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Letter to the Editor

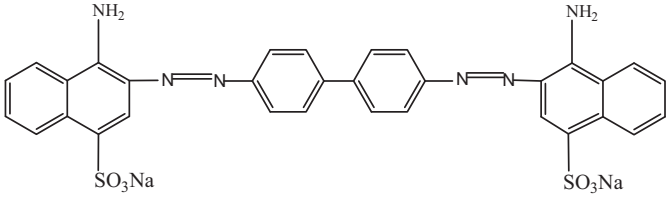
Comments on the method of using maximum absorption wavelength to calculate Congo Red solution concentration published in J. Hazard. Mater.

Dear Editor,

As a disazo anionic direct dye, Congo Red (CR) contains NH_2 and SO_3 functional groups (molecular formula = $C_{32}H_{22}N_6Na_2O_6S_2$, C.I. = 22,120, FW = 696.7). The molecular structure of CR is shown in Scheme 1. Removal of CR from aqueous solutions has been reported by many scientists in the past years. Recently we read, with great interest, the papers with "Congo Red (CR)" published by *J. Hazard. Mater*. Those studies are significantly helpful and informative to researchers interested in this field. However, it has come to our attention that an obvious error in determining the maximum absorption wavelength to calculate Congo Red solution concentration has been found in these articles. In Section 3.2 of paper [1], it is stated that "The measurement is done at a wave length of 499 nm for pH range of 5–12 and at 560 nm at pH 2", but only 497 nm (or 498, 499, 500, 502 nm) was used in the other papers [2–11]. The different maximum absorption wavelengths used to calculate CR solution concentration implied that some articles must be erroneous.

In order to determine the reliable λ_{max} value for CR dye, experiments were carried out in this laboratory over the same solution concentration with adjustments being made using the same amount of different concentrations of HCl or NaOH over a pH range of 2.18–12.05 (Mettler Toledo Seven Easy S20K pH meter), and then the UV–vis absorption spectra of the solutions were recorded with a UV–vis spectrophotometer (Agilent 8453, USA). As shown in the spectra (Fig. 1), it is evident that the λ_{max} is 576 nm at pH 2.18–3.16, 567 nm at pH 3.86, and 496 nm at pH ≥ 4.71, for the different structure of CR molecules at different pH. CR is very sensitive to the pH and would change from red to blue, due to π–π^* transition in azo group shift to higher wavelength because of protonation (see Scheme 2). This experiment revealed that at lower pH it becomes cationic and shows two tautomeric forms of protonated CR, i.e. ammonium rich variety and azonium variety [12].

The results of λ_{max} are similar to those in the literature [1,12,13]. However, we would like to point out that, even with the same concentration, the value of absorbance at λ_{max} is different when the values of pH were 4.71, 4.99, 5.39 and 6.32, respectively. The experiments show that, for calculating the accurate solution concentration, pH-specific standard calibration curves should be generated at these maximum absorption wavelengths and used in its respective pH range. According to Fig. 1, it can be concluded that the calculated concentration (C_{cal}) (corresponding to the absorbance) would be well below the actual concentration (C_{act}) (corresponding to the maximum absorbance at pH 6.32) of CR solution if C_{cal} was determined from the calibration curve (λ_{max} 496 nm) in the condition of pH ≤ 5.39.



Scheme 1. Chemical structure of CR.

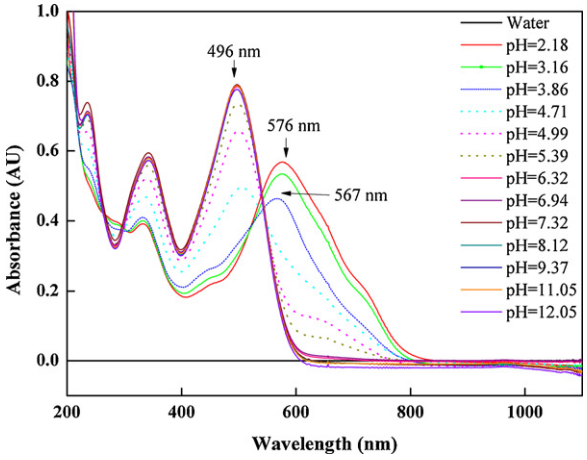


Fig. 1. UV–vis spectra of CR solution at different pH (50 mg L^{-1}, 25 °C).

Thus, if only 497 nm (or 500, 498, 499 nm) is utilized as the λ_{max} to determine the CR solution concentration, or the standard curve at pH ≥ 6.32 is used to calculate the concentration of CR solution at pH ≤ 5.39, or the changes of pH_{final} versus $pH_{initial}$ have not been taken into account, one thing is certain: *the results from the base-case calculations are definitely wrong*. From other relevant papers about λ_{max} of Congo Red published in other Journals, such as *Desalination* [14], *Applied Surface Science* [12], *Bioresource Technology* [15], etc., similar mistakes have been found.

It should be noted that a correct method of using maximum absorption wavelength to calculate dyes solution concentration is very important for researchers. Also, from the scientific point of view, it is always a must to inform all the authors who have not found the changes of λ_{max} of CR solution with pH. If we have not pointed out the errors in the above calculation of CR solution concentration, the subsequent researchers would be likely to refer to these erroneous references and continue to make the same mistakes.

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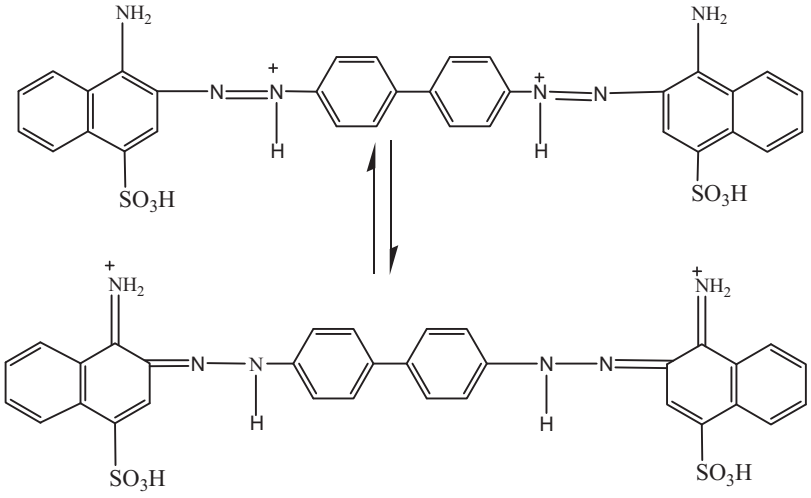

Scheme 2. Protonated CR.

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Zhou Qi
School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan 430070, PR China

Xie Chuanxin
SINOPEC Research Institute of Safety Engineering, Qingdao 266071, PR China

Gong Wenqi*
Xu Nian
Zhou Wenjun
School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan 430070, PR China

* Corresponding author.
E-mail address: gongwenqi@yahoo.com.cn
(W. Gong)

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