Combination of adsorption and biological treatment in a SBR for color elimination in municipal wastewater with discharges of textile effluents

E. Ferrer-Polonio, A. Iborra-Clar, J.A. Mendoza-Roca, M.I. Iborra-Clar

Instituto de Seguridad Industrial, Radiofísica y Medio Ambiente
Universitat Politècnica de València
Camino de Vera s/n
46022 Valencia
Tel. +34 963877630 Fax +34 96 3877639
e-mail address: jamendoz@iqn.upv.es

Abstract.

In most cases, conventional activated sludge processes do not eliminate wastewater color. This is due to the fact that aerobic bacteria do not degrade azo-dyes, which are the most used dyes in textile mills. In this way, discharges of textile wastewaters to municipal wastewater treatment plants (MWWTPs) entail presence of color in the final effluent what causes a negative impact on the environment and, additionally, hinders an efficient disinfection by UV lamps. In this work, a combined process consisting in the addition of powdered activated carbon (PAC) to a sequencing batch reactor (SBR) was studied. The main objective was to reduce the wastewater color in order to obtain transmittance values in the final effluent above 60%, measured at a wavelength of 254 nm, with the aim of ensuring the disinfection with UV-lamps. Experiments were performed both with simulated wastewater including the azo-dye Reactive Black 5 and with wastewater from a MWWTP receiving discharges from a textile mills area located in Valencian Region (Spain). The concentration of PAC needed to have a final effluent with a transmittance value above 60% was 250 and 400 mg/L for the simulated effluent and for the wastewater, respectively. PAC had to be periodically added to cover its loss in the waste sludge and in the treated wastewater stream.

Keywords: Color removal; Powder activated carbon; Remazol Black 5; SBR

INTRODUCTION

Discharge of colored wastewater from textile industry into Municipal Wastewater Treatment Plants (MWWTPs) with conventional activated sludge processes entails colored treated effluents. This is due to the fact that reactor biomass is not able to degrade reactive dyes. They are normally azo-based chromophores combined with different types of reactive groups e.g., vinyl sulphone, chlorotriazine (Aksu and Dönmez, 2003).

In spite of the low concentrations of dyes in the MWWTPs effluents, color can be optically observed. An operational problem is associated with the residual color independently of the eventual dye toxicity: the loss in the performance of the disinfection by means of UV radiation. This compels to the plant manager to take measures leading to color removal before the disinfection stage.

Upgrading MWWTPs for color elimination is not an easy task. Although many techniques have been reported in the bibliography, most of them are not economically feasible when high wastewater volumes have to be treated. Advanced oxidation techniques by Fenton’s reagent (Su et al., 2011), ozone (Colindres et al.,2010) or photocatalysis (Mahadwad et al., 2011) have been proposed by several authors in order to eliminate reactive dyes in wastewater, in particular Reactive Black 5, which is the dye studied in this work. However, at industrial scale, the cost of these processes and the eventual formation of partially oxidized substances that can be dangerous have limited their application.

Membranes are also processes that separate dyes from wastewater. In particular, nanofiltration and reverse osmosis separate low molecular weight organic substances. Nevertheless, membrane fouling phenomena and reject streams management are drawbacks to take into account. In fact, current research is focusing on fouling minimization (Fersi et al., 2099; Van der Bruggen et al., 2005).

Other authors have studied color elimination by implementing a double biological stage. It is well known that biological mineralization of azo-dyes requires the integration of an anaerobic process that degrades the azo-bond to aromatic amine intermediates and an aerobic process for their total degradation (Harrelkas et al., 2008; Melgoza et al., 2004; Venkata et al., 2007).

Color separation is also carried out by adsorption with activated carbon. Activated carbon (AC) can be added in a WWTP for color removal as powder (PAC) or as granular carbon (GAC). The application of the AC can carried out by dosing to the biological reactor to mix it with the biological sludge or as a tertiary treatment after the biological treatment. The last alternative is more difficult to implement once the WWTP is working due to the space required.

In the bibliography, some studies have been published about application of AC to a biological reactor, mainly to membrane bioreactors (MBRs) and to sequencing batch reactors (SBR). These works show the performance enhancement of the pollutants removal in different applications. They are mainly focused on particular pollutants removal such as micropollutants (Li et al., 2011; Serrano et al., 2011) and hexavalent chromium (Ferro et al., 2011) and on the improvement in the removal of organic matter in high polluted wastewaters like leachates (Maranon et al., 2009; Rivas et al., 2006).

Focusing on color removal, there are hardly references in the literature. Only Asadi et al. (2010) reported about the effect of the addition of GAC to an aerobic SBR for Brill Blue NR dye removal from wastewater. They observed an approximately additional 20% of the dye removal after adding GAC to the reactors (Asadi et al., 2010).

In this work, adsorption with PAC added to a SBR for color elimination both in a simulated wastewater with Reactive Black 5 (RB-5) and in a wastewater from a MWWTP that treats both municipal and textile mills effluents was studied. Unlike the combination of PAC and MBR, settling problems of PAC have to be studied, what is also carried out in this work.

MATERIALS AND METHODS

Wastewater

Experiments were carried out with simulated municipal wastewater consisting of 270 mg/L of peptone (Panreac) and 270 mg/L of meat extract (Panreac) solved in tap water. Its COD was 600 mg/L. Reactive Black 5 (RB-5; CAS 17095-24-8; Sigma-Aldrich) was added in the concentration that mimicked the color in terms of transmittance of the effluent from a MWWTP receiving discharges from a textile mills area located in Valencia Region. The molecular weight of this azo-dye is 991.82 g/mol.

Activated carbon

Two commercial activated carbons have been used in the experiments. Clarimex 061 (Chiemivall) is a carbon made from pine wood, chemically activated with phosphoric acid. GMI 835/05 from GALAQUIM is a mineral carbon provided in a granular form. For the tests, the granular carbon was grinded to a size similar to the Clarimex 061 (minimum of 80% lower than the 400 mesh size in US standard sieve, equivalent to 37 microns). Both activated carbons were tested in a jar-test apparatus from SELECTA. The procedure consisted in introducing 500mL of 10 mg/L of RB-5 solution samples in the jars, then the activated carbon was added and rapidly mixed (180 rpm) during 30 min. Before each measurement, the base line of spectrophotometer was calibrated against solvent. The maximal length of RB-5 was found to be 597nm at the solution pH. Absorbances were measured with a Hewlett Packard model 8453 spectrophotometer.

Laboratory plant

A 25 L volume reactor was used as SBR for the experiments. The reaction volume used was of 12 L in all the experiments. The SBR operation was controlled by timers programmed for changing the cycle phase at the required time. Mixing was provided via a Heidolph mechanical stirrer. Air was supplied by means of an air blower (Eheim de GmbH & Co. KG) for a maximum air flow rate of 400 L/h and was diffused through porous ceramic diffusers into the reactor. Dissolved oxygen was measured with a Crison OXI 330 and its concentration was maintained between 2 and 3 mg/L in the aerobic phases. Masterflex pumps (Millipore) were used for feed and draw phases, respectively.

Analysis

Transmittance at 254 nm was measured to determine the suitability of the final effluent to be treated by UV lamps. Color was determined by measuring the absorbance values of the samples at three wavelengths (440, 520 and 600 nm), corresponding to the maximal absorbance of yellow, red and blue colors, respectively. These measures were performed with a Hewlett Packard model 8453 spectrophotometer.

Once the absorbances at the three wavelengths were measured, a color index (CI) was calculated according Döepkens et al. (2001) (Eq. 1)

$$\mathrm{CI} = \frac{(\mathrm{A}_{436}^2 + \mathrm{A}_{525}^2 + \mathrm{A}_{620}^2)}{(\mathrm{A}_{436} + \mathrm{A}_{525} + \mathrm{A}_{620})} \qquad \mathrm{Eq.\,1}$$

Where A_{436}, A_{525} and A_{620} are the absorbance values at wavelengths of 436 nm, 525 nm and 620 nm, respectively. COD was determined by means of cell tests from Merck after 0.45 microns filtration. Mixture liquor suspended solids (MLSS) and mixture liquor volatile suspended solids (MLVSS) were measured following APHA [2].

Operating strategy

The laboratory SBR was operated according to the strategy detailed in Table 1. As it can be seen the hydraulic retention time was 1 day, i.e. the reactor was operated as an extended aerated activated sludge process. The reaction phase was divided into anoxic and aerobic. The operation of the SBR was divided into four experiments: start-up of the plant with neither dye nor activated carbon addition, with dye addition but without activated carbon to study the adsorption of the dye on the biological flocs, with dye and 300 mg/L of activated carbon and with dye and 400 mg/L of activated carbon. The laboratory SBR was operated during 70 days.

Table 1. Operation strategy of the SBR

Duration of the cycle phases	
Phase	Time (min)
Filling	21
Anoxic reaction	60
Aerobic reaction	294
Sedimentation	90
Draw	7
Idle	8
Operating parameters	
Hydraulic retention time (HRT)	24 hours
Cycles per day	3
Volume exchange ratio (VER)	1/3

RESULTS AND DISCUSSION

Start-up of the SBR laboratory plant (no addition of dye and PAC)

As commented in the materials and methods section, the SBR plant was fed with simulated municipal wastewater in the starting-up. The reactor was seeded with mix liquor of a MWWTP. Thus, acclimation was very quick and after 6 days it was decided to add the RB-5. Table 2 illustrates the values of the main parameters determined in the biological process.

Table 2. Characteristics of the biological process after the starting-up of the laboratory SBR

Parameter	
COD removal	92.5 %
pH of SBR effluent	8.02
Conductivity of the SBR effluent	1294 µS/cm
Mixed Liquor Suspended Solids (MLSS)	2500 mg/L
Volatile mixed liquor suspended solids (VMLSS)	87.5 (%)
Organic load	0.24 gCOD/(gSS·d)

Selection of PAC and concentration

Jar-tests for the selection of PAC type and concentration were carried out at 20ºC and at pH = 8.2 (pH of the solution of 10 mg/L of RB-5 in tap water). Figure 1 shows the results in terms of percentage removal of RB-5 in water after the tests with different PAC concentration. Absorbances values were measured at a wavelength of 597 nm.

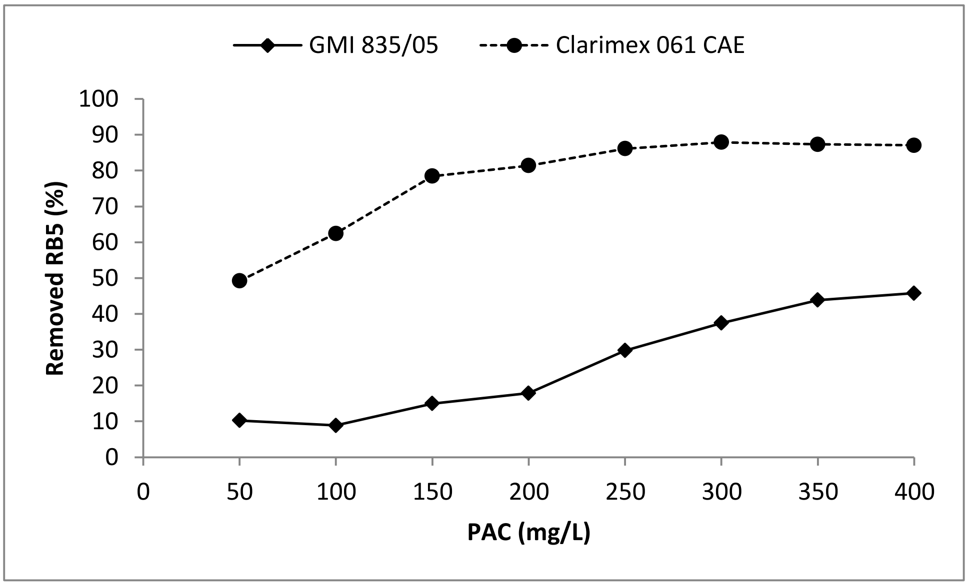


Figure 1. Elimination of RB-5 by GMI/835-05 and CLARIMEX 061 CAE carbons.

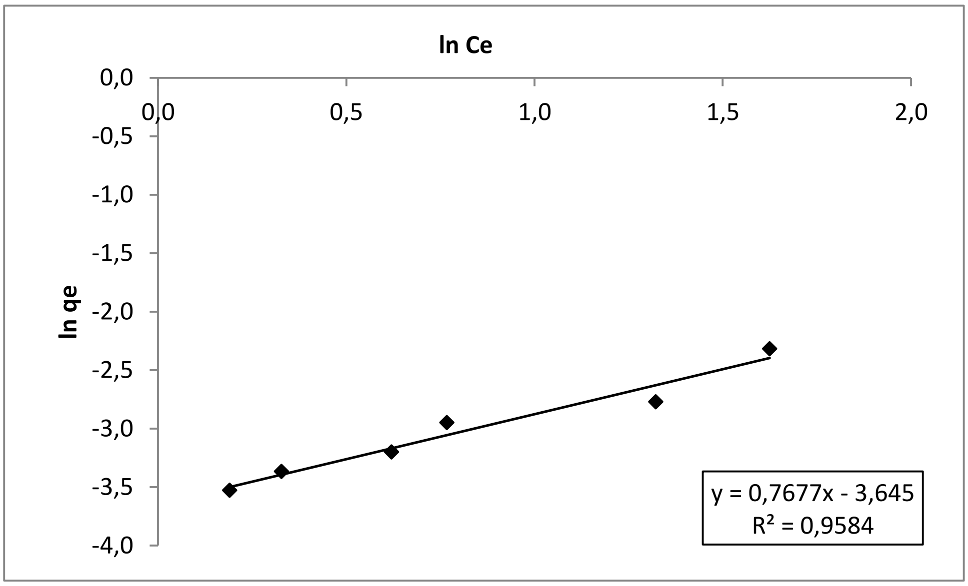
It is evident that GMI carbon is not appropriate for the elimination of RB-5, meanwhile more than 90% of the dye is eliminated with a concentration of 300 mg/L of CLARIMEX CAE. It was decided to select this concentration as initial one in the SBR experiments. Results were adjusted to a Freundlich isotherm. The Freundlich equation is:

$$q_e = K_F \cdot C_e^{1/n} \qquad \text{Eq. 2}$$

where q_e is the quotient between the masses of adsorbate and activated carbon (mg/mg), C_e is the concentration of RB-5 remaining in the solution (equilibrium concentration in mg/L) and K_F and n are the Freundlich constants. K_F is roughly an indicator of the adsorption capacity and n is related to the intensity of the adsorption. Eq.2 can be linearized by taking logarithms to find out the parameters K_F and 1/n.

For the selected carbon (Clarimex CAE) the linear plot of $\ln(q_e)$ versus $\ln(C_e)$ give a linear regression with a correlation coefficient (R^2) of 0.95 (Figure 2).

Figure 2. Linearization of Freundlich equation for the data obtained with Clarimex 061 CAE.

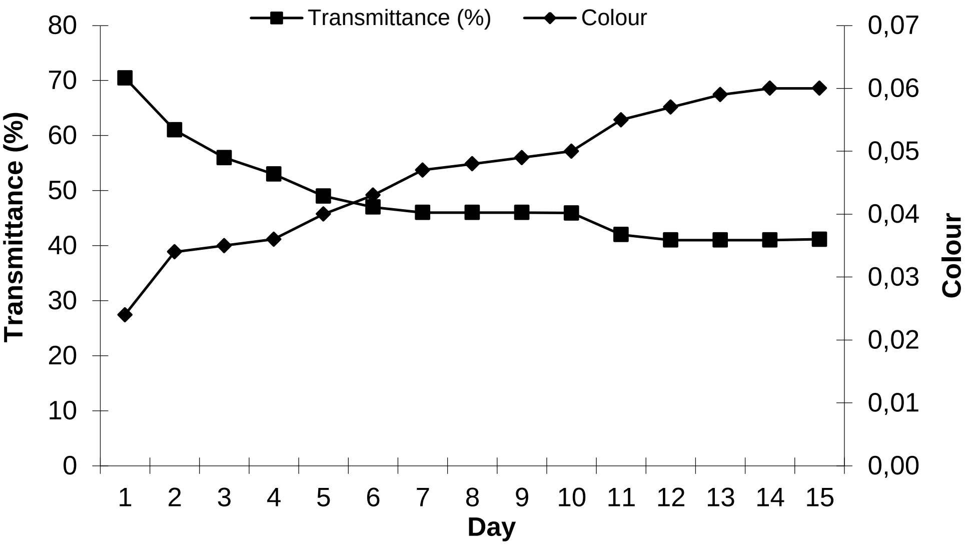


Thus, K_F = 0.026 (mg RB-5/mg CAP)·(mg CAP/L)$^{-0.7677}$ and n = 1.30. This value of n > 1 indicates favourable conditions for adsorption (McKay et al., 1982; Saha et al., 2011).

Experiments with azo-dye and PAC

Once 300 mg/L of PAC were dosed to the tank, transmittance and color were daily measured. In this part of the study it was aimed to find out the period of time in which the effluent would recover the initial conditions (41% of transmittance and 0.074 of color). Sludge withdrawal was carried out when the measured MLSS was near 3500 mg/L so that the sludge load could not be too high. Figure 3 shows the results in this period of time (15 days).

Figure 3. Evolution of transmittance (254 nm) and colour after PAC addition.



It can be observed that transmittance decreased very quickly in the first 5 days. This was not due to the carbon saturation but to the loss of activated carbon in the effluent. Its poor settling properties implied suspended solid concentrations in the effluent near 40 mg/L. After these initial days, the decrease in the effluent transmittance was not so sharp. The value was maintained practically constant near 46%. After the only sludge withdrawal in this period (in day 11) the effluent transmittance decreased as expected since activated carbon was withdrawn together with the sludge. Finally, after 15 days the initial transmittance value was measured again. Concerning color, although it was increasing with the time as expected, the final value was lower than the initial one. This can be due to the change in the tonality of the brown color of the sludge, since the biomass seeded in the reactor came from a MWWTP and the feeding with simulated wastewater changes its optical properties. Concerning COD of the treated effluent, it has to be mentioned that a COD of 64 mg/L was measured the day after adding the activated carbon as a consequence of the PAC in the treated wastewater. However, COD decreased in the following days and it was constant until the end of the period with a value near 30 mg/L.

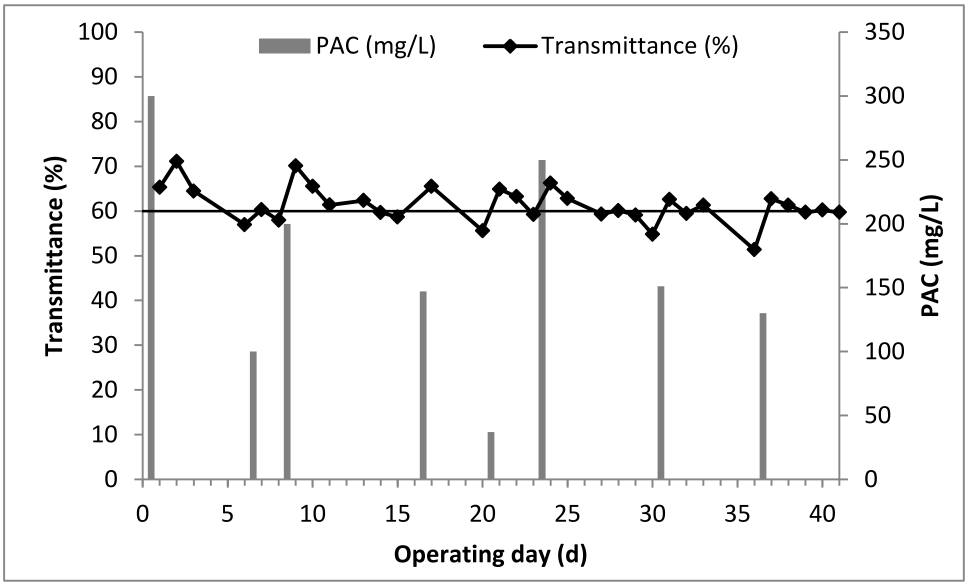
After this period of 15 days, the system was operated with a different strategy. Activated carbon was dosed trying that the transmittance was higher than 60%, i.e. PAC was added when the transmittance was lower than this threshold. At the beginning of this part of the tests the dosed PAC concentration was 300 mg/L again. Since the aim was only to reach the 60% of transmittance, it was considered to decrease the PAC to be dosed. However, it was not possible to establish an optimal concentration to satisfy the requirement. This was due to the fact that both sludge withdrawal and treated wastewater caused PAC withdrawal from the system. In this way, it was decided to estimate the PAC dose to be added as a function of the sludge withdrawal and the presence of suspended solids in the effluent. Recently, it has been reported in the bibliography the difficulty in measuring the activated carbon in the effluent when PAC is added to the activated sludge reactor (Vu et al., 2012); thereby it was considered for the estimation that the presence of suspended solids in the effluent was due exclusively to the activated carbon. In this way, the equation estimating the necessity of the system, i.e. the concentration of activated carbon to be dosed, was calculated according Eq.3.

$$\mathrm{PAC_T} = \frac{(\mathrm{V_W} \cdot \mathrm{PAC_{T-1}})}{\mathrm{V_R}} + \frac{\left(\mathrm{n_{T-1,T}} \cdot \mathrm{V_D} \cdot \mathrm{SS_D}\right)}{\mathrm{V_R}} \qquad \mathrm{Eq.\,3}$$

Where, V_W is the volume of withdrawn sludge in L, PAC_{T-1} is the concentration of PAC dosed in the earlier addition (mg/L), V_R is the reaction volume (12 L), $n_{T-1,T}$ is the number of cycles between PAC additions, V_D is the decanting volume per cycle (4 L) and SS_D is the suspended solids concentration in the effluent.

It is clear that the PAC concentration is being overestimated with the application of this equation if it is aimed to maintain the PAC concentration in the reactor. However, it has to be highlighted that the objective was also to cover the renewal of the saturated PAC. Figure 4 shows the evolution of the transmittance of the treated water with the time and the PAC dosing.

Figure 4. Evolution of the transmittance at 254 nm (%) with the operating day in the tests with periodical PAC addition



From the 17th day, the concentration of PAC to be dosed was calculated as explained above, except from the addition of day 24th, since it was considered to add a higher concentration (200 mg/L) to renew the saturated PAC (the system was already working 39 days, considering the fifteen days when the dosing of 300 mg/L was tested).

The loss of PAC in the effluent was low, since the mean values of the daily measured suspended solids concentration in the effluent was 7.9 mg/L. Thus, unlike the starting phase of the addition of PAC no remarkable sedimentation problems have been observed. Concerning COD removal, the mean value of the COD in the effluent was 38 mg/L (standard deviation of 11 mg/L). Thus, the average COD removal efficiency was 93.7% and no problem with the biological process were detected. Results demonstrate that the additions of PAC led to maintain the transmittance higher than 60%. If the total mass of RB-5 entering the SBR and the total mass of PAC added in this part of the experiment (41 days), the relation of both is 4.92 g RB-5/15.78 g PAC, i.e. 0.3g/g.

CONCLUSIONS

RB-5 is an azo-dye that is not degraded in a conventional wastewater treatment plant. A SBR treating simulated wastewater with 10 mg/L of RB-5 only could reduce the color in a 50% by dilution and adsorption in the activated sludge. The transmittance of the treated wastewater was round 40%. After tests with two PACs, CLARIMEX 061 CAE was selected as the most appropriate one to separate the dye. After addition of different PAC concentrations it was concluded that the addition of PAC could be performed according to a calculation depending on the loss of PAC by sludge withdrawal and by its presence in the final effluent. The overestimation of the PAC lost from the system covered the saturated PAC and the transmittance could be maintained over 60% with a relation between RB-5 and PAC to reach the aimed treated water transmittance was of 0.3 g/g.

Acknowledgement

Authors thank Depuración de Aguas del Mediterráneo S.A. for its support in the work.

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