A study on decolourisation of Reactive Red-180 dye and dye effluent containing Reactive Red-180 using H_2O_2 solar assisted photodegradation process.

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Received: February 13, 2019 Accepted: March 25, 2019

ABSTRACT: *The degradation of Reactive Red-180 dye and dye effluent containing Reactive Red-180 dye was investigated using H_2O_2 solar assisted photodegradation process (H_2O_2/Solar Light). The photodegradation process was carried out in 250 ml conical flasks with side arms with a dye solution with concentration of 100 mg/l with 50% H_2O_2 irradiated with sun light in the lux intensity range of 60,000-90,000 lux.100% decolourisation was achieved in both RR-180 dye and 75% diluted effluent containing RR-180 whereas 96.18% decolourisation was achieved for undiluted effluent containing RR-180 under optimum reaction conditions. An optimum pH of 7 with H_2O_2 concentration of 700 mM is required for complete decolourisation of both RR-180 dye and effluent containing RR-180. Therefore H_2O_2/ Solar light is proved to be a more appropriate method for decolourisation of the azo dye Reactive Red-180.*

Key Words: *Reactive Red-180, H_2O_2/Solar Light, H_2O_2 solar assisted photodegradation process*

1. Introduction

Azo dyes are used as colouring agents in a wide range of industries like textile, leather, plastics, food, and pharmaceuticals. They are found to contain the azo group(-N=N-) attached to two organic substituents, mainly benzene or naphthalene derivatives[1]. Reactive Red-180 is an azo dye which is used for dyeing cellulose fibre fabric and in manufacturing of printing inks[2]. After finishing the dyeing process with them, the effluent containing azo dyes are directly discharged into water bodies.

Textile wastewater containing reactive azo dyes on discharging into rivers and streams is found to be one of the major water pollutant. They are also toxic to aquatic life as it affects the aquatic organisms.[3]. Therefore they are subjected to decolourisation and degradation. Oxidation processes, Biological processes and various physical/ chemical processes (coagulation, adsorption by activated carbon, flocculation) were used to decolourise textile wastewater containing various categories of dyes and they are found to be conventional methods[4].

Among the different category of dyes, reactive azo dyes and the industrial waste water containing them are found to be recalcitrant towards the conventional effluent treatment methods and they become a threat to environment as they are resistant towards degradation by the conventional methods. Conventional effluent treatment methods are not suitable for treatment of azo dyes and effluent containing azo dyes as the azo double bonds of reactive dyes are resistant towards biological treatment as the degradation of azo dyes is difficult [5]. Azo dyes are converted into toxic aromatic amines after their degradation by aerobic waste treatment and the removal rate of amines is very low which also causes environmental concern [6].Hence we are in need of some alternate methods for their colour removal.

Advanced Oxidation Processes (AOPs) has been found to be an alternate method for the treatment of azo dyes and effluent containing azo dyes. AOPs disintegrate the chromophore of the dye and completely decolourise the dye solution and effluent containing dye [4]. Many AOPs such as UV/H_2O_2, O_3, O_3/H_2O_2, H_2O_2/Solar Light, Fenton and Photo Fenton have been used to treat such dyes and textile wastewater containing those dyes. Hydroxy radicals, formed from various AOPs have a higher oxidation potential of 2.8 V than hydrogen peroxide of 1.78 V and involved in decomposition of chromophore of dye [4]. Among those, H_2O_2/Solar light has been found to be more effective towards treatment of effluent containing azo dyes because of its high efficiency and low cost.

In this study solar assisted Photodegradation using H_2O_2 (H_2O_2/solar light) was carried out to decolourise an azo dye Reactive Red-180 and dye effluent bath containing Reactive Red-180 and their reaction conditions were optimised. The optimised parameters were pH, H_2O_2 concentration and dye concentration.

2. Materials and methods.

Experiments were conducted on the dye solution containing 100 mg/l of RR-180.H_2O_2 of 50% concentration(526mM) was used with a volume of 3 ml. Dye solutions along with 3 ml of 50% H_2O_2 was taken in 250 ml conical flasks along with side arms and irradiated with sunlight. Light intensity was fixed to be in the range of 60,000- 90,000 lux and its intensity was measured using lux meter[7].Lux meter of model UA1010B was used to measure the lux intensity of range 200-2,00,000 lux. Decolourisation was evidenced by measuring the absorbance of decolourised dye solutions in the time interval of 1 or 1.5 hrs using µp photo colorimeter of model 1311.

To optimise the pH, dye solution of 100 mg/l concentration along with 3 ml of 50% H_2O_2 (526mM) was tested with glycine, citrate and phosphate buffer. Glycine buffer was prepared and its pH was found to be 11[8]. 50 ml of the Glycine buffer was mixed with dye solution of 100mg/l concentration containing 3 ml of 50% H_2O_2(526mM) to check the effect of basic pH of 11in decolourisation of RR-180. Similarly phosphate buffer with pH 7 was mixed with dye solution of 100 mg/l concentration with3 ml of 50% H_2O_2 (526mM) to check the effect of neutral pH of 7 in decolourisation. Similarly citrate buffer in acidic pH of 3 was mixed with dye solution of 100 mg/l concentration with 3 ml of 50% H_2O_2 (526 mM) to check the effect of acidic pH in decolourisation. Similarly RR-180 dye in its own pH of 6 was also irradiated with sunlight with 50% H_2O_2 (526 mM) without any type of buffer. pH was measured using the digital pH meter of model AI-102.

To optimise the H_2O_2 concentration, dye solution of 100 mg/l concentration with optimised pH was treated with different concentrations of H_2O_2 (50 mM-1000 mM). Similarly to optimise the concentration of dye solution, dye solutions with different concentrations (50 mg/l to 500 mg/l) was treated with H_2O_2 of optimised concentration with optimised pH.

Similarly the reaction conditions were optimised for effluent containing RR-180 and its decolourisation percentage was measured. Fig.1 shows the structure of Reactive Red 180.

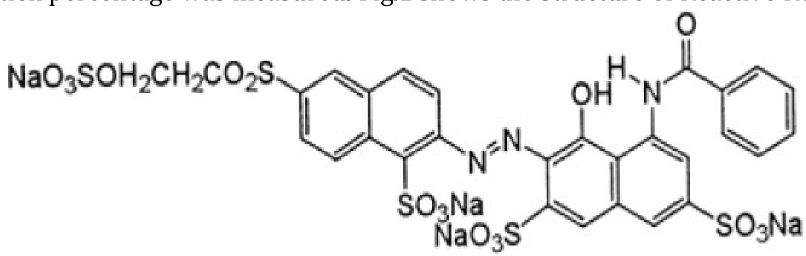

Fig 1. Structure of Reactive Red 180

Characteristics of Reactive Red
Other name: Remazol Brilliant Red F3B
Molecular Formula: C_{29} H_{19} N_3 Na_4O_{17} S_5
Molecular Weight: 933.76
Type: Azo dye
Chemical Name: 5-(Benzoylamino)-4-hydroxy-3-[-2-[1-sulfo-6-[[2-(sulfooxy)ethyl]sulfonyl]-2-naphthalenyl]diazenyl]-2,7-naphthalenedisulfonic Acid Sodium Salt.
λ_{max}:520 nm.
pH: 6

3. Results and discussion:

3.1. Effect of various parameters on decolourisation of RR-180 using solar assisted H_2O_2 degradation process.

3.1.1. Effect of pH

Effect of pH on decolourisation was studied by treating RR-180 dye solutions of 100 mg/l concentration with H_2O_2 of 526 mM concentration (3 ml of 50% H_2O_2)with Glycine buffer, Citrate buffer, Phosphate buffer and without any buffer. Glycine buffer was added with dye solution of 100 mg/l with

526mM concentration of H_2O_2 to investigate the decolourisation of RR-180 Dye in Basic pH of 11. Phosphate buffer was added with dye solution of 100 mg/l with 526mM concentration of H_2O_2 to investigate the decolourisation of RR-180 Dye in Neutral pH of 7.RR-180 solution with H_2O_2 of 526mM without any buffer was investigate the decolourisation of RR-180 Dye in its original pH of 6.Further acidification to get a pH of 4 by treating dye solution with citrate buffer did not work out well for the decolourisation of RR-180 as there was no decolourisation on exposing dye to sunlight along with 526mM H_2O_2. Results have shown that the 100% decolourisation of RR-180 was occurred in 11 hrs in acidic pH of 6, 9 hrs in neutral pH of 7. Only 19.2% decolourisation was produced in case of dye solution with Glycine buffer (basic pH of 11) and the reaction time is also found to be 11 hours for that. Hence the optimum pH for complete decolourisation of RR-180 is 7 with dye solution concentration of 100 mg/l and H_2O_2 concentration of 526mM.

In basic pH condition, production of the conjugate base of H_2O_2 (HO_2^-) increases. This conjugate anion (HO_2^-) reacts with nondissociated molecule of H_2O_2 which forms dioxygen and water, instead of forming hydroxyl radicals. Therefore the concentration of produced $OH^\cdot$ radicals is lower than expected concentration. Also in basic pH condition self-decomposition rate of H_2O_2 is high which leads to the formation of water and oxygen. Hence at basic pH condition abundance of H_2O_2 molecules to react with the dye molecules is lower than the expected. Hence we concluded that in basic pH condition obtained by addition of Glycine buffer with RR-180 dye solution, the decolourisation percentage is found to be very low of only 19.2%[9].Also at high pH values scavenging effect of hydroxyl radicals by H_2O_2 was produced so that they cannot react with dyes[10].

Similarly in acidic pH condition, H_2O_2 spontaneously decomposed into water and oxygen rather than producing hydroxyl radical. [11].

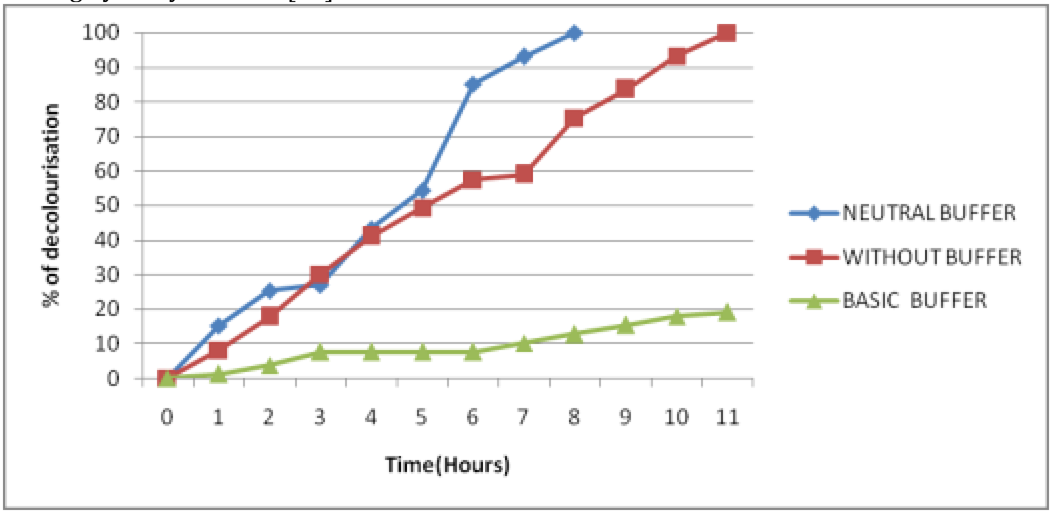

Fig. 2.Effect of pH on decolourisation of RR-180

Figure 2 :Effect of pH: Reaction conditions- (i) Dye solution of concentration 100 mg/l with neutral buffer(Phosphate buffer) with pH 7(neutral condition) and H_2O_2 of concentration of 526 mM(ii) Dye solution of concentration 100 mg/l without any buffer with pH 6(acidic condition) and H_2O_2 of concentration of 526mM(iii) Dye solution of concentration 100 mg/l with alkaline/basic buffer(Glycine buffer) with pH 11(basic condition) and H_2O_2 of concentration of 526 mM.

3.1.2.Effect of H_2O_2 Concentration

Effect of H_2O_2 concentration on decolourisation of RR-180 dye solution was studied by treating RR-180 dye solution of 100 mg/l concentration with optimum pH of 7 with different H_2O_2 concentrations ranging from 100 mM to 1000 mM. Results have shown that 100 % decolourisation of RR-180 was observed in shorter period time of 13 hours in case of RR-180 dye solution with 700 mM concentration of H_2O_2.Hence the optimised H_2O_2 concentration was also found to be 700 mM. Kinetic studies have also provided an evidence for that.

The $OH^\cdot$ free radicals formed on photolysis reaction of H_2O_2 with sunlight can react with excess of H_2O_2. It makes an inhibitory effect on the decolourisation of RR-180 dye. Reaction of $OH^\cdot$ free radicals with excess of H_2O_2 leads to formation of oxygen and water. Hence the availability of sufficient $OH^\cdot$ free radicals to react with dye molecules is very lower than the expected one. It leads to lower decolourisation of RR-180 dye with higher concentration of H_2O_2. Similarly at low concentration of H_2O_2 generation of $OH^\cdot$ radicals is very low and its abundance to react with dye molecule is also very low. Hence we concluded that decolourisation % is maximum in case of RR-180 dye with optimised 700mM concentration of H_2O_2[9].

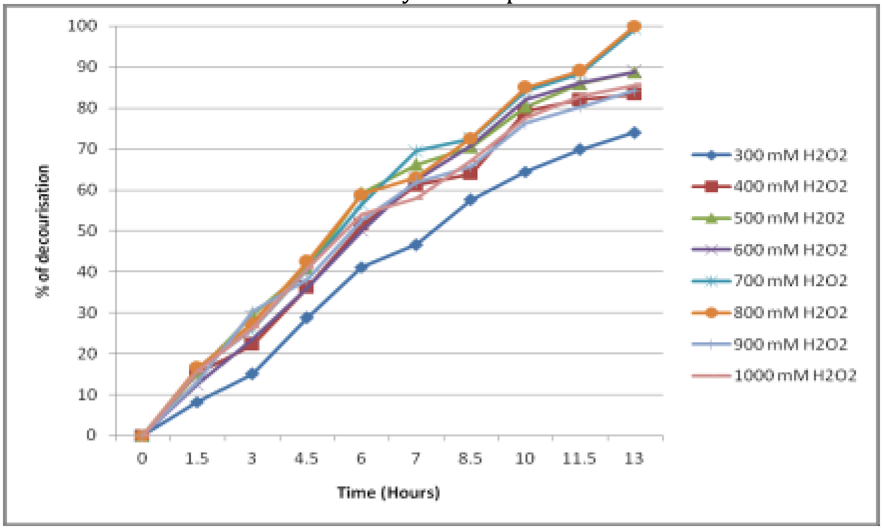

Fig. 3 Effect of H_2O_2 on decolourisation of RR-180

Figure 3:Effect of H_2O_2concentration : Reaction conditions- Dye solution of concentration 100 mg/l with neutral buffer(Phosphate buffer) with optimum pH 7(neutral condition) and H_2O_2 of different concentrations from 300 mM to 1000 mM

3.1.3. Effect of Dye Concentration

Effect of Dye concentration on decolourisation of RR-180 dye solution was studied by treating RR-180 dye solution of different concentrations ranging from 50 mg/l to 500 mg/l with optimised pH of 7 and optimised H_2O_2 concentration of 700 mM. Results have shown that lower the concentration of RR-180 dye solution lower the time taken for 100% decolourisation was[12]. 100% decolourisation was observed in case of RR-180 dye solution of 50 MM concentration in a time period of 5.5 hrs. It was because of change in RR-180 dye concentration even though the concentration of H_2O_2 is found to be optimised. It is because of the consideration that both dye and H_2O_2 absorb solar radiation in the same range. Increase in dye concentration increases internal absorbance and the solution becomes more and more impermeable to solar radiation[12]. Hydrogen peroxide can only be irradiated by a smaller portion of solar light and it leads to formation of lower $OH^{\cdot}$ radicals. Hence we can concluded that it leads to lower colour degradation rate of RR-180 with higher concentration [10].

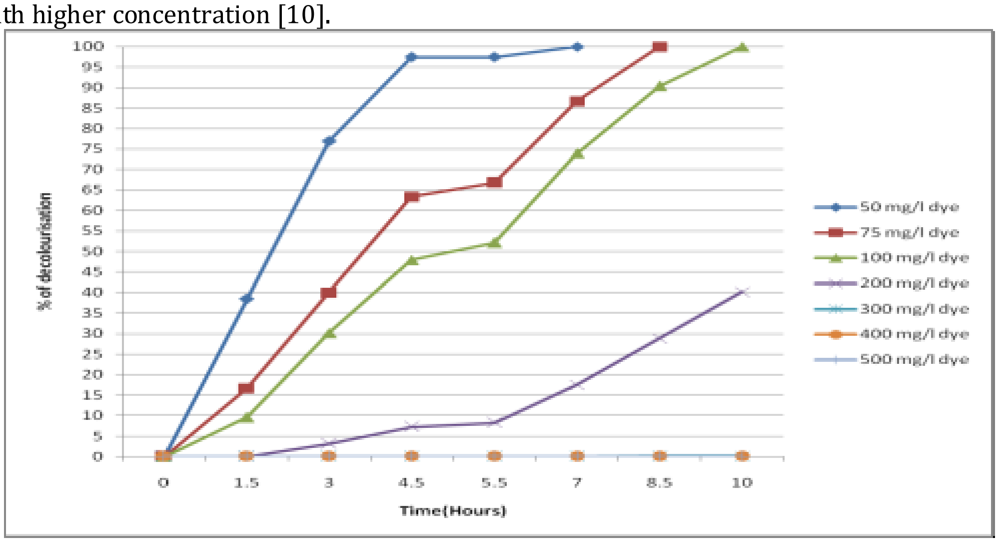

Fig.4 Effect of dye concentration on decolourisation of RR-180

Fig.4: Effect of Dye concentration: Reaction conditions- Dye solution of different concentrations from the range of 50 mg/l to 500 mg/l with neutral buffer (Phosphate buffer) with optimum pH 7(neutral condition) and H_2O_2 of optimum concentration of 700 mM.

3.1.4.Kinetic studies: Effect of Hydrogen Peroxide concentration on the kinetics of RR-180 decolourisation.

The order of the reaction is found to be first order with respect to the dye concentration, viz,
$\ln (A_t) - \ln (A_0) = -kt$

where k is the rate constant, t is the irradiation time and A_0 and A_t are the initial and final absorbance values of the dye solution respectively.[13]

We can optimise the H_2O_2 concentration also by studying the effect of Hydrogen Peroxide concentration on Kinetics of RR-180 decolourisation. We can get the rate constants by plotting the Time of Decolourisation against ln (A_t/A_0)[14].

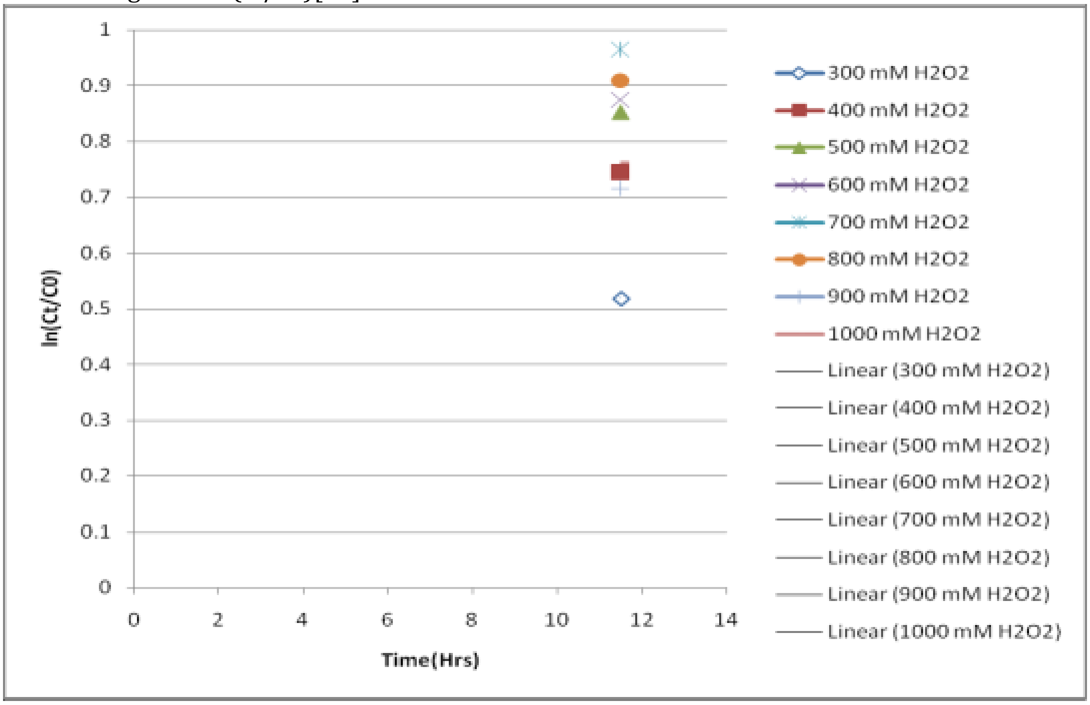

Fig. 5. Kinetic studies

Fig.5 :Kinetic studies: Plot of Time of decolourisation of RR-180 at different concentrations of H_2O_2 vs ln (C_t/C_0)

On plotting the concentration of H_2O_2vs rate constants, we can get a curve which gets maximum over that point of H_2O_2 concentration of 700 mM and it drops down after that concentration. Thus it can be concluded that there exists a maximum rate at H_2O_2 of 700 mM concentration and thus the optimum concentration of H_2O_2 was also finalised to be 700 mM.[13]

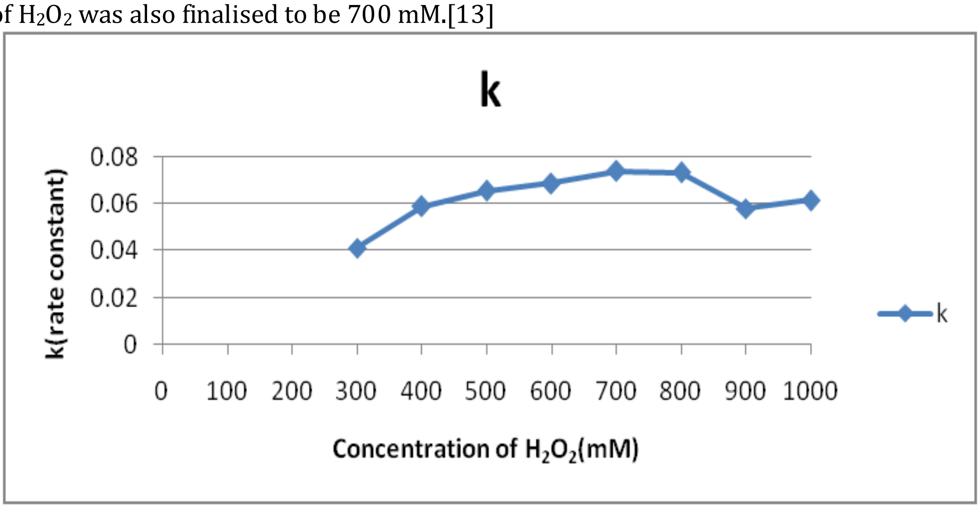

Fig. 6. Plot of Concentration of H_2O_2 vs rate constant

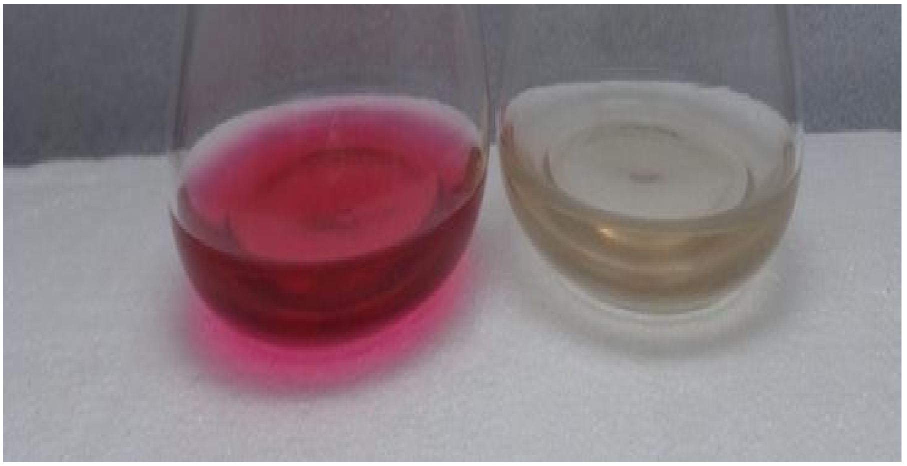

Fig. 7 Pictorial representation of Reactive Red 180 before and after decolourisation by H_2O_2/ Solar light

3.2. Testing the optimised parameters on decolourisation of effluent containing RR-180.

3.2.1. Effect of pH on decolourisation of 75% diluted effluent containing RR-180

Effect of pH on decolourisation of effluent containing RR-180 with 700 mM H_2O_2 can be studied by treating 75% diluted effluent with 5 ml of neutral buffer(phosphate buffer)and its decolourisation efficiency is compared with 75% diluted effluent without phosphate buffer. Results have shown that the decolourisation of 100% is same in case of both of the effluents with phosphate buffer and without phosphate buffer.

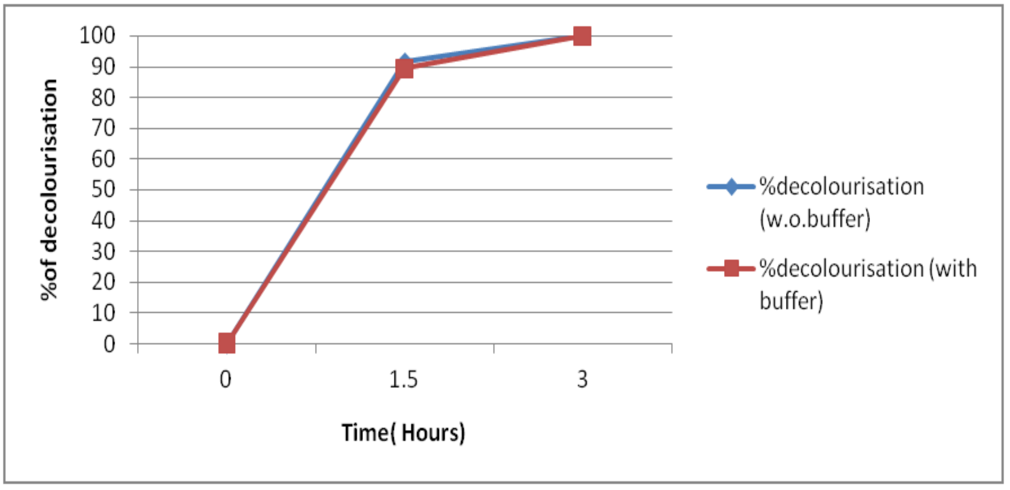

Fig. 8 Optimisation of pH on 75% diluted effluent

Fig.8:Optimisation of pH on 75% diluted effluent: Reaction conditions: (i) 100 ml of 75% diluted effluent sample containing RR-180 without (w.o) neutral buffer (phosphate buffer) (ii) 100 ml of 75% diluted effluent sample containing RR-180 with neutral buffer(phosphate buffer) in neutral condition of pH 7

3.2.2. Effect of pH on decolourisation of undiluted effluent containing RR-180

Similarly the decolourisation efficiency of undiluted effluent samples containing RR-180 was studied by treating the samples with and without phosphate buffer with 700mM H_2O_2.The maximum decolourisation efficiency obtained to 95.90% in case of sample without phosphate buffer and 96.18% in case of sample with phosphate buffer.[15,16]

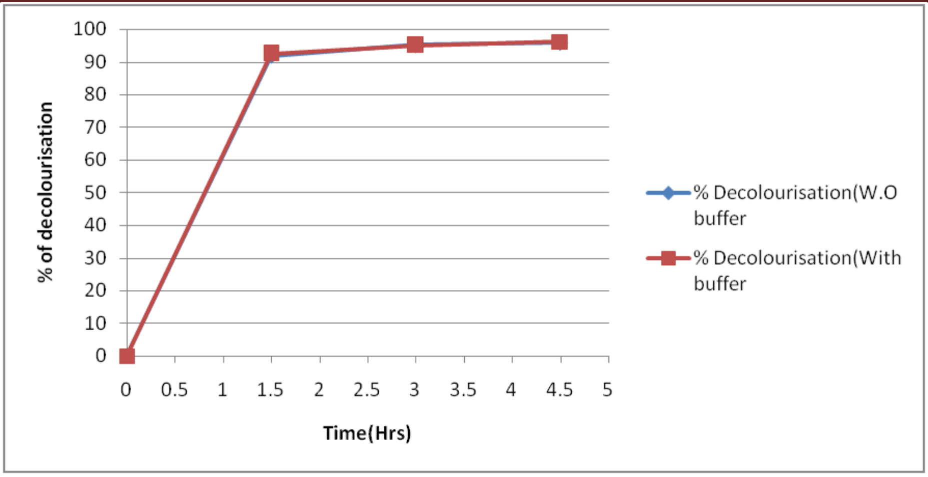

Fig. 9. Optimisation of pH on decolourisation of undiluted effluent

Fig.9 :Optimisation of pH on decolourisation of undiluted effluent: Reaction conditions: (i) 100 ml of undiluted effluent sample containing RR-180 without (w.o) neutral buffer(phosphate buffer) (ii) 100 ml of undiluted effluent sample containing RR-180 with neutral buffer(phosphate buffer) in neutral condition of pH 7

Conclusion:

This solar assisted H_2O_2 degradation process was found to effective method for complete degradation of Reactive Red 180 dye solution and also for effluent containing RR-180 with the optimised conditions of pH 7, H_2O_2 concentration of 700 mm as there was complete degradation of 100% in both cases. Previous literatures on UV/H_2O_2 have ensured that it was an environmentally friendly procedure and also it causes no sludge. Being the similar method of using solar light instead of UV, this method also proved to be an effective method based on the above investigations and it is found to be economical among the different AOPs[17].

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