



## Decolourisation of the Dyes in Aques Solution Using a New Combined System (UV/H<sub>2</sub>O<sub>2</sub>/biosorbent)

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Received: August 24 2013

Accepted: September 10 2013

### ABSTRACT

In this research, Comparison of decolorization of Reactive black B dye that have the most application in the Iranian textile industries, by using of advanced oxidation UV/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>/ biosorbent were investigated. The nonliving biomass of Penicilliumcamembertiwas used as a biosorbent for the sorption of dye from anaqueous solution. In the first stage, dye removal by UV/H<sub>2</sub>O<sub>2</sub> in continues system was investigated. The results showed that removal efficiency, in the optimum condition , pH=6.25 , dye concentration= 30mg/L , hydrogen peroxide concentration= 500mg/L and irradiation time 35 min were 84.34%. the same condition COD and TOC removal (%) were 77.3% and 35% respectively. In the second stage , dye removal by UV/H<sub>2</sub>O<sub>2</sub>/biosorbent was studied. For this purpose The immobilized Penicilliumcamemberti (biosorbent) fitted in polyetelen filter then filter of biosorbent was packed into a reactorThe results showed that removal efficiency , in the optimum condition ( pH=6.25 , [RBB]= 30mg/L , [H<sub>2</sub>O<sub>2</sub>]= 500mg/L and irradiation time 15 min were 96.46%. COD and TOC removal (%) were 90.22% and 56% respectively. Electrical energies per order (EE/O) estimated for both the processes.

**KEY WORDS:** biosorbent, Penicilliumcamemberti, COD, TOC, Electrical energies per order (EE/O)

### 1. INTRODUCTION

Azo dyes are widely used in the textile industry. Approximately 12% of the wastewater are dyes, textile effluent why the most polluted industrial wastewater are classified (1). Azo dyes are comprised of an (–N=N–) group, and when attached to molecules they become monoazo, diazo or polyazo dyes. Azo dyes currently represent around 60% of the world's market for dyes and are widely used in the dyeing of textile fibers (2). The removal of color from dye-bearing effluents is a major problem due to the difficulty in treating such wastewaters by conventional treatment methods (3).

Many research reports are available, which explain successful decolorization of the dyes using purified microbial cultures. But these findings do not find much application in practical treatment system due to complexity and heterogeneity of chemical compounds present in textile wastewater (4). For instance, screened several fungal and yeast isolates for the biosorption of reactive dyes and identified that *Saccharomyces cerevisiae* and *Rhizopusnigricans* performed well with uptake capacities in the range of 112–204 mg/g biomass. Recently, inactive *Corynebacteriumglutamicum* has been identified as a potent reactive dye biosorbent(5). *Penicillium* is one of the most widespread fungi in the terrestrial environment. *Penicillium* has been widely used for dye removal viabiodegradation or biosorption. Dried *Penicilliumrestrictum* had been recently used for biosorption of Reactive Black 5 (6).

Most of azo dye compounds are resistant to bacterial activity, and direct biological treatment is not effective. Consequently, alternative technology must be developed to solve the problem. Advanced oxidation processes (AOPs) have been developed for the destruction of certain pollutants in water (7). AOPs are characterized by the fact that no more toxic compound can be produced during the degradation process and the possibility to achieve a complete mineralization of the organic contaminant (8). Most of them, including heterogeneous photocatalytic oxidation, treatment with ozone (often combined with H<sub>2</sub>O<sub>2</sub>, UVA or both), and H<sub>2</sub>O<sub>2</sub>/UV systems, involve the generation of highly reactive hydroxyl radicals (•OH) (9).

physical, chemical and biological processes applied individually are generally limited to degrade the recalcitrant organic matter completely (10). Latest investigations on the degradation of organic pollutants are

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focused on the combination of biological and physical-chemical treatments. It was shown that combined processes had higher treatment efficiency than those of individual processes (11).

Some combination of the AOP and biological systems for the treatment of toxic and non-biological degradation, biological degradation of the materials and the methods are placed under the complete oxidation (12). In this study we assessed the efficiency, in terms of color removal and organic matter reduction of the dyes. The treatment system consisted of a combined process of UV/H<sub>2</sub>O<sub>2</sub> and biological treatment with a biomass.

## 2. EXPERIMENTAL AND METHODS

### 2.1. Material

Hydrogen peroxide was obtained from Fluka Chemical (30 % w/w). dye Reactive Black B (RBB) was obtained from Alvan Sabet Co. without further purification. The chemical characterization of C.I. Reactive black B is shown in Table. 1.

The color removal of RBB was determined using a UV-Vis spectrophotometer (UV-1700 Pharaspe). The pH of the solution was adjusted using sodium hydroxide (NaOH) or by hydrochloric acid (HCl).

### 2.2. Photoreactor

Experiments were performed in a photoreactor with a total volume of 2 L. The reactor is a continuous column circulation photo reactor fitted with a 15-W electric power high-pressure mercury lamp.

The UV irradiation source was installed inside a cylindrical quartz tube. The liquid level in the radiation column was kept constant at 1600 ml. The treated wastewater was returned to the reservoir and then left to circulate back to the reactor column at a constant flow rate of 4ml min<sup>-1</sup>. The immobilized *Penicilliumcamemberti* (biosorbent) fitted in polytetra filter then filter of biosorbent was packed into a reactor

Table1: Main characteristics of the Reactive Black-B

structure	Molecular Formula	$\epsilon$ (L mol <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{max}$	$M_w$
	C <sub>26</sub> H <sub>25</sub> N <sub>5</sub> O <sub>19</sub> S <sub>6</sub>	29740	957	991.8

### 2.3. Preparation of biosorbent

The nonliving biomass of *Penicilliumcamemberti* was used as a biosorbent for the sorption of dye from aqueous solution. The fungus was cultivated in a liquid medium using the shake flask method. The growth medium consisted of (g/l of distilled water): SABOURAUD- 2% Glucose- Bouillon. Once inoculated, flasks were incubated on an orbital shaker at 150 rpm for two days at 44 °C. Once inoculated, flasks were incubated on an orbital shaker at 150 rpm for 72 h at 35 °C. After incubation, the biomass was collected from the medium and washed with distilled water.

Then it was boiled for 15 min in 500 ml of 0.3 N NaOH solutions. Hydrogen chloride – pretreated biomass was ground and sieved through filtration using glass fiber filter papers (Whatman GF-C), and it was washed with deionised water until the pH of the wash solution was in near neutral range (pH7.0±7.2). It was then dried at 60 °C in an oven for two days and powdered in a mixer Fig.1.(13).

### 2.4. Preparation of immobilized *Penicilliumcamemberti* beads (biosorbent)

*Penicilliumcamemberti* was immobilized in sodium alginate polymer beads. Immobilization of fungal biomass was carried out by the entrapment method. Based on technique of drop wise addition of cells suspended in sodium alginate solution into calcium chloride solution that the cells are immobilized in calcium alginate gel. Alginate solution of 2.1% (w/v) was prepared by dissolving 8 g of sodium alginate in 420 ml of hot deionised water into the stirred tank. The mixed powdered biomass by different percentage proportions with 100 ml alginate (sodium) 2.1 % (

w/v) was shaken in shaker to have a uniform mixture. The mixture was extruded by a syringe into 0.2M calcium cholorid solution under shaking by using a peristaltic pump. After 35 min, the beads were amassed from solution and washed with deionised water. Then beads placed into a solution of calcium cholorid (0.2M) for 10 min, through  $\text{Ca}^{2+}$  diffused into the beads and produced the gelification on the bead surface. After that, the beads were washed with deionised water and keep in a solution of calcium cholorid (0.2M) for 60 min at 4°C and finally, washed with NaCl 0.7% (13).

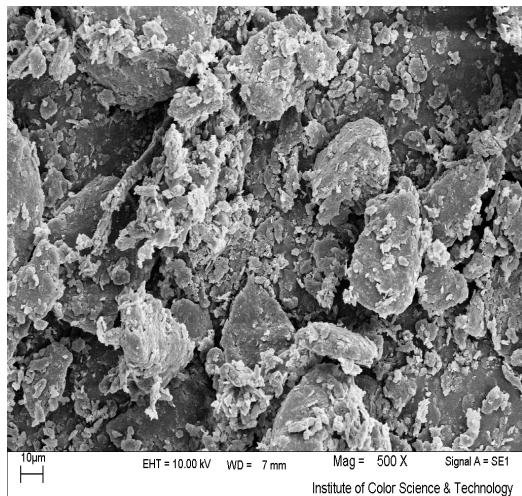


Figure 1. SEM of *Penicilliumcamemberti*

### 2.5. analysis

The concentration of the residual dye in solution was calculated by Beer Lambert law using the optical density and molar extinction observed at the characteristic wavelength ( $\lambda = 597 \text{ nm}$ ). Chemical Oxygen demand (COD), Total carbon organic (TOC) and %COD removal are selected as a criterion to monitor the degradation processes. The efficiency of color removal and dye mineralization were defined by the following expressions:

$$\text{Decolorization (\%)} = \left( 1 - \frac{[\text{RBB}]}{[\text{RBB}]_0} \right) * 100 \quad (1)$$

$$\text{COD removal (\%)} = \left( 1 - \frac{[\text{COD}]}{[\text{COD}]_0} \right) * 100 \quad (2)$$

$$\text{Mineralization (\%)} = \left( 1 - \frac{[\text{TOC}]}{[\text{TOC}]_0} \right) * 100 \quad (3)$$

where [RBB], [COD] and [TOC] are dye, COD and TOC concentrations at time  $t$ , respectively.  $[\text{RBB}]_0, [\text{COD}]_0$  and  $[\text{TOC}]_0$  are dye, COD and TOC initial concentrations, respectively(14).

## 3. RESULTS AND DISCUSSION

The absorption spectrum of the sample is characterized by three main bands, one in the visible range ( $\lambda_{\text{max}} = 597 \text{ nm}$ ) responsible for the maroon colour and other one in the UV region ( $\lambda_{\text{max}} = 320 \text{ nm}$ ). The 597 nm bands arises from chromophore structure ( $-\text{N}=\text{N}-$ ) of azo dyes and 320 nm bands are characteristics of the individual aromatic rings of the dyes.

### 3.1. Effect of UV alone

In our preliminary study, the decoloration of C.I. Reactive Black B (RBB) by ultraviolet radiation alone, or by hydrogen peroxide oxidation alone, or by immobilized *Penicilliumcamemberti* (biosorbent) alone showed that neither could degrade azo dye significantly. The results show the low efficiency of the alone system as presented in Fig.2.

### 3.2. $\text{UV}/\text{H}_2\text{O}_2$ :

The  $\text{H}_2\text{O}_2/\text{UV}$  oxidation process is one of the AOP, and it has potentially practical importance. The main reactions of this process are producing OH radicals and oxidizing of dye molecule and occurred as follows (15)



We have presented the normalized absorbance at 597 nm as a function of the irradiation time in Figs. 3 by UV/H<sub>2</sub>O<sub>2</sub> processes.

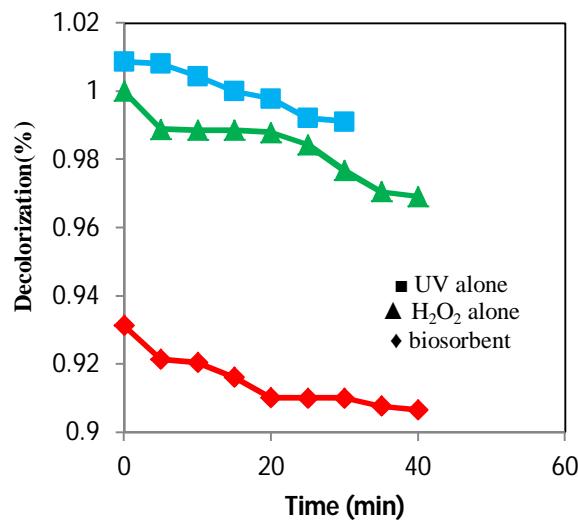


Figure 2. Decolourisation of RBB dye in wastewater by H<sub>2</sub>O<sub>2</sub> alone, UV alone and biosorbent ([H<sub>2</sub>O<sub>2</sub>]=500 mg/L, dye=30 mg/L)

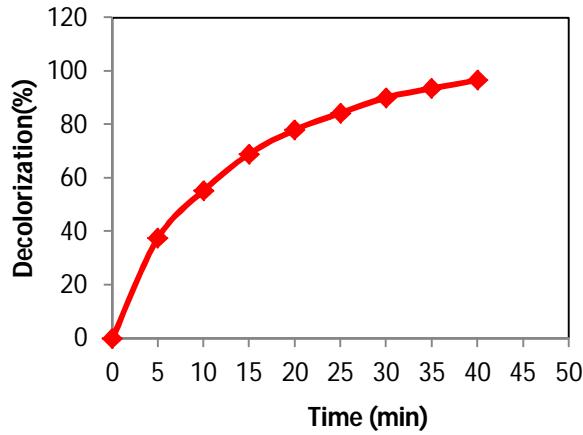


Figure 3. Decolourisation of RBB dye by UV/H<sub>2</sub>O<sub>2</sub> (dye=30mg/L, [H<sub>2</sub>O<sub>2</sub>]=500 mg/L)

### 3.2.1. Effect of H<sub>2</sub>O<sub>2</sub> concentration H<sub>2</sub>O<sub>2</sub>/UV

One of the important parameters on Advanced Oxidation Processes is the concentration of H<sub>2</sub>O<sub>2</sub> during the UV irradiation of the sample. Studies have been conducted to determine the optimum concentration of H<sub>2</sub>O<sub>2</sub> for the oxidation of various organic compounds (16).

To study the effect of the  $\text{H}_2\text{O}_2$  concentration on the efficiency of degradation of Reactive Black B in ultrapure water was investigated by adding 90, 100, 200, 300, 400, 500 and 600 mg/L of  $\text{H}_2\text{O}_2$  to the dye solution (30mg/L) at the same applied UV dose Fig.4.(17).

The rate of decomposition of Reactive Black-B increased with increasing  $\text{H}_2\text{O}_2$  concentration from 90 to 600 mg/L. According to Figure.4. it can be seen that the removal efficiency increases with increasing concentration , This increase will continue until the concentration of 500 mg  $\text{l}^{-1}$ , Although the removal rate remains constant after the concentration. $\text{H}_2\text{O}_2$  causes an increase in the production of hydroxyl radicals that are produced as a result of UV rays collid with  $\text{H}_2\text{O}_2$  and decolonization are causing. But the concentration of 500 mg/L, the removal rate is reduced blatantly due to hydroxyl radicals recombination or hydroxyl radicals react with  $\text{H}_2\text{O}_2$  effectively, and produces perhydroxyl radicals that are less active than the hydroxyl radicals.(18). Samples at the  $\text{H}_2\text{O}_2$  concentration of 500ppm were found to show the highest dye decolourisation and were thus considered to be the optimum concentration for use in the current system.

### 3.2.2. Effect of initial dye concentration

The decolorization experiments of RBB dye were carried out with 10, 20, 30, 40 and 50 mg/L initial concentrations at pH 6.25 One can notice in Fig. 5. that the more dilute the initial concentration, the faster is the decolorization as expected (15). Some researchers reported that the observed rate constant ( $k_{\text{obs}}$ ) increases by decreasing initial dye concentration (19).

An increase in dye concentration induces a rise of the internal optical density and the solution becomes more and more impermeable to UV irradiation. The fraction of hydrogen peroxide were irradiated and the formation of free radicals is reduced. In addition, there is higher concentration of intermediate

compounds. These compounds are highly reactive free radicals by comparison. Thus , competition between RBB dye and intermediate compounds for hydroxyl radicals , reducing the bleaching efficiency (18).

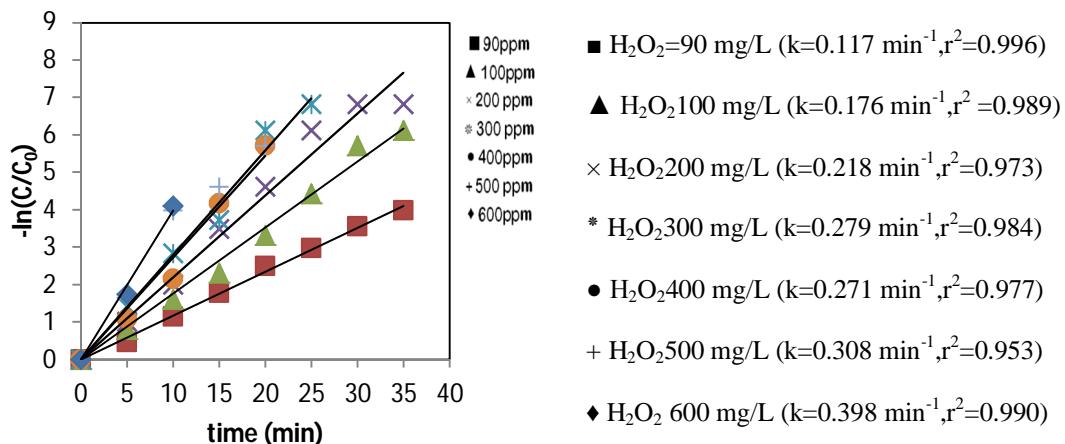


Figure 4. The first order rate representation of RBB versus time under various hydrogen peroxide concentration from 90 to 600ppm at pH= 6.25 in UV/ $\text{H}_2\text{O}_2$ process .. [RBB]= 30 mg/L,  $I_0=15 \text{ W m}^{-2}$ ,

### 3.3 UV/ $\text{H}_2\text{O}_2$ /immobilized Penicillium (biosorbent):

The concept of combining AOPs as a pre-treatment stage to enhance biodegradability and reduce toxicity with biological post-treatment has gained a lot of attention over the past several years (20).

The main goal of combined AOP with biological , wastewater containing pollutants resistant to biodegradation, in addition biodegradation, their treatment by advanced oxidation processes . AOP in the decomposition process is one of the most effective compounds are resistant. The complete mineral compounds by this method requires a long reaction time and high concentration of oxidizing agent , so combining with a biological method is advantageous (14). For this purpose the combined system in addition to UV/ $\text{H}_2\text{O}_2$  immobilized Penicillium fitted in polytetelen filter and put into the reactor. In these reactors , the dye solution is cyclic and alternating in and out . we sampled from the reactor for analysis. The results show the high efficiency of the two UV/ $\text{H}_2\text{O}_2$  immobilized Penicillium system as presented in Fig.6.

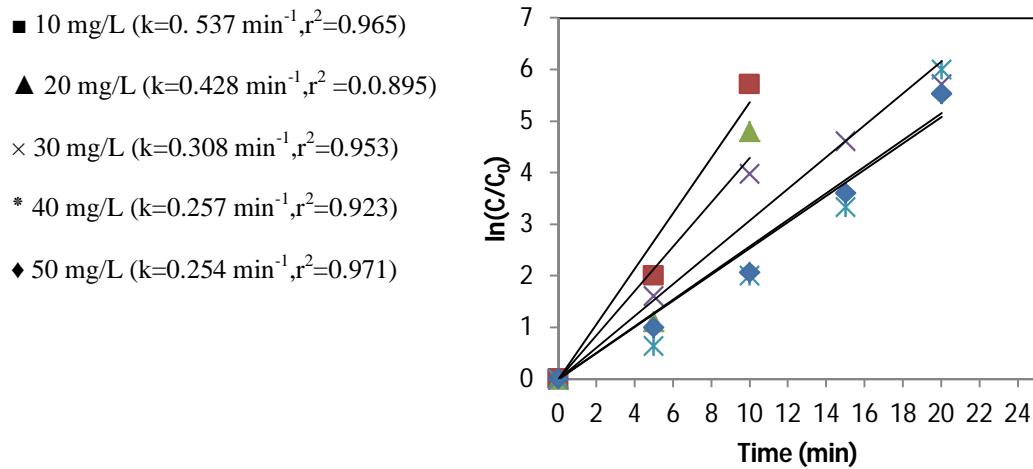


Figure .5.The first order rate representation of RBB versus time under various dye concentration from 10 to 50 mg/L at pH= 6.25 in UV/H<sub>2</sub>O<sub>2</sub> process .. [H<sub>2</sub>O<sub>2</sub>]= 500mg/L, I<sub>0</sub>=15 W m<sup>-2</sup>,

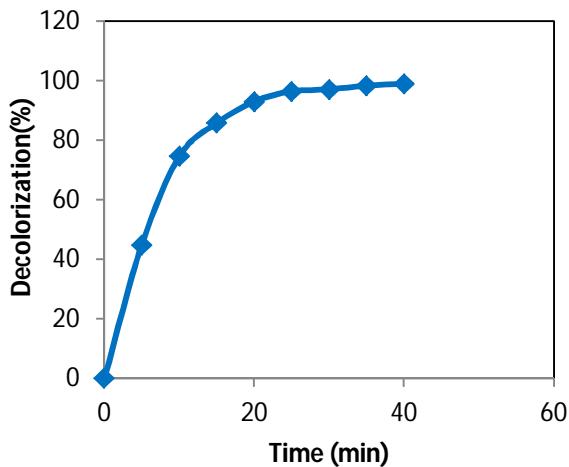


Figure 6.Decolourisati of RBB dye by UV/H<sub>2</sub>O<sub>2</sub>/biosorbent ([H<sub>2</sub>O<sub>2</sub>]=500 mg/L, dye=30 mg/L)

### 3.4. Kinetic study

Although the fast degradation of dyes in some of the experiments, especially in ,UV/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>/biosorbent process, required pseudo-first-order kinetics assumption, most of the degradation curves were found to obey first-order kinetics. There-fore, all constants were determined based on the first-order kinetics assumption (Eq. (9)).

$$\ln \left( \frac{C_f}{C_i} \right) = -k_1 * t \quad (9)$$

Where  $C_i$  is the initial dye concentration,  $C_f$  the concentration of dye at time  $t$  and  $k$  the overall rate constant (time<sup>-1</sup>)

In Fig. 7.the logarithmic variations of the dye concentration as a function of the UV irradiation time is illustrated. The dye destruction is a pseudo-first order reaction with respect to dye concentration. For each dye solution, color removal apparent rate constants ( $k_{app}$ ) were evaluated using a linear regression of the plot of color degradation with time and presented in Table 2.

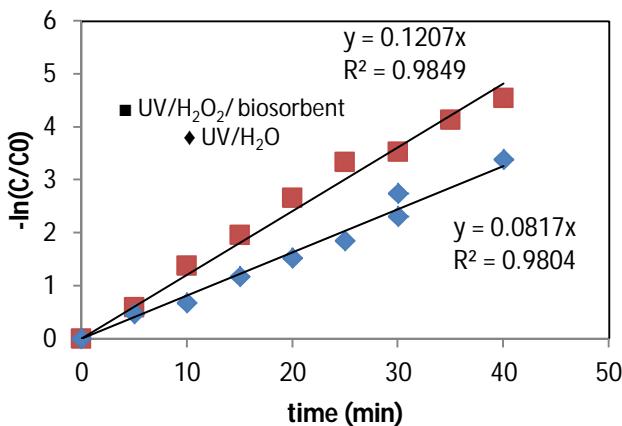


Fig.7. First order plot of color degradation of RBB solutions as a function of UV irradiation time by UV/H<sub>2</sub>O<sub>2</sub>/biosorbent ([H<sub>2</sub>O<sub>2</sub>]=500 mg/L, dye=30 mg/L)

Table 2. Characteristics of the RBB solution,  $R^2$  and  $k$  values for decolorization ([H<sub>2</sub>O<sub>2</sub>]=500 mg/L,[RBB]=30 mg/L

	$K_{app}(\text{min}^{-1})$	$R^2$
UV/H <sub>2</sub> O <sub>2</sub>	0.081	0.980
UV/H <sub>2</sub> O <sub>2</sub> / (biosorbent)	0.120	0.984

### 3.5. Mineralization studies

Since the intermediate products of their toxic and non-biodegradable organic compound are destroyed by these compounds should also be considered (21). It is known that complete decolorization of RBB does not mean that the dye is completely mineralized into CO<sub>2</sub> and H<sub>2</sub>O. The longer lived reaction intermediates formed may be more toxic than the original dye. Hence, it is necessary to simultaneously investigate the mineralization process. To achieve this goal, COD and TOC removal (%) of the reaction mixture as a function of time was measured (22).

Fig. 8 depicts the variations of chemical oxygen demand, %COD removal with time for decolorization process of reactive black-B by UV/H<sub>2</sub>O<sub>2</sub> and combined UV/H<sub>2</sub>O<sub>2</sub>/immobilized Penicillium (biosorbent). It can be seen from the figure that the reduction in COD using UV/H<sub>2</sub>O<sub>2</sub>/ immobilized Penicillium (biosorbent) is about 90.2% which is larger than that of UV/H<sub>2</sub>O<sub>2</sub> process, which is about 77.3% (14)..

As shown in Fig. 8 plots of ln (COD)/(COD)<sub>0</sub> versus  $t$  gives straight lines with correlation coefficient of about  $R^2 = 0.992$ , , 0.999 and The first-order rate constant,  $k$ , is 0.012, 0.019 for decolorization of RBB by UV/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>/biosorbent, respectively. The UV/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>/immobilized Penicillium processes percent TOC removal measured and it was found that the TOC removal ratio increases significantly by UV/H<sub>2</sub>O<sub>2</sub>/ immobilized Penicillium (biosorbent) After 30 min of UV irradiation time, we can observe about 35 and 56% TOC removal, respectively, in UV/H<sub>2</sub>O<sub>2</sub> and combined UV/H<sub>2</sub>O<sub>2</sub>/immobilized Penicillium (biosorbent) (21).

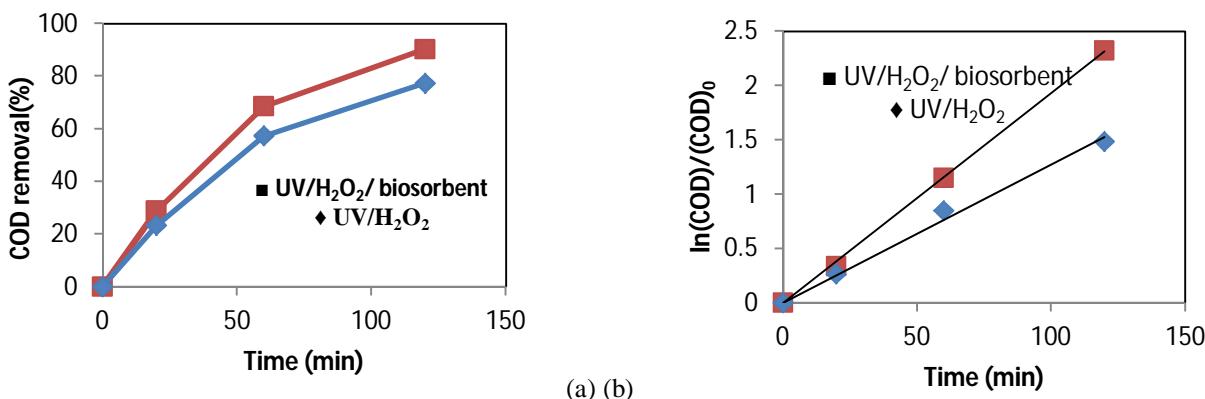


Figure 8. (a) %COD removal of RBB by UV/H<sub>2</sub>O<sub>2</sub>/ immobilized Penicillium (biosorbent) and UV/H<sub>2</sub>O<sub>2</sub> (b) Determination of first-order rate constants (k) for decolorization of dye-RBB by UV/H<sub>2</sub>O<sub>2</sub>/biosorbent and UV/H<sub>2</sub>O<sub>2</sub>

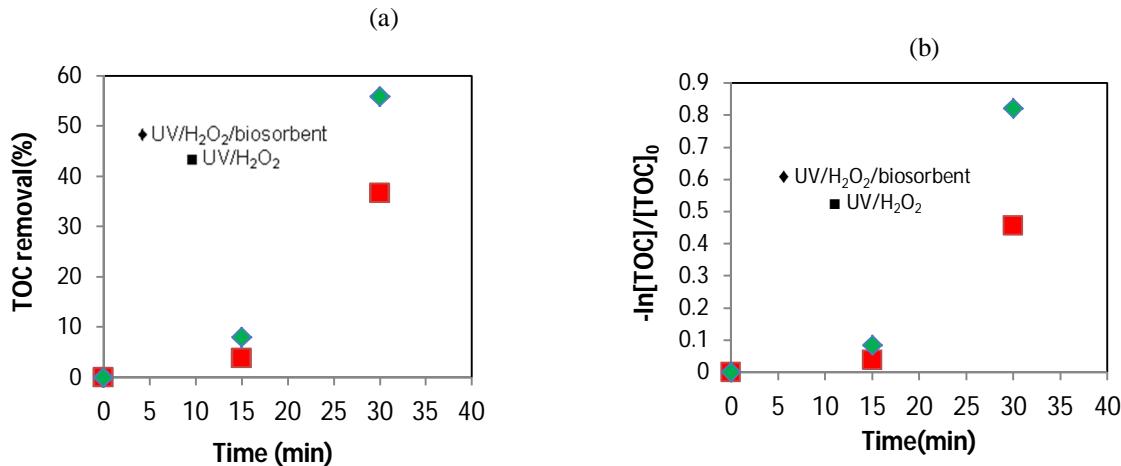


Figure 9.(a) %TOC removal of RBB by UV/H<sub>2</sub>O<sub>2</sub>/ immobilized Penicillium(biosorbent) and UV/H<sub>2</sub>O<sub>2</sub> (b) Determination of first-order rate constants (k) for decolorization of dye-RBB by UV/H<sub>2</sub>O<sub>2</sub>/biosorbent and UV/H<sub>2</sub>O<sub>2</sub>

As shown in Fig. 9.plots of  $\ln (\text{TOC})/(\text{TOC})_0$  versus  $t$  gives straight lines with correlation coefficient of about  $R^2 = 0.775, , 0.789$  and The first-order rate constant,  $k$ , is 0.012, 0.023 for decolorization of RBB by UV/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>/biosorbent, respectively

### 3.6. Evaluation of electrical energy per order

There are a number of important factors in selecting a waste treatment technology, inducing economics, economy of scale, regulations, effluent quality goals, operation (maintenance, control, safety) and robustness (flexibility to change/upsets). Although these factors are important, economics is often paramount. Since photo degradation of aqueous organic pollutant is an electric-energy-intensive process, and electric energy can represent a major fraction of the operating costs, simple figures-of-merit based on electric energy consumption can be very useful and informative. These figures-of-merit are based on electrical energy consumption within two phenomenological kinetic order regimes: one for high contaminant concentration (electrical energy per mass, EE/M) and one low concentration (electrical energy per order of magnitude perm<sup>3</sup>, EE/O). Simple understanding of the overall kinetic behavior of organic degradation in wastewater (i.e., whether zero or first order reaction) is necessary for describing meaningful electrical efficiencies. In the case of low pollutant concentrations (pseudo-first order reactions), which applies here, the appropriate figure-of-merit is the electrical energy per order (EE/O), defined as the number of kWh of electrical energy required to reduce the concentration of a pollutant by 1 order of magnitude (90%) in 1m<sup>3</sup> of contaminated water. The EE/O (kWhm<sup>-3</sup> order<sup>-1</sup>) can be calculated from the following equations:

$$\text{EE}/\text{O} = \frac{\text{P} * \text{t} * 1000}{\text{V} * 60 * \log\left(\frac{\text{C}_i}{\text{C}_f}\right)} \quad (10)$$

$$\ln\left(\frac{\text{C}_i}{\text{C}_f}\right) = k_{app} * t \quad (11)$$

where  $P$  is the rated power (kW) of the AOP system,  $t$  the irradiation time (min),  $V$  the treated wastewater volume (l),  $C_i$  and  $C_f$  the initial and final pollutant concentrations and  $k$  is the pseudofirst order rate constant ( $\text{min}^{-1}$ ) for the decay of the pollutant concentration From Eqs. (10) and(11), EE/O can be written as follows (22,23).

$$E_{EO} = \frac{38.4P_{el}}{V k_{app}} \quad (12)$$

However, EE/O parameters are inversely proportional to fundamental efficiency factors, such as the lamp efficiency, the fraction of the emitted light flux that is absorbed in the wastewater and the quantum yield of generation of active OH radicals. For UV/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>/ biosorbent total electrical energy required is 3.428 kWhm<sup>-3</sup> and 2.504 kWhm<sup>-3</sup>, respectively (22). From the economical point of view, the H<sub>2</sub>O<sub>2</sub>/UV process electrical energyforRBB decolorization (EE/O=59.25 kWhm<sup>-3</sup>) very higher than by the UV/H<sub>2</sub>O<sub>2</sub>/biosorbent process (EE/O=40 kWhm<sup>-3</sup>) (24). For a full-scale system, these costs strongly depend on the flow rate of the effluent and the configuration of the

reactor as well as the nature of the effluent. Cost evaluation for UV processes was based on electrical energy per order (EE/O) using the formula(10). Cost evaluation is given in Table 3 (25).

Table 3

	K(min <sup>-1</sup> )	EE/O (kWhm <sup>-3</sup> )	Cost( Rs)
UV/H <sub>2</sub> O <sub>2</sub> / biosorbent	0.120	40	16000
UV/H <sub>2</sub> O <sub>2</sub>	0.081	59.25	23700

### Conclusion

In this study, combined chemical oxidation with biological treatment processes were applied to treat pesticides from aqueous solutions. The high cost of advanced processes and low efficiency of biological processes make the use of combination of both the processes a viable option available.

The results have shown that the removal efficiency both in terms of decolorization and mineralization is negligible when UV, H<sub>2</sub>O<sub>2</sub> or biosorbent are used alone. Among combining AOP with- biological process schemes tested, we found that the UV/H<sub>2</sub>O<sub>2</sub>/biosorbent process was the most effective in reducing the COD, color and TOC of decolorization. The UV/H<sub>2</sub>O<sub>2</sub>/biosorbent process is capable of reducing the COD removal (%) content of the RBB by 90.22% in 120 min at pH 6.25. By comparison, the UV/H<sub>2</sub>O<sub>2</sub> treatments under the same conditions reduced the COD removal(%) by approximately 77.3%, and TOC removal (%)in the UV/H<sub>2</sub>O<sub>2</sub>/immobilized Penicillium is more. The kinetics of decolorization was found to follow first order reaction rules. The electrical energy needed for mineralization process can be notably reduced by using UV/H<sub>2</sub>O<sub>2</sub>/biosorbent

### Acknowledgment

The authors declare that they have no conflicts of interest in the research.

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