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Fenton degradation of azo dyes

An overview

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Abstract

This review provides a general idea of Fenton oxidation of azo dyes. The effect of temperature or initial pH on the degradation process of some azo dyes in aqueous solution was investigated. From this study, it can be concluded that Fenton oxidation process is an effective method for azo dye removal.

Keywords: azo dye, Methylorange, Methyl red, Congo red, Fenton oxidation

INTRODUCTION

Industrial effluent is one of the important sources of water contamination [1]. Azo dyes present in dye industrial wastewater are toxic to aquatic organisms and mutagenic for humans [2]. These dyes are also very resistant to natural biological degradation [3]. There are several studies related to the use of Fenton reaction for the removal of azo dyes from wastewaters [4-6].

In this review, the influence of pH and temperature on chemical degradation by Fenton reagent of 3 azo dyes is presented. The studied dves are: Methylorange [7], Methyl red [8] and Congo red [9].

All experimental determinations were performed for aqueous solutions of azo dyes at different temperatures and initial pH values [7-9]. The chemical structures and the wavelengths corresponding to the maximum absorbance values (λ_{max}) for the studied azo dyes are shown in Table 1.

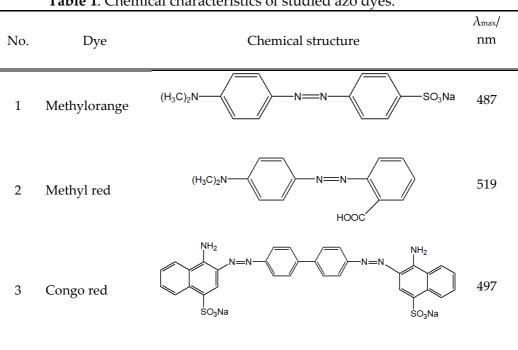


Table 1. Chemical characteristics of studied azo dyes.

1. Methylorange

The degradation process of Methylorange azo dye (Table 1) in aqueous solution by Fenton oxidation at different temperatures (25 °C, 35 °C, 45 °C, 55 °C, 65 °C) and pH = 3.5 has been investigated. The UV-Vis spectra of Methylorange were recorded from 200 to 800 nm and the wavelength corresponding to the maximum absorbance value (λ_{max}) was 487 nm. The absorbance value at 487 nm, which is due to the $n \rightarrow \pi^*$ transition in -N=N- group (the colour of dye solution), was used to monitor the Methylorange discolouration. The absorbance value of the dye solution at $\lambda_{max} = 487$ nm was measured at 1 minute time intervals.

UV-Vis spectra obtained during the Methylorange degradation at pH = 3.5 and temperatures of 25 °C and 65 °C are presented in figure 1. From figure 1 it can be observed that absorbance decreased in time, the most pronounced decrease being obtained at temperature of 65 °C at the same reaction times.

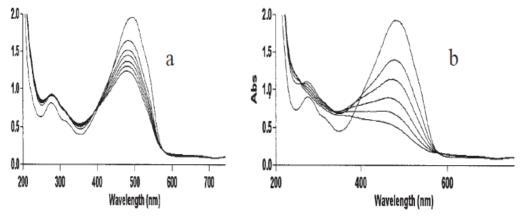


Figure 1. UV-Vis spectral changes of Methylorange azo dye at pH = 3.5 and temperature values of 25 °C (a) and 65 °C (b), respectively

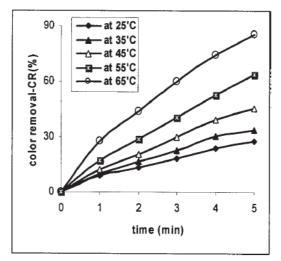


Figure 2. Dependence of colour removal on time at different temperature values and pH = 3.5

The effect of temperature on the Fenton oxidation of Methylorange azo dye is presented in figure 2. The graph in figure shows an increase of colour removal from 27.9 % at 25 °C to 85.5 % at 65 °C, after 5 min of reaction.

2. Methyl red

The Fenton oxidation process was also used to study the effect of initial pH on degradation of Methyl red azo dye in aqueous solution. The effect of initial pH on Methyl red degradation by the Fenton process was studied at different initial pH values (2.5, 3, 3.45, 4) and temperature of 25 °C.

The UV–Vis spectrum of Methyl red, recorded before the treatment (figure 3), showed one band in the ultraviolet region at 285 nm (this peakwas ascribed to the absorption of the $\pi \rightarrow \pi^*$ transition related to the aromatic ring bonded to the –N=N– group in the dye molecule) and one band in the visible region at 519 nm (this peak was attributed to the absorption of the n $\rightarrow \pi^*$ transition related to the –N=N– group and it is due to the colour of Methyl red solution). The absorbance at 519 nm was used to monitor the discolouration of azo dye ($\lambda_{max} = 519$ nm).

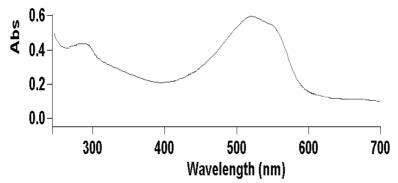


Figure 3. UV-Vis initial spectrum of azo dye Methyl red

The UV-Vis spectra recorded at different initial pH values are presented in figure 4. It can be observed from figure 4 that the adsorption peak at 519 nm diminished and nearly completely disappeared after 45 min at pH= 3.45 and after 72 min at pH = 2.5.

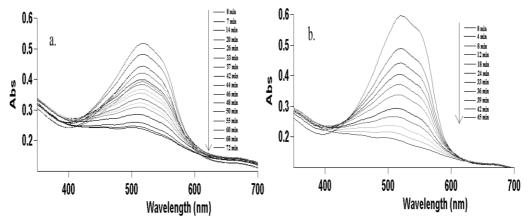


Figure 4. UV–Vis spectral changes of Methyl red by Fenton oxidation at the initial pH values of 2.5 (a) and 3.45 (b), respectively (temperature was 25 °C)

The dependence of colour removal on time is shown in figure 5. From figure 5 it can be observed an increase of colour removal from 49.8 % (at pH value of 2.51) to 83.54 % (at pH value of 3.45). Also, with increase of pH value from 3.45 to 4, the colour removal decreases from 83.54 % to 58.5 %. It can be concluded that the optimum pH value for Methyl red degradation by Fenton reagent is 3.45.

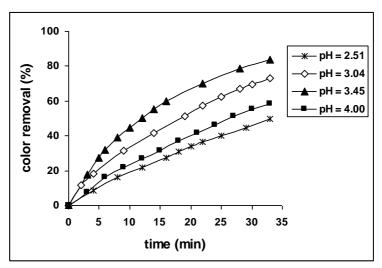


Figure 5. Dependence of colour removal on time at different initial pH values and temperature of 25 °C for Methyl red discolouration

3. Congo red

The degradation of Congo red azo dye by Fenton oxidation process in aqueous solution was studied at different temperatures: 25 °C, 35 °C, 45 °C and 55 °C, respectively and pH = 3.

It can be observed in the initial UV–Vis spectrum of Congo red (figure 6) a peak at 497 nm which was attributed to the absorption of the $n \rightarrow \pi^*$ transition related to the –N=N– group and a peak at 318 nm which was ascribed to the absorption of the $\pi \rightarrow \pi^*$ transition related to the aromatic ring bonded to the –N=N– group in the Congo red molecule.

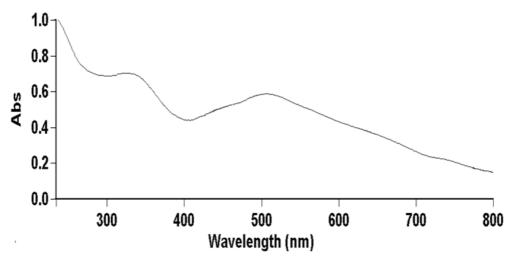


Figure 6. Initial UV-Vis spectrum of azo dye Congo red

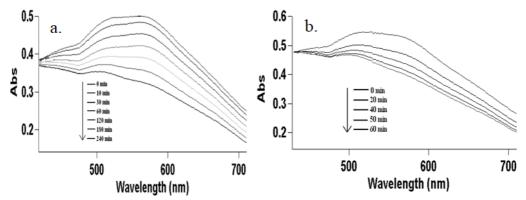


Figure 7. UV–Vis spectral changes of Congo red by Fenton oxidation at pH = 3 and temperature values of 25 °C (a) and 55 °C (b), respectively

It can be seen from the spectral changes registered during the Fenton oxidation of Congo red (figure 7) that peak at 497 nm nearly disappeared after 240 min at temperature of 25 °C and after 60 min at 55 °C.

From the dependence of colour removal on time at different temperature values (figure 8) it can be observed that colour removal increased from 5.04 % to 16.3 % with increase of temperature from 25 °C to 55 °C within 4 min of Congo red discolouration process.

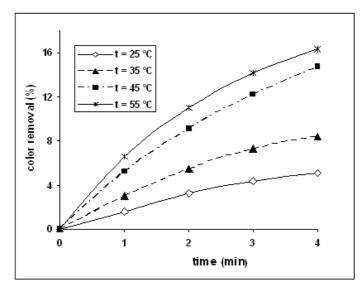


Figure 8. Dependence of colour removal on time at different temperature values and pH 3 for Congo red discolouration

CONCLUSION

The azo dyes can be effectively degraded by Fenton oxidation process.

In case of Methylorange oxidation by Fenton reagent, it was observed that an increase of temperature from 25 °C to 65 °C leads to an increase of colour removal from 27.9 % to 85.5 %, after 5 min of reaction.

The influence of pH on Fenton oxidation of Methyl red was also studied. It was observed an increase of colour removal from 49.8 % to 83.54 % with increase of pH value from 2.51 to 3.45 and a decrease of colour removal from 83.54 % to 58.5 % with increase of pH value from 3.45 to 4.

The study of Congo red Fenton oxidation shows that colour removal increased from 5.04 % to 16.3 % with increase of temperature from 25 °C to 55 °C after 4 min of reaction.

REFERENCES

- M. S. I. Afrad, M. B. Monir, M. E. Haque, A. A. Barau and M. M. Haque, J. Environ. Healt Sci. Eng., 18 (2020) 825.
- [2] V. Selvaraj, T. Swarna Karthika, C. Mansiya and M. Alagar, *Journal of Molecular Structure*, 1224 (2021) 129195.
- [3] M. Sudha, A. Saranya, G. Selvakumar and N. Sivakumar, Int. J. Curr. Microbiol. App. Sci, 3 (2014) 670.
- [4] N. A. Youssef, S. A. Shaban, F. A. Ibrahim and A. S. Mahmoud, J. Sci. Res. Sci., 32 (2015).
- [5] N. C. Fernandes, L. B. Brito, G. G. Costa, S. F. Taveira, M. S. Cunha-Filho, G. A. R. Oliveira, R. N. Marreto, *Chemico-Biological Interactions*, 291 (2018) 47.
- [6] A. J. Feuzer-Matos, R. C. Testolin, S. Cotelle, E. Sanches-Simoes, W. Pimentel-Almeida, G. Niero, G. C. Walz, R. Ariente-Neto, C. A. Somensi, C. M. Radetski, J. Environ. Sci. Healt A Tox. Hazard. Subst. Environ. Eng., 56 (2021) 1019.
- [7] M. Dumitru, A. Samide, M. Preda, A. Moanta, Rev. Chim (Bucuresti), 60 (2009) 957.
- [8] M. Drăgoi, A. Moanță, M. Preda, Annals of the University of Craiova, The Chemistry Series, XXXIX (2010) 21.
- [9] M. Drăgoi, A. Moanță, Annals of the University of Craiova, The Chemistry Series, XLI (2012) 14.