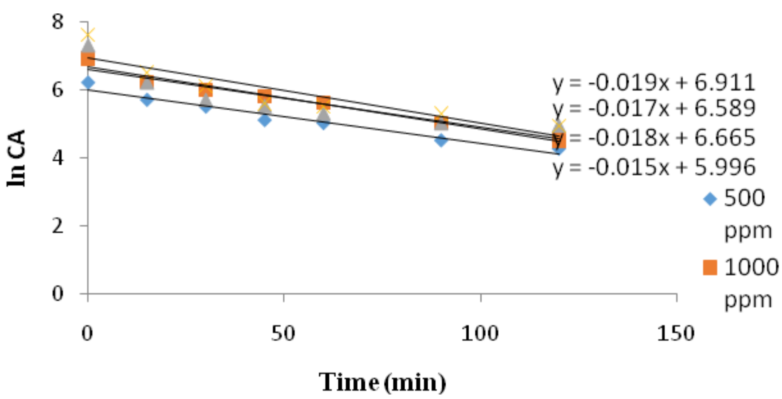


Fig 5: First order kinetics

Sludge Characterization

The sludge obtained from the Fenton and Photo Fenton process was analyzed by Energy-dispersive X-ray spectroscopy (EDAX) for elemental composition determination (Fig 6 - 8). It confirms that the chromophore of the dye is broken down and the decolorization is seen (**Table 1**).

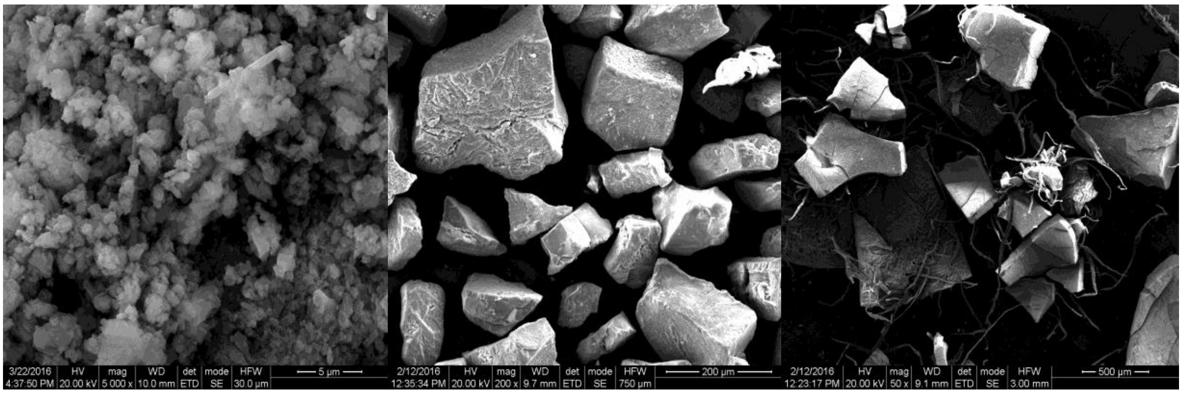


Fig 6: SEM Image for Congo red dye, sludge from Fenton and Photo--Fenton's process

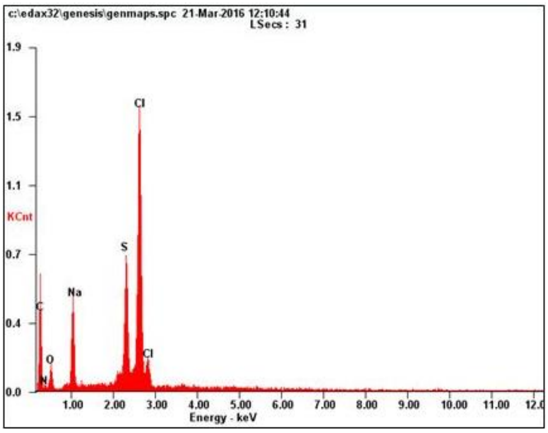


Fig 7: EDAX Report for Congo red Dye

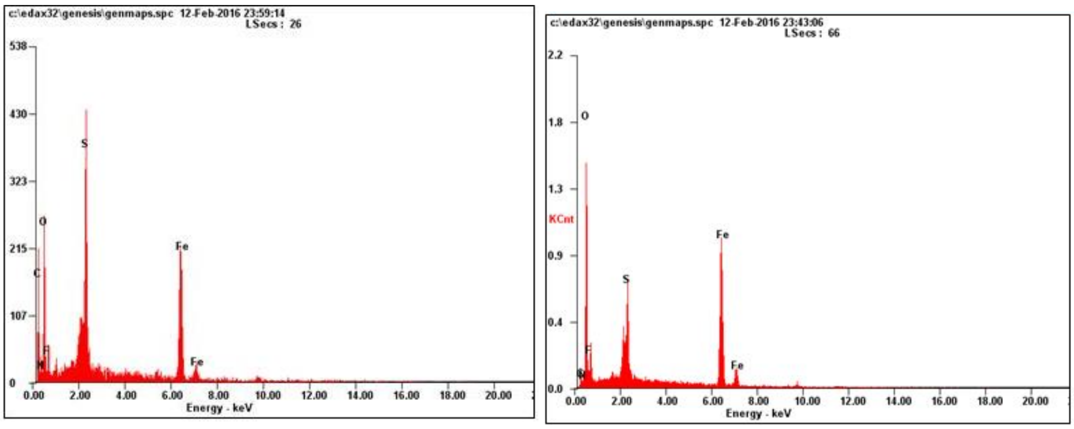


Fig 8: EDAX Report for Fenton's and Photo Fenton's process

Table 1: Comparison of Elements Composition.

Elements	Dye (wt%)	Sludge composition (wt%)	
		By Fenton	By Photo Fenton
Carbon (C)	63.08	35.58	08.66
Nitrogen (N)	06.76	07.10	02.54
Oxygen (O)	09.07	21.14	33.71
Sodium (Na)	07.10	-	-
Sulphur (S)	04.10	09.19	07.00
Chlorine (Cl)	09.98	-	-
Iron (Fe^{+2})	-	23.99	41.78
Fluorine (F)	-	02.81	06.31

CONCLUSION

To comply with the discharge permits, waste generations have to consider alternatives before disposal of their effluents. In this work the decolorization efficiency of Congo red was analyzed by AOP's such as Fenton and Photo Fenton processes. From the results it was concluded that Fenton along with artificial UV radiation gave highest decolourisation efficiency compared to visible and solar radiations. The optimum condition for both the process was found to be 60°C for 1000mg/L at the pH of 2 to 3 with the molar ratio of 1: 5 of Fe^{2+}:H_2O_2, the degradation reaction follows the first order kinetics with the rate constant of 0.01725 min^{-1} and the EDAX report confirmed the mineralization of the dye occur.

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