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*Full Length Research Paper*

# Improvement of COD and TOC reactive dyes in textile wastewater by coagulation chemical material

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**This study was designed to investigate the removal of reactive dyes, Samofix Red V-RBL and Samofix Green V-G from wastewater using a two step Al (III) coagulation/activated carbon adsorption method. The effects of pH and coagulant dosage as well as the effects of contact time and a powdered activated carbon dosage on dye removal were studied. The process was optimized with reasonable consumption of coagulant and quantity of obtained sludge. Coagulation as a main treatment process followed by adsorption achieved almost total elimination of both dyes from wastewater with significant reduction (90%) of chemical oxygen demand (COD), total organic carbon (TOC) and absorbable organic halide (AOX). Besides high efficiency of dye removal, the combined treatment process offers many advantages for potential application such as coagulant savings, minimal amount of sludge formation and also an economic feasibility since it does not require high costs for chemicals and equipments.**

**Key words:** Reactive dye, textile wastewater, coagulation material, COD, TOC.

## INTRODUCTION

Wastewater generated by the dye production industry and many other industries which use dyes and pigments is characteristically high in both colour and organic content. About 10,000 different commercial dyes and pigments exist, and over 7 x $10^5$ tonnes are produced annually worldwide. It was estimated that about 10 - 15% of these dyes are released in effluents during dyeing processes (Gejdzicki, 1998).

Reactive dyes represent an increasing market share (currently about 20 - 30%) of the total market for dyes because they are used to dye cotton which makes up about half of the worlds fibre consumption. A large fraction, typically around 30%, of applied reactive dye is wasted because of dye hydrolysis in the alkaline dyebath. Conventional wastewater treatment plants which rely on aerobic biodegradation have low removal efficiency for reactive and other anionic soluble dyes (Arslan, 2001). The discharge of highly colored waste is not only aesthetically displeasing, but it also impedes light penetration thus upsetting biological processes within a stream.

In addition, many dyes are toxic to some organisms and may cause direct destruction of aquatic communities. Hence, removal of dyes from such wastewaters is a major environmental problem; complete dye removal is necessary because dyes will be visible even at low concentrations (Perez et al., 2002).

During the last few years, new and stricter regulations coupled with increased enforcement concerning wastewater discharges were established in many countries. In the past, legislation has controlled the discharge of organic material by setting limits on permissible biological and chemical properties of effluents; limits can include the degree of coloration of the effluent (Bhattacharya, 1992). The ability to reclaim dye wastewater for discharge or reuse would also be a giant step toward overall waste reduction.

There are many processes available for wastewater treatment in these industries: chemical oxidation, foam flotation, electrolysis, biodegradation, adsorption, chemical coagulation and photocatalysis. Advanced oxidation processes are possibly the best technologies to totally eliminate organic carbons in wastewater, but these processes are only effective in wastewater with very low concentrations of organic dyes (Montazer, 2001). Thus, significant dilution is necessary as a facility requirement. In addition, these processes are too expensive and com-

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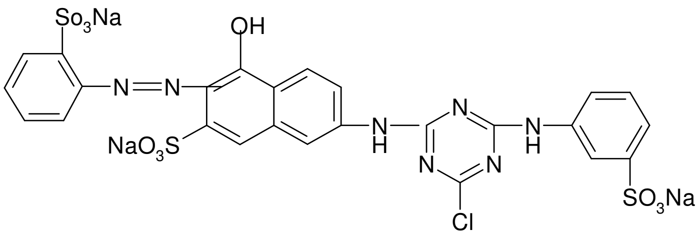
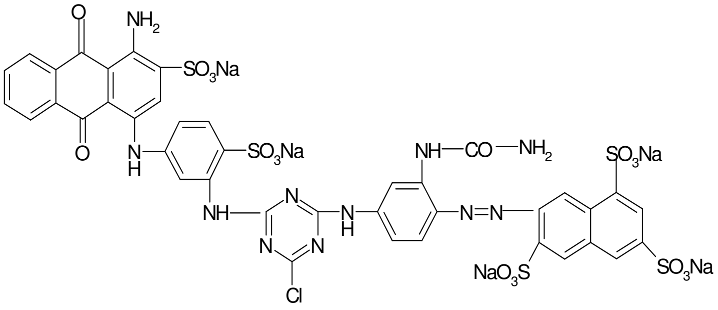
**Table 1**. Dye structures and their max values.

| Dye | Structure | Max (nm) |
|---|---|---|
| Samofix red -RBL<br>(C. I reactive Red 45) |  | 520 |
| Samofix greenv-G<br>(C. I reactive Green 8) |  | 430 |

plex at the present level of their development. The coagulation/flocculation process is in extensive use for premain or post-treatment and full decolourization is possible by this process. The limitations of coagulation/ flocculation are that it is not always effective and there are problems associated with sludge disposal; hence the interest in coagulant recovery stems, not only from the potential savings in chemical costs but also from substantial reductions in sludge volume. Some research has been conducted to show the feasibility of recycling the coagulants (Legrini et al., 1993).

In the present study, the removal of reactive dyes from wastewater by the combination of Al (III) coagulation and activated carbon adsorption was investigated. Low cost adsorbents like those obtained from waste materials have an economic advantage, but they are much less effective than activated carbon (Neamtu et al., 2002). two commercial reactive dyes, Samofix Red V-RBL and Samofix Green V-G were chosen for this study. The purpose of the present work was to lower the coagulant consumption using activated carbon in the final polishing step and to achieve complete dye removal. This approach offers a simple and economic "end of pipe'' solution to the challenges set by new legislation covering dye wastewater discharges. Water reuse may be possible as well (Yediler et al., 2000).

## MATERIALS AND METHODS

As in previous studies, the experiments were conducted using two commercial reactive dyes (Samofix red V-RBL) and (Samofix Green V-G) manufactured by Colour and Chemical Switzerland Co. The chemical structures and $\lambda_{max}$ values are shown in Table 1.

Calibration curves were made for each dye at its absorbance maximum. The synthetic wastewater was prepared by dissolving the dyes into distilled water. The concentration of the dye solutions was 1 $gl^{-1}$. The jar test procedure was applied at room temperature which ranged from 20 - 25°C and at various coagulant dosages (0.4 - 5.0 $gl^{-1}$) and pH conditions (3 - 5 units). The coagulant used was alum chloride $AlCl_3.6H_2O$ having a gram molecular weight of 241.45. The coagulant was added to 500 ml beakers containing synthetic wastewater and mixed using magnetic stirrers at 300 rpm for 1 min. The pH was varied by adding HCl or $Na_2CO_3$ (Kemika) after coagulant addition. The stirring speed was adjusted thereafter to 50 rpm for the next 20 min. Sedimentation period followed and after 2 h, the height of sludge was measured and the dye concentration of the supernatant determined using SPEKOL 210 MA 9525- Iskra spectrophotometer. The height of the precipitate was measured and the percentage of the sludge volume in the overall treated wastewater volume was calculated. The adsorption experiments were conducted by adding different amounts (0.05, 0.10, 0.25, 0.50, 1.00, 1.50 and 2.50 g) of powdered activated carbon (PAC) by Kemika, into the flask containing 100 ml of synthetic wastewater after a chosen coagulation treatment and pH adjustment to pH 6. After magnetic stirring at a constant temperature (20°C) for a certain period (1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 h), the sample taken from the flask was filtered through a Whatman's glass microfiber filter. The filtrate was then measured for the dye concentration. The results of adsorption experiments were used to determine equilibrium isotherms for both dyes. A standard method based on oxidation of oxidable components in the sample has been used for chemical oxygen demand (COD) measurements. The reaction is made in the closed ampule and the oxygen quantity is measured colorimetricaly with a spectrophotometer at 600 nm with standard. The concentrations of the total organic carbon (TOC) were determined using TOC-VCPN, Total Organic Carbon Analyzer 5000 a, Shimadzu. The concentrations of the adsorbable organic halide (AOX) were measured using Halide Analyzer DX-2000.

**Table 2.** The effect of coagulant dose and pH on removal of RR V-RBL dye[a] (%).

| pH | Coagulant dose | | | | |
|---|---|---|---|---|---|
| | **0.3 $gl^{-1}$** | **0.6 $gl^{-1}$** | **1.3 $gl^{-1}$** | **2.5 $gl^{-1}$** | **4.5 $gl^{-1}$** |
| 3.5 | 17.1 | 58.9 | 59.9 | 39. 9 | 42.9 |
| 4 | 35.9 | 70.9 | 79.9 | 59.8 | 50.9 |
| 4.5 | 65.1 | 97.9 | 98.8 | 99.2 | 99.1 |
| 5 | 83.2 | 99.0 | 98.9 | 88.0 | 73.5 |
| 5.5 | 62.9 | 95.8 | 99.7 | 98.8 | 98.4 |

[a] The numbers in bold are the highest percentages of dye removal achieved with particular coagulant doses

**Table 3.** The effect of coagulant dose and pH on removal of RGV-G dye[a] (%).

| pH | Coagulant dose | | | | |
|---|---|---|---|---|---|
| | **0.3 $gl^{-1}$** | **0.6 $gl^{-1}$** | **1.3 $gl^{-1}$** | **2.5 $gl^{-1}$** | **4.5 $gl^{-1}$** |
| 3.5 | 32.9 | 73.9 | 71.1 | 64.9 | 75.8 |
| 4 | 47.8 | 87.8 | 72.9 | 99.1 | 97.0 |
| 4.5 | 83.7 | 95.9 | 97.1 | 99.0 | 91.0 |
| 5 | 56.9 | 98.6 | 99.6 | 99.4 | 92.9 |
| 5.5 | 66.8 | 83.9 | 90.9 | 99.0 | 76.1 |

[a] The numbers in bold are the highest percentages of dye removal achieved with particular coagulant doses.

## RESULTS AND DISCUSSION

The combined coagulation/carbon desorption process for reactive dye removal from synthetic wastewater was performed as a two step process whereby coagulation was followed by adsorption. Chemical coagulation using Al (III) as a coagulant was shown to be highly effective in the removal of both dyes. The interdependence of optimum pH, coagulant dose and dye removal are shown in Tables 2 and 3. It can be seen that to achieve good dye removal (higher than 90%) the pH should be between 3.5 and 5.0 and coagulant dose should be greater than 0.4 $gl^{-1}$. The appearance of the maximum in dye removal could be explained by the combined effect of; 1) the ionisation of sulpho, amino and hydroxy groups in the dye molecule, which increases with pH and; 2) the decrease in the concentration of dissolved Al (III) hydrolysis products when pH increases. The magnitude of the maximum dye removal and the pH value at which the maximum occurs depends on the coagulant dose. A broad optimal pH range does not occur for all applied coagulant doses. The broadest pH range is at coagulant doses of 3.0 and 1.3 $gl^{-1}$ for RR V-RBL and RGV-G, respectively. From the results presented in Tables 2 and 3, it can be seen that almost complete dye removal (99.6% RR V-RBL and 99.7% RGV-G) could be achieved with 1.3 $gl^{-1}$ alum coagulant at pH 4.5 - 5.5. Similar results were obtained for treatment of the same wastewater with $Fe_3$ coagulation. These large percentages of dye removal lead to residual dye concentrations under 0.001 $gl^{-1}$ that satisfy regulatory requirements. Since the presence of a dye in wastewater can be observed at very low dye concentration, 0.001 $gl^{-1}$ is visible; it is necessary to achieve complete dye removal using an efficient treatment process.

It has to be emphasized that for maximum dye removal with coagulant treatment, a large volume of sludge is formed which can be seen in Figure 1. Although a large percentage of dye removal (99.7%) could be achieved by coagulation; for industrial application it is necessary to optimize the process by means of reasonable consumption of coagulant and quantity of obtained sludge. Results of the present work showed that approximately half of the coagulant dose 0.6 $gl^{-1}$ leads to significantly less sludge in comparison with that used for the maximum dye removal 1.3 $gl^{-1}$. Therefore, the percentage of dye removal is decreased by only 1%, from 99.6 to 98.6% for RR V-RBL and from 99.7 to 99.0% for RGV-G (Tables 2 and 3) while the sludge volume is significantly decreased from 18 to 8% RR V-RBL and from 13 to 6% for RGV-G (Figure 1). Concerning coagulant savings and the decrease in sludge volume, the use of the coagulation process in combination with other

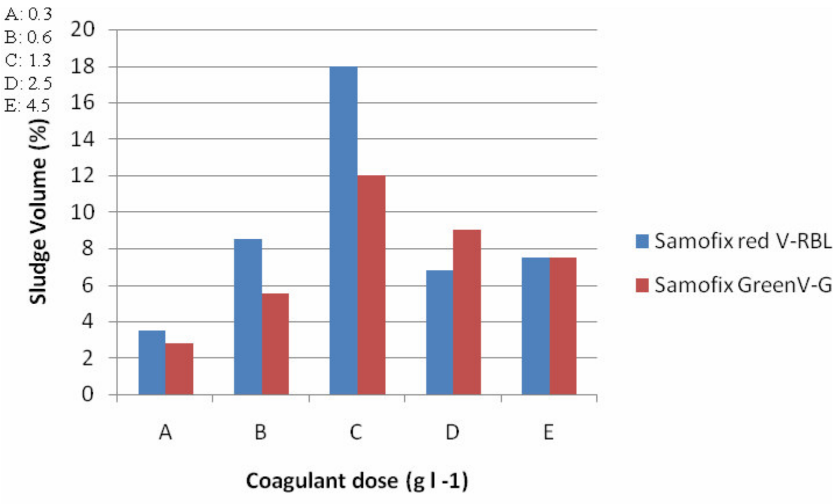


**Figure 1.** The volume of sludge formed at maximum removal of RR V-RBL and RG V-G using different coagulant doses

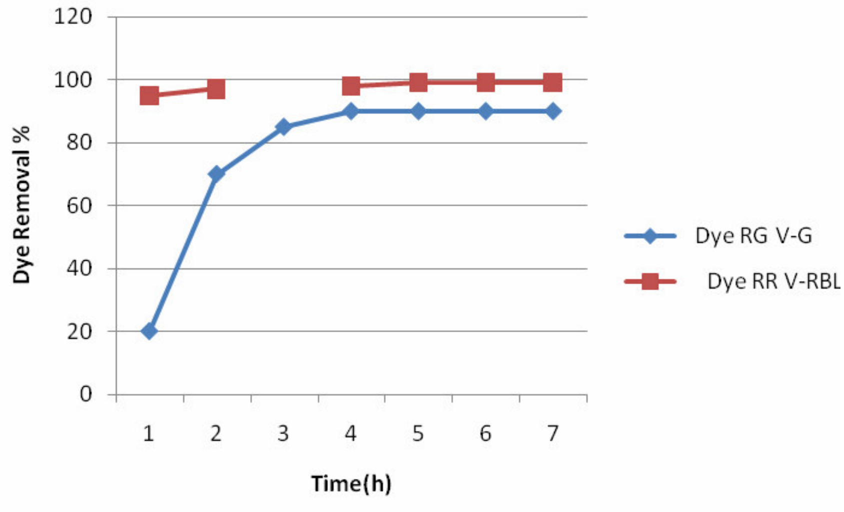


**Figure 2.** Kinetics of dye removal by PAC (1.5 gl$^{-1}$) at concentration of residual dye in water after coagulation treatment (0.012 gl$^{-1}$ RR V-RBL and 0.010 gl$^{-1}$ RG V-G).

processes is recommended. Because the dyes are visible even at very low concentrations, the treatment process has to provide complete removal of dye from the wastewater. In the present work, adsorption onto PAC was applied as a finishing and a polishing step after coagulation with half the coagulant dosage of 0.6 gl$^{-1}$. The removal of RR V-RBL and RG V-G by PAC as functions of contact time is shown in Figure 2. Under the conditions of the experiment, both cases approached equilibrium within 2 h contact times for which maximal dye removals of 98% for RR V-RBL and 91% for RG V-G were achieved. The effect of PAC dosage on dye removal can be seen from Figure 3, which shows that dye removal increases with dosage rate up to a maximum after which an increase in the amount of PAC used does not improve dye removal.

The experimental data have been used to evaluate the experimental constants of the Freundlich adsorption isotherm equations. The equation is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface. The equation for this type of adsorption isotherm is given by:

$$X/M = kce1/n \qquad (1)$$

where ce is equilibrium concentration of impurity in solution (mg l$^{-1}$), x/m is the amount of impurity adsor-

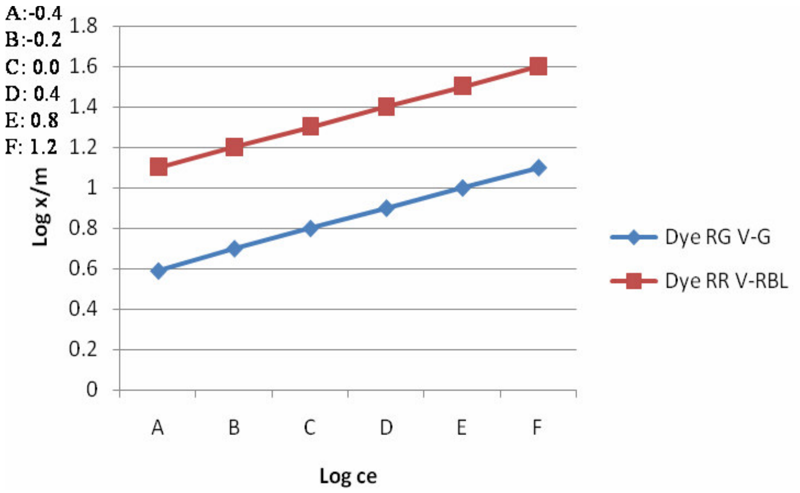


**Figure 3.** The percentage of dye removal PAC dosage at concentration of residual dye in water after coagulation (0.012 gl$^{-1}$ RR V-RBL and 0.010gl$^{-1}$RG V-G).

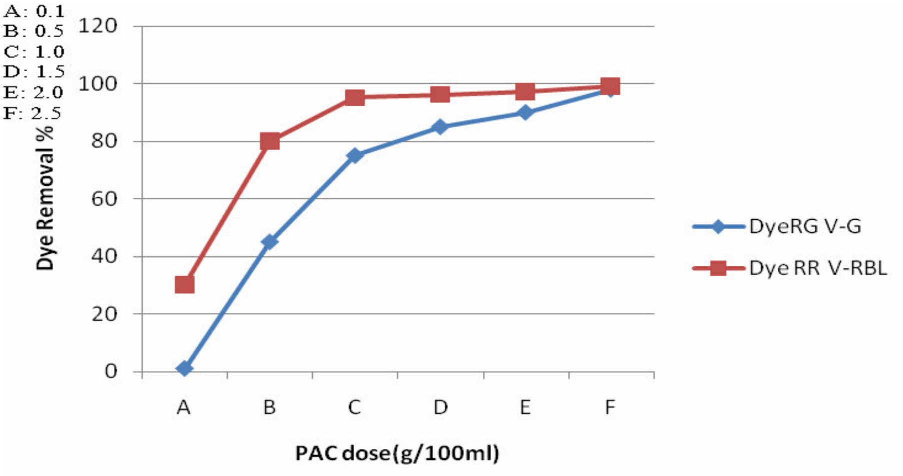


**Figure 4.** Freundlich plots for the adsorption of dyes RR V-RBL and RG V-G on PAC.

**Table 4.** Freundlich isotherm parameters for dyes RR V-RBL and RG V-G adsorption from aqueous solutions (pH 6 and 20°C) on PAC.

| RR V-RBL | Samofix Green V-G |
|---|---|
| K = 2.722<br>1/n = 1:192<br>a*$R^2$ = 0.989 | K = 2.005<br>1/n = 0:795<br>$R^2$ = 0.989 |

bed per unit of adsorbent (mg gl$^{-1}$), k represents the quantity of impurity adsorbed in mg gl$^{-1}$ adsorbent for a unit equilibrium concentration of the compound under test (that is, ce= 1), and 1/n is a measure for the adsorption intensity.

Freundlich adsorption plots of dyes RR V-RBL and RG V-G on PAC are shown in Figure 4. The adsorption capacity of RR V-RBL is much higher than that of RG V-G. The greater affinity of RR V-RBL for PAC than RG V-G can be attributed to the chemical structure of the dyes. The molecular structures of the dyes have a significant effect on the extent to which they will adsorb to activated carbon. In general, adsorbability is enhanced by increasing molecular size and aromaticity, and by decreasing solubility, polarity and carbon chain branching. RG V-G is a larger molecule than RR V-RBL (Table 1) but it contains more sulphonic acid groups which decreases adsorbability on PAC.

The Freundlich adsorption parameters of both dyes on PAC are listed in Table 4. The R2 values indicate the Freundlich type of isotherm and its adsorption

**Table 5.** The efficiency of coagulation (Treatment 1) and combined process coagulation/carbon adsorption (Treatment 2) in reactive dye wastewater treatment expressed by percentage of dye concentration, TOC, COD and AOX reduction.

| Treatment | Before treatment | After Treatment 1 | After Treatment 2 |
|---|---|---|---|
| Samofix Red V-RBL c ($gl^{-1}$) | 1.0 | 1.2 $10^{-2}$ | 2.4 $10^{-4}$ |
| c reduction (%) | – | 98.8 | 99.9 |
| TOC ($mgl^{-1}$) | 755 | 13 | 3 |
| TOC reduction (%) | - | 98.3 | 99.8 |
| COD ($mgl^{-1}$) | 892 | 58 | 37 |
| COD reduction (%) | – | 93.2 | 95.5 |
| AOX ($mgl^{-1}$) | 5530 | 37 | 9 |
| AOX reduction (%) | – | 99.2 | 99.7 |
| Samofix Green V-G c ($gl^{-1}$) | 1.0 | 1.0 $10^{-2}$ | 9.0 $10^{-4}$ |
| c reduction (%) | – | 98.9 | 99.8 |
| TOC ($mgl^{-1}$) | 383 | 12 | 3 |
| TOC reduction (%) | – | 96.9 | 99.2 |
| COD ($mgl^{-1}$) | 470 | 76 | 41 |
| COD reduction (%) | – | 83.8 | 91.3 |
| AOX ($mgl^{-1}$) | 4262 | 20 | 7 |
| AOX reduction (%) | - | 99.5 | 99.7 |

experimental data.

Almost complete removal of these dyes from synthetic wastewater was achieved by using Al (III) coagulation pretreatment followed by carbon adsorption as can be seen in Table 5. With a single coagulation treatment (Treatment 1), more than 90% reduction of ecological parameters (TOC, COD, and AOX) was obtained. This reduction was improved further after the PAC finishing step (Treatment 2). The most significant result is that the combination of coagulation and adsorption resulted in water quality where the dye was no longer visible (that is, < 1 $mgl^{-1}$). The same water quality could be obtained by coagulation only, but with a much larger quantity of coagulant as well as a much greater volume of sludge. It would be of more practical and economic significance to operate such a combined process because of the capability of total de-colourization, coagulant savings and the minimal amount of sludge formation. The consumption of PAC is not large and can be calculated from the maximal adsorption capacity (X/M). The maximum carbon capacities are 41.0 $mgl^{-1}$ for RR V-RBL and 11.8 $mgl^{-1}$ for RG V-G, which can be seen in Figure 4. The quantities of carbon required to treat 1 L of wastewater are 0.24 g for RR V-RBL and 0.85 g for RG V-G.

Chemical coagulation is applied as a pre- and main- process for the treatment of municipal, pulp and paper and tannery effluents. For treatment of effluents resulting from dye manufacturing and textile industry, coagulation is applied as a post-treatment process. There is a lack of established data and there are no comparative studies on dye coagulation, particularly of reactive dyes present in wastewaters. On the other hand there is much research data concerning the degradation of dyes in wastewater by advanced oxidation processes (AOPs).

In the present investigation coagulation was applied as a main treatment process because of the high concentration of reactive dyes in wastewaters and requirements for not only complete decolourization but also for the removal of organic content to obtain acceptable values of ecological parameters in treated water. Sarasa et al. (1998) studied a combined ozone/chemical coagulation treatment of wastewater resulting from dye manufacturing and established that ozone is not very effective in removing azo dyes, but coagulation treatment is very active in removing the remaining compounds of ozonaton including those from azo dyes. They used $Ca(OH)_2$ as a coagulant with consumption of 787 $mgl^{-1}$. The results of their experimental work show that ozonation offers an excellent means for decolourization of textile wastewater, but it is relatively ineffective in reducing the COD in a short time period.

Chemical coagulation is rather effective in reducing the COD content after ozonation and the COD removal efficiency was between 41 and 66%. The COD concentration above 300 $mgl^{-1}$ of the treated wastewater indicated the need for activated sludge treatment to further reduce COD. Similar studies on dye house effluents containing commercially important reactive dyes were carried out by Arslan et al. (2001). Complete decolourization was achieved after only 5 min of ozonization with 8% TOC and 25%

COD removal. In the present study, coagulation as a main treatment process followed by activated carbon adsorption achieved almost total elimination of both dyes from wastewater as well as 95.5 and 91.3% COD, 99.8 and 99.2% TOC and 99.7% AOX removal in RR V-RBL and RG V-G wastewater. The ecological parameters of synthetic wastewater treated by the combined process of coagulation/carbon adsorption (Table 5) imply that the water can be discharged into the environment or reused as process water.

## Conclusions

The applied process, Al (III) coagulation/carbon adsorption, achieved complete decolourization and almost total elimination (99.9%) of both reactive dyes from wastewater as well as 95.5 and 91.3% COD, 99.8 and 99.2% TOC and 99.7% AOX reduction in RR V-RBL and RG V-G wastewater, respectively. This result was obtained with half the coagulant consumption and lower volume of sludge formation in comparison with dye removal by coagulation only and by small amounts of activated carbon. This combined treatment process offers many advantages for potential industrial use such as high efficiency, coagulant savings, minimal amount of sludge formation, high quality of treated water, possibility for the potential reuse of water and also economic feasibility since it does not require high costs for chemicals and equipments.

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