4

Alkaline Degradation of Some Basic Dye Due to Sodium Hypochlorite and the Fate of COD Load in Aqueous Environment

Mitali Sarkar, Mahadeb Das
University of Kalyani, India

1. Introduction

Textile industry is an important industry among the different industries in India. A variety of synthetic complex organic dyes is often used by textile industries as the coloring materials of the textile goods for their bright and attractive look. Subsequently due to discharge, the textile wastewater contains a huge amount of dye, causing a great extent of pollution [1]. Recent estimates indicate that approximately 12% of synthetic dyes used every year are lost during manufacture and processing operations and enters the aqueous environment [2]. Dyes include a broad spectrum of different chemical structures, primarily substituted aromatic compounds with heterocyclic groups. Most of these are the suspected carcinogens [3]. Due to their complex chemical structure the organic dyes remain fast for the lifetime of the fabric, do not breakdown on exposure to sunlight, water, soap, etc. and therefore the treatment of dye wastewater is very difficult [4÷9]. Color in wastewater is an obvious indicator of water pollution due to dye and pigment [10]. The characteristics of the wastewater from a dye house are highly variable from day to day, and even hour to hour, depending on the type of dye, the type of fabric and concentration of the fixing agents added. The discharge of dye house wastewater into the environment is aesthetically displeasing, impedes light penetration, damages the quality of the receiving stream and may be toxic to treatment process, to food chain organisms and to aquatic life. As the degradation of dye molecules in the environment by microorganisms is likely to be slow [11], it is possible for high levels of dye to persist, and potentially accumulate. Further, it is difficult to eliminate color from wastewater by conventional flocculation or biodegradation. The development of ecologically and economically viable method for reactive dye removal is therefore a worthwhile task to meet the high specific water demand of the textile finishing industry.

Several techniques ranging from physico-chemical to biological methods for dye removal are available. The performance operation depends largely on the dye load, presence of other chemical components as well as the organic load. Post dying wastewater treatment following co precipitation and sorption processes are evaluated by Anielak in a recent review [12]. Other chemical processes are oxidative degradation using O_3, H_2O_2, Peracids, Fenton's reagent as well as electrochemical oxidation, alum treatment and adsorption [13÷16]. Biodegradation potential of different dyes as well as their influence upon the work of activated sludge can be assessed from the work of Anielak [17]. Alkaline fading of some azo dyes are reported in the literature [18, 19]. The present study deals with alkaline fading of malachite green, a triphenylmethne dye, from aqueous solution using sodium hypochlorite solution and the fate of COD load for this operation.

2. Materials and methods

All the chemicals of the present investigation were of AnalR grade. The dye, malachite green (formula weight 364.9) or C.I. Basic green 4 (C.I. 42,000) was obtained from E. Merck Limited, India. The dye was further purified by recrystallisation. Solution of NaOCl (approximately 4% w/v available chlorine) was obtained from BDH, E. Merck Limited, India. The desired concentrations of NaOCl for the experiments were made subsequently. A Shimadzu UV-VIS recording spectrophotometer (model no. UV-2401PC) was used for the absorbance measurement.

3. Experimental procedure

With the pure malachite green, a stock solution ($5.01.10^{-5}$ $mol.dm^{-3}$) was made dissolving it in de-ionized water. An aliquot of 20 cm^3 of MG solution is pipetted into test tube, kept in a water bath equipped with a contact thermometer. Sodium hypochlorite solution of desired concentration was added to it and the dye concentration at a regular interval of time was evaluated from the absorbance value at 617 nm. The volume of NaOCl is so maintained that the dilution effect is negligible. The blank experiment shows further that there is no adherence or adsorption of MG on the container walls. Three sets of experiments were performed as follows:

- varying dye concentration for a fixed concentration of NaOCl and the temperature,
- varying NaOCl concentration for a fixed concentration of dye and the temperature,

- varying temperature for a fixed concentration of dye and a fixed concentration of NaOCl and at each case the dye concentration in the solution is measured.

4. Results and discussion

Malachite green (MG), an important member of the triphenylmethane dyes shows the absorption maxima (λ_{max}) at 617 nm. The intense color of dye is caused by the extended conjugated system among three phenyl rings. The absorbance of malachite green is directly proportional to its concentration and follows the Lambert Beer's law in the concentration range $2.0.10^{-5}$ to $1.0.10^{-6}$ moldm^{-3}. Five replicate determinations of the dye absorbance value at 617 nm indicate the reproducibility with standard deviation 0.005. The modeling of fading of MG with time requires the optimization of operational variables like concentration of both the dye and NaOCl, time and temperature. The study involves variation of one variable at a time and keeping all other variables fixed.

4.1. Effect of initial dye concentration on the fading pattern of MG

The fading behavior of MG in aqueous solution by NaOCl was studied by monitoring the change of dye absorption at 617 nm. With lapse of time, the absorbance value was found to decrease as shown in Fig 1. The data for the absorbance-time profile can well be fitted to a polynomial of 5th degree with a correlation factor of 0.9986 for dye concentration $1.05.10^{-5}$ moldm^{-3} and NaOCl concentration $1.0.10^{-4}$ moldm^{-3}. Similar nature of curves but with different absorbance values were observed for other dye concentrations ranging from $1.19.10^{-5}$ to $5.7.10^{-6}$ moldm^{-3}. The data corresponding to each curve was fitted in the 5th degree polynomial in a variable time (t) in the following equation (1),

$$Abs = a_0 + a_1.t + a_2.t^2 + a_3.t^3 + a_4.t^4 + a_5.t^5 \qquad (1)$$

The corresponding coefficients a_0-a_5 for the polynomial were evaluated (Table 1) from the work spread sheet of Excel Microsoft computer programming.

The absorbance data from the figure 1 were utilized to calculate the percent decrease in dye concentration, correspond to fading or decolorization, which was plotted against time in Fig 2. It is observed that the extent of dye fading is different and depends on the initial dye concentration taken. For a fixed concentration of NaOCl, more the dye concentration less is the extent of fading. Further, it is evident from the figure that about 93.6% fading occurs in 30 minutes for $1.05.10^{-5}$ moldm^{-3} dye. Within the dye concentration range from $1.19.10^{-5}$ to $5.7.10^{-6}$ moldm^{-3} and fixed NaOCl concentration ($1.0.10^{-4}$ moldm^{-3}) fading was however found to increase from 91.8 to 98.3%.

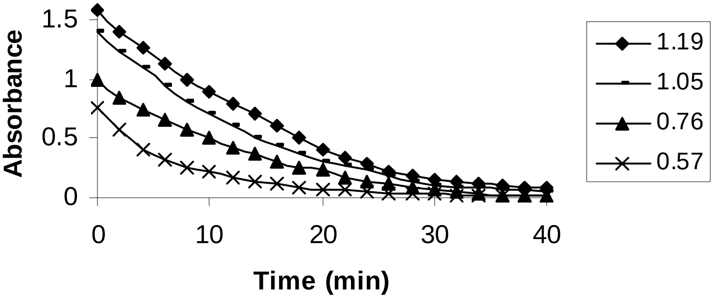

Fig. 1. Degradation pattern for variable dye and fixed hypochlorite concentration
Rys. 1. Krzywe obniżki dla zmiennego stężenia barwnika i stałego stężenia podchlorynu

Table 1. Coefficient of the polynomial and correlation coefficient values for fixed $[OCl^-]$ and variable [MG] at 303K
Tabela 1. Wartości współczynników wielomianu oraz współczynników korelacji dla stałego stężenia OCl^- i zmiennego stężenia zieleni malachitowej (ZM) w temperaturze 303K

$[MG].10^5$ $(moldm^{-3})$	a_0	$-a_1.10^2$	$a_2.10^3$	$-a_3.10^5$	$a_4.10^5$	$-a_5.10^8$	R^2
1.19	1.587	9.586	4.236	21.189	0.585	5.736	0.9982
1.05	1.401	8.759	1.728	-1.232	-0.104	-1.239	0.9988
0.76	0.993	7.213	3.180	11.900	0.264	2.291	0.9899
0.57	0.496	5.703	0.579	-1.622	-0.006	-0.545	0.9897

$[OCl^-] = 1.0.10^4$ $moldm^{-3}$

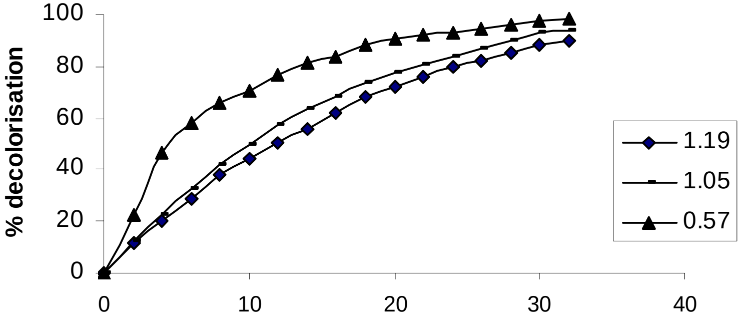

Fig. 2. Percent decolorisation for variable dye and fixed hypochlorite concentration
Rys. 2. Odbarwienie w % dla zmiennego stężenia barwnika i stałego stężenia podchlorynu

4.2. Effect of NaOCl concentration on the fading of MG

The effect of NaOCl concentration on the fading of MG was investigated keeping the dye concentration fixed ($1.05.10^{-5}$ $moldm^{-3}$) and varying the NaOCl concentration ($1.0.10^{-4}$ to $2.75.10^{-5}$ $moldm^{-3}$). The corresponding absorbance–time profile is presented in figure 3. The absorbance data are fitted to a polynomial of degree 5, similar to equation (1). The polynomial coefficients (a'_1-a'_5) corresponding to each curve are presented in table 2. The correlation factors are found to be > 0.9897. This suggests that the data can be well fitted to the 5th degree polynomial. The percent decrease of dye concentration or the extent of dye fading for each NaOCl concentration is plotted against time in figure 4. A greater extent of dye fading is observed in case of NaOCl with higher concentration. In a typical experiment with a fixed dye concentration ($1.05.10^{-5}$ $moldm^{-3}$) as the NaOCl concentration increases from $1.0.10^{-4}$ to $2.75.10^{-5}$ $moldm^{-3}$, extent of dye fading increases from 64.3 to 93.6%.

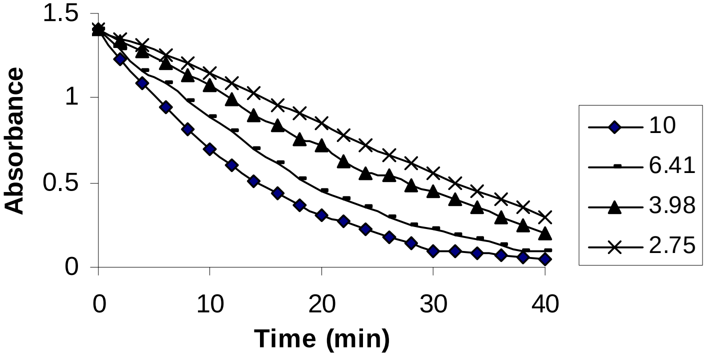

Fig. 3. Degradation pattern for fixed dye and variable hypochlorite concentration
Rys. 3. Krzywe obniżki dla stałego stężenia barwnika i zmiennego stężenia podchlorynu

Table 2. Coefficient of the polynomial and correlation coefficient values for fixed [MG] and variable [OCl^-] at 303K
Tabela 2. Wartości współczynników wielomianu oraz współczynników korelacji dla stałego stężenia ZM i zmiennego stężenia OCl^- w temperaturze 303K

$[OCl^-].10^5$ ($moldm^{-3}$)	a'_0	$-a'_1.10^2$	$a'_2.10^3$	$-a'_3.10^5$	$a'_4.10^5$	$-a'_5.10^8$	R^2
10.01	1.401	8.759	1.728	-1.232	-0.104	-1.239	0.9988
6.42	1.394	5.270	0.002	-8.041	0.005	1.085	0.9898
3.98	1.395	2.801	-0.752	-1.247	0.007	1.502	0.9977
2.75	1.400	2.388	0.002	2.878	0.115	1.253	0.9989

$[MG] = 1.05.10^5$ $moldm^{-3}$

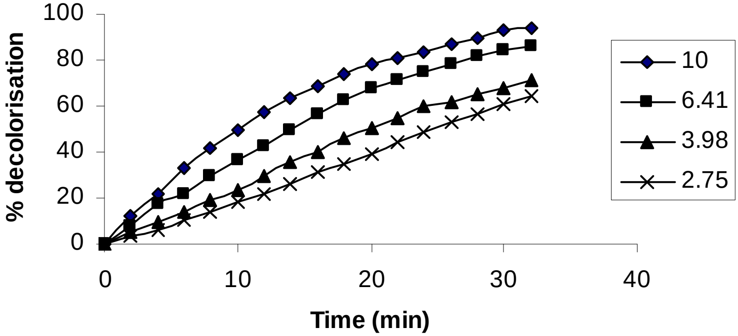

Fig. 4. Percent decolorisation for fixed dye and variable hypochlorite concentration
Rys. 4. Odbarwienie w % dla stałego stężenia barwnika i zmiennego stężenia podchlorynu

4.3. Effect of temperature

In order to investigate the effect of temperature on MG fading, the study was made for a fixed dye ($1.05.10^{-5}$ moldm^{-3}) and NaOCl ($1.0.10^{-4}$ moldm^{-3}) concentration at four different temperatures from 293 to 308 K. A blank experiment was performed for each temperature. This shows no change in dye concentration itself due to temperature variation. The absorbance-time profile curve for each temperature is presented in figure 5. The absorbance data were fitted to a polynomial of 5th degree, similar to equation (1). The corresponding polynomial coefficients (a''_1-a''_5) and the correlation factors are given in table 3. Higher values of correlation factors (> 0.9987) were obtained. Figure 6 represents the extent of dye fading (the percent decrease in dye concentration) with lapse of time. It is observed that the extent of dye fading increases as the temperature increases. With temperature increase from 293 to 308 K the extent of dye fading increases from 69.3 to 98.6% within 22 minutes for the present MG ($1.05.10^{-5}$ moldm^{-3}) and NaOCl ($1.0.10^{-4}$ moldm^{-3}) system.

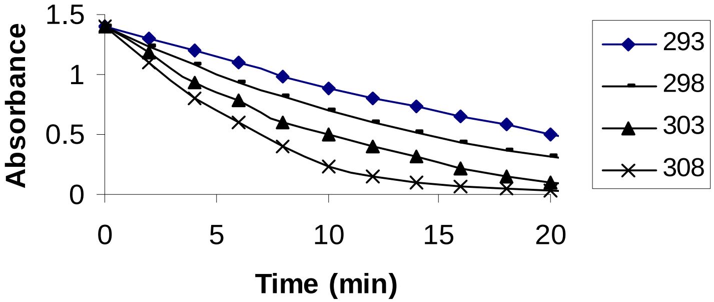

Fig. 5. Degradation pattern at different temperatures
Rys. 5. Krzywe obniżki przy różnych temperaturach

Table 3. Coefficient of the polynomial and correlation coefficient values for fixed [OCl$^-$] and [MG] at variable temperatures

Tabela 3. Wartości współczynników wielomianu oraz współczynników korelacji dla stałego stężenia OCl$^-$ i ZM w przy różnych temperaturach

Temp (K)	a''_0	$-a''_1.10^2$	$a''_2.10^3$	$-a''_3.10^5$	$a''_4.10^5$	$-a''_5.10^8$	R^2
293	1.402	17.442	10.527	114.674	9.287	250.441	0.9994
298	1.403	11.805	- 1.426	-81.448	-4.986	-96.331	0.9987
303	1.401	8.759	1.728	-1.232	-0.104	-1.239	0.9988
308	1.406	5.484	0.213	-2.429	-0.007	-0.779	0.9989

[MG] = $1.05.10^5$ moldm^{-3} ; [OCl$^-$] = $1.0.10^4$ moldm^{-3}

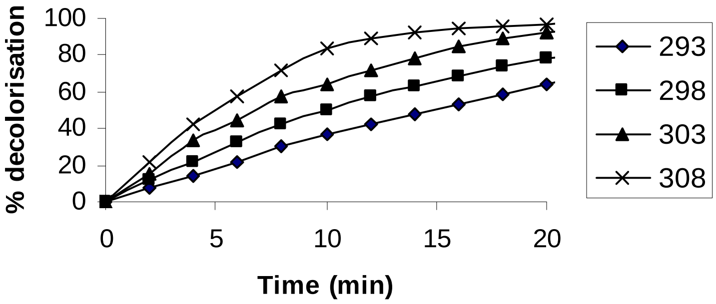

Fig. 6. Percent decolorisation at different temperatures

Rys. 6. Odbarwienie w % przy różnych temperaturach

4.4. Kinetics of fading

It is observed from figure 2 that the $t_{1/2}$, the time required for 50% of the total fading of $1.05.10^{-5}$ moldm^{-3} MG requires only 10 minutes and 80% degradation occurs in 22 minutes. This indicates that the process is fast and kinetically feasible. The rate of reaction was measured by monitoring the absorbance of the dye solution at 617 nm where all other substances including the reaction products are transparent and no attempts were made to detect any intermediates or reaction products. Only dye concentration was calculated at different times and not the NaOCl concentration. It is found that the decrease in dye absorbance was faster at the initial stage with respect to color intensity of pure dye. The dye decolonization was much sluggish at the subsequent stages. The ‘initial rate’ method was adopted in the present situation for fitting the absorbance time data in the rate equation.

The initial degradation rate of the dye by NaOCl could be obtained as the negative of the differential coefficient of each of the fitted equations at time zero i.e. $-a_1$ from the polynomial (1) [as $-d/dt(\text{absorbance})_{t\rightarrow 0} = a_1$]. The double logarithmic plot of $-a_1$ against the dye concentration gives a straight line with a slope 1.003 as shown in fig 7. This implies that the fading of MG by NaOCl is proportional to the first power of [MG] at the initial stage of reaction. The initial rate of fading of MG under the condition of an excess of $[NaOCl]_0$ to $[MG]_0$ and constant $[MG]_0$ similarly can be obtained as $–a'_1$ from polynomial equation [table 2]. The double logarithmic plot of - a'_1 against [NaOCl] again yields a straight line with a slope of 0.9998 (Fig 8) indicating that the fading of dye is proportional to the first power of [NaOCl] at the initial stage of reaction.

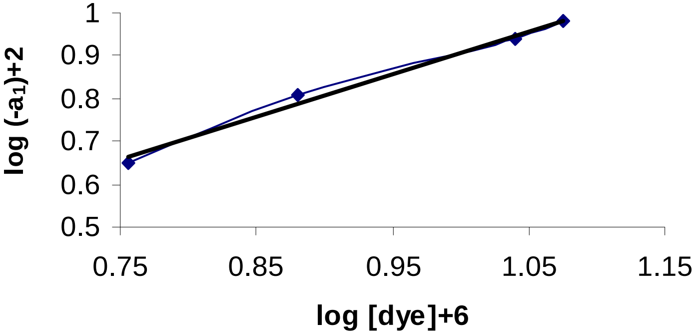

Fig. 7. Logarithmic plot between $–a_1$ and initial dye concentration
Rys. 7. Wykres logarytmiczny $–a_1$ w funkcji początkowego stężenia barwnika

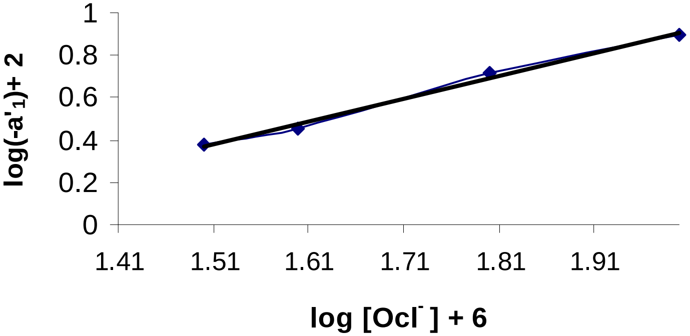

Fig. 8. Logarithmic plot between $-a'_1$ and added hypochlroite concentration
Rys. 8. Wykres logarytmiczny $–a'_1$ w funkcji stężenia dodanego podchlorynu

Thus, a kinetic model for fading of dye was assumed as being first order with respect to both [dye] and $[OCl^-]$.

$$Rate = -dC_D/dt = k_1.[dye].[OCl^-] \tag{2}$$

where k is the rate constant ($dm^3mol^{-1}sec^{-1}$); C_D is the dye concentration ($moldm^{-3}$).

Under the condition of large excess of NaOCl, integration of equation (2) yields,

$$\ln C_t = \ln C_0 - k't \qquad (3)$$

where k' is the observed rate constant (= $k_1[OCl^{-1}]$)

A plot of $\ln C_t$ vs time yields a straight line with a slope k' (Fig. 9) with high regression parameter ($R^2 > 0.9984$). The rate constant value subsequently evaluated from k' is found to be 17.76 $dm^3mol^{-1}sec^{-1}$ at 303 K. The rate constant parameters for different temperatures were similarly evaluated from the corresponding rate equation. The rate constant value was found higher at the higher temperature. In order to find out the activation energy a plot of $\ln k_1$ vs. 1/T was made (Fig. 10) according to Arrhenius equation (4)

$$\ln k_1 = \ln A - E/RT \qquad (4)$$

where A is the frequency parameter, T is the absolute temperature, R is the universal gas constant and E is the activation energy. The activation energy thus obtained from the slope of the Arrhenius plot was found to be 16.48 $kcalmol^{-1}K^{-1}$.

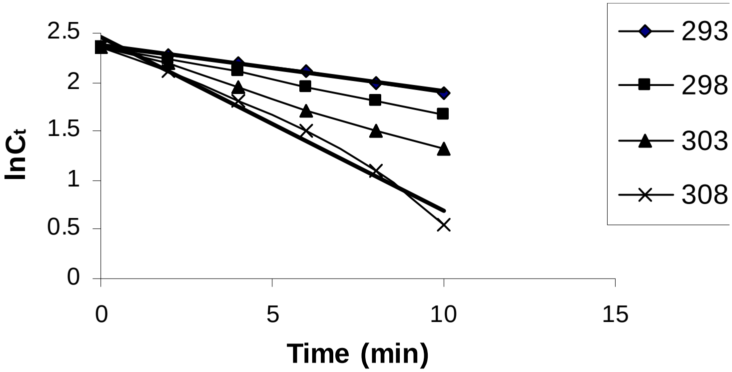

Fig. 9. Plot for evaluation of rate constant parameter
Rys. 9. Wykres do oceny stałej szybkości reakcji

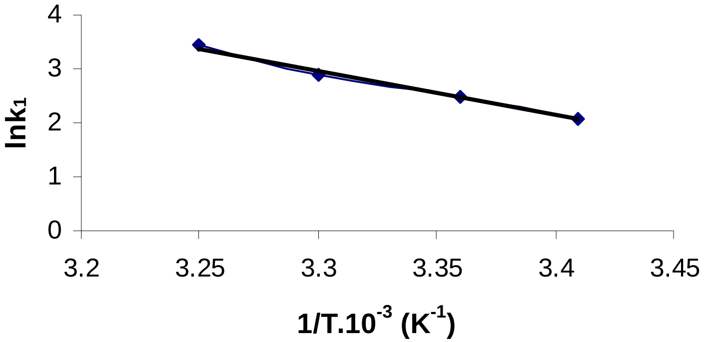

Fig. 10. Arrhenius plot for activation energy
Rys. 10. Wykres Arrheniusa dla energii aktywacji

4.5. Comparison of dye decolorization and COD removal

All the results reported so far are based on the color decay at 617 nm. In order to find out the fate of organic load due to dye degradation by NaOCl the COD of the dye solution at different times were measured by dichromate sulphuric acid oxidation method [20]. Percent COD removal was calculated as a ratio of the difference in the COD values of the pure dye and that at any time during the reaction, and for the pure dye. It is expected that with progress of dye removal with lapse of time, COD should also decrease. A comparison between the COD removal and dye degradation is presented in figure 11. It is interesting to note that at each time the dye removal is more than the COD removal. The difference between the percent dye degradation and percent COD removal during alkaline degradation reaction is probably be due to generation of some colorless intermediate organic products that contribute to COD value. Such discrepancies have also been reported for the oxidative degradation of Methylene blue and phenol [21].

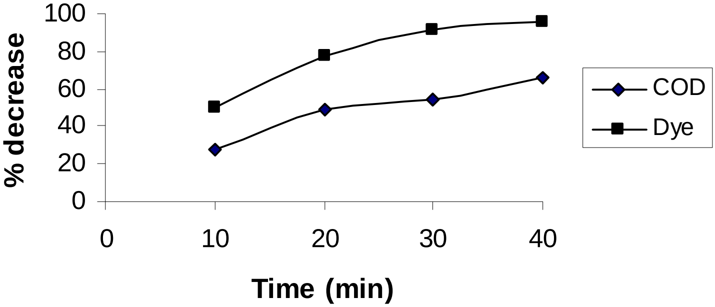

Fig. 11. Comparison between percent decrease of dye and COD
Rys. 11. Porównanie procentowej obniżki stężenia barwnika i ChZT

References

1. **Sarkar M., Poddar S.:** *Study of the Adsorption of Methyl Violet onto Fly Ash,* Anal Proc Anal Commun. 31, 213÷215. 1994.
2. Ecological sub committee project E3016 *Ecological and Toxicological Association of the Dyestuffs manufacturing Industry*. 1984.
3. **Leonas K. K., Leonus M. L.:** *Textile Process Wastewater Permits: An Update and Strategies,* Am. Dyers Rep 83, 26÷34. 1994.
4. **Chern J., Wu C.:** *Desorption of dye from activated carbon beds: Effect of temperature, pH and alcohol,* Wat Res. 17, 4159÷4165. 2001.
5. **Ko D. C., Tsang D. H. K., Porter J. F., Mckay G.:** *Application of Multipore Model for the Mechanism Identification during the Adsorption on Activated Carbon and Bagasse Pith***,** Langmuir. 19, 722÷730. 2003.
6. **Schoonheydt R. A., Jacobs K. Y.:** *Time dependence of the Spectra of Methylene Blue – Clay Mineral Suspensions,* Langmuir. 17, 5150÷5155. 2001.
7. **Sarikaya H. Z., Sevimli M. F.:** *Ozone Treatment of Textile Effluents and Dyes: Effect of Applied Ozone Dose, pH and Dye Concentration,* J. Chem. Technol. Biotechnol. 77, 842÷850. 2002.
8. **Yoo E. S.:** *Chemical Decolorisation of the Azo Dye CI Reactive Orange 96 by arious Organic/Inorganic Compounda*, J. Chem. Technol. Biotechnol. 77, 481÷485. 2002.
9. **Perez M., Torrades, F., Domenech X., Peral J.:** R*emoval of Organic Contaminants in Paper Pulp Effluents by AOPs: An Economic Study,* J. Chem. Technol. Biotechnol. 77, 525÷532. 2002.
10. **ICI Watercare.:** Color in Textile Effluent, Environmental brief No.1.In: *Introduction to the Environmental Brief.* ICI Colors Textile Dyes Technology Group.
11. **Kapdan I. K., Kargi F.:** *Biological Decolorisation of Textile Dyestuff Containing Wastewatere by Coriolus versicolor in a Rotating Biological Contactor,* Enzyme Microbiol. Technol. 39, 195÷199. 2002.
12. **Anielak A. M.:** *Post Dying Wasterwater Treatment in Co-Precipitation and Sorption Process,* Technical University of Koszalin, 123. 1995.
13. **Al-Qodah Z.:** *Adsorption of Dyes using Shale Oil Ash,* Wat. Res. 17, 4295÷4303, 2000.
14. **Sarkar M., Das M.:** *Design and Performance of Fixed Bed Adsorber for the Treatment of Malachite Green as Single Solute as well as in Bisolute Composition,* The Env Prot. 3, 129÷137. 2001.
15. **Chu W.:** *Dye Removal from Textile Dye Wastewater using Recycled Alum Sludge,* Wat. Res. 35, 3147÷3152. 2001.
16. **Hawkyard C. J., Hassan M. M.:** *Decolorisation of Aqueous Dyes by Sequential Oxidation Treatment with Ozone and Fenton's Reagent,* J. Chem. Technol. Biotechnol. 77, 834÷841. 2002.
17. **Anielak A. M.:** *Phenomena Occurring on Phase Boundary in a Process of Coagulation and Co-Precipitation,* Environmental Science Research, Volume 51, 179÷192.1996, Serie Editor Herbert S. Rosenkranz. University of Pittsburg 130 De Soto Street, Pennsylvania. Plenum Press – New York and London.

18. **Oakes J., Gratton P.**: *Kinetic Investigations of the Oxidation of Arylazonaphthnol Dyes in Hypochlorite Solutions as function of pH*, J. Chem. Soc. Perkin Transc. 2, 2201÷2206. 1998.
19. **Oakes J., Gratton P.**: *Kinetic Investigations of Azo Dye Oxidation in Aqueous Media*, J. Chem. Soc. Perkin Transc. 2, 1857÷1864. 1998.
20. APHA-AWWA-CPWF *Standard Methods foe the Examination of Water and Wastewater*, Washington DC, 19th Ed., 1998.
21. **De A. K, Bhattacharya S., Chowdhuri B.**: *A Comparison Study of Phenol Degradation using Reagents*, J. Inst. Engg. (India). 29, 4÷11. 1998.

Alkaliczna degradacja wybranego zasadowego barwnika przez zastosowanie podchlorynu sodowego oraz pozostałość ChZT w środowisku wodnym

Streszczenie

Włókiennictwo jest ważnym przemysłem wśród innych gałęzi przemysłu w Indiach. Wiele różnych syntetycznych kompleksowych organicznych barwników jest często używana zakłady włókiennicze do barwienia towarów włókienniczych aby poprawić ich wygląd. Następnie z powodu zrzutu barwników, ścieki włókiennicze zawierają ogromną ilość barwników, powodując duży wzrost zanieczyszczenia. Niedawne szacunki wskazują, że około 12% barwników syntetycznych używanych co roku jest tracone podczas produkcji oraz procesów przetwarzania i trafia do środowiska wodnego.

Istnieje szereg dostępnych metod usuwania barwników od fizyko-chemicznych do biologicznych. Inne stosowane procesy chemiczne to: utlenianie przy zastosowaniu O_3, H_2O_2, nadkwasów, odczynnika Fentona jak również elektrochemiczne utlenianie, stosowanie ałunu i adsorpcja.

Przedstawione w artykule badania dotyczą alkalicznej degradacji zieleni nauka zadaje zasadowy spierając się z zieleni malachitowej, barwnika trifenylometanowego, z roztworu wodnego przy zastosowaniu roztworu podchlorynu sodowego a także zmiany ładunku ChZT w czasie reakcji. Wykonano trzy etapy badań, w których badano degradację barwnika przy: zmiennym stężeniu barwnika oraz stałym stężeniu NaOCl i stałej temperaturze, zmiennym stężeniu NaOCl przy stałym stężeniu barwnika i stałej temperaturze, zmiennej temperaturze przy stałych stężeniach barwnika i NaOCl. W każdym przypadku mierzono stężenie barwnika w roztworze.

Analizując wyniki można zauważyć, że wzrost usunięcia barwnika jest różny i zależy od jego początkowego stężenia. Zauważono również, że wraz ze wzrostem stężenia NaOCl wzrasta stopień usunięcia barwnika oraz, że wraz ze wzrostem temperatury wzrasta również stopień usunięcia barwnika. Interesujące jest spostrzeżenie, że w każdym badanym przypadku stopień usunięcia barwnika jest większe niż obniżka ChZT. Różnica pomiędzy procentowym usunięciem barwnika i procentową obniżką ChZT podczas reakcji zasadowej degradacji jest prawdopodobnie spowodowana powstawaniem bezbarwnych pośrednich produktów organicznych, które przyczyniają się do wzrostu wartości ChZT. Podobne zależności uzyskano również podczas utleniania błękitu metylenowego i fenolu.