



# Influence of clay minerals on curcumin properties: Stability and singlet oxygen generation<sup>☆</sup>



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## ABSTRACT

Curcumin (CUR) has showed promising photophysical properties regarding to biological and chemical sciences. However, the main barrier for those applications are their low solubility and stability in aqueous solution. The effects of two different clay minerals, the montmorillonite (SWy-2) and the Laponite RD (Lap) nanoclay, on the stabilization of Curcumin were investigated. Their effects were compared with two well-established environments (acidic and neutral aqueous media). CUR/clay hybrids were prepared using a simple and fast method, where CUR solution was added into clay suspensions, to obtain well dispersed hybrids in water. The degradation process of CUR and CUR/clays hybrids was investigated using UV–Vis spectroscopic. For both studied hybrids, the CUR degradation process was suppressed by the presence of the clay particles. Furthermore, the Lap showed a great stabilization effect than SWy-2. This behavior was due to the smaller particle size and higher exfoliation ability of Lap, providing a large surface for CUR adsorption compared to SWy-2. The degradation process of CUR solutions and CUR/clay hybrids was also studied in the presence of light. CUR photodegradation process was faster not only in the aqueous solution but also in the clay suspension compared to those studied in the dark. The presence of clay particles accelerated the photodegradation of CUR due to the products formation in the reactions between CUR and oxygen radicals. Our results showed that the singlet oxygen quantum yield ( $\Phi_{\Delta}$ ) of CUR were about 59% higher in the clay suspensions than CUR in aqueous solution. Therefore, the formation of CUR/clay hybrids, in particularly with Lap, suppressed the degradation in absence light of CUR and increased the singlet oxygen generation, which makes this hybrids of CUR/clay a promising material to enlarge the application of CUR in the biological sciences.

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## 1. Introduction

Curcumin (1,7-bis(4-Hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione) is a natural yellow pigment that can be isolated from the rhizome of turmeric (*Curcuma longa L*) [1]. As shown in Scheme 1, the CUR structure consists in two rings with phenolic OH groups bonded by an unsaturated diketone. The diketone structure undergoes to keto-enol tautomerism depending on the environment [2–4]. In acidic and neutral solution the  $\beta$ -diketo form is predominant, on the other hand, a keto-enol form can be observed in alkaline medium [5].

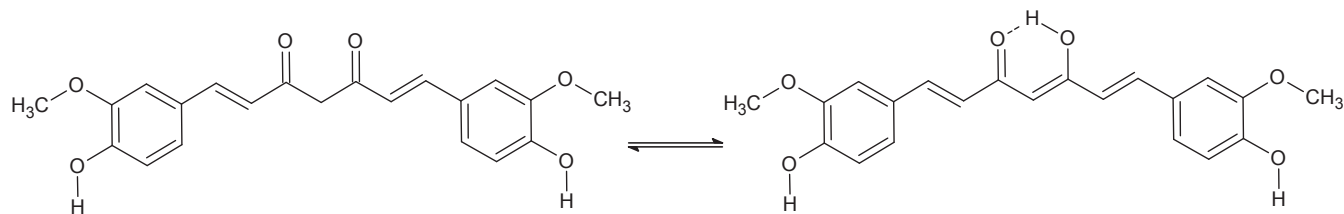
In the last few years, CUR was investigated in wide range applications in biological sciences due to the potential anticancer [6,7] and anti-inflammatory [8] properties. Besides, CUR is also a potential photosensitizer in antimicrobial photodynamic therapy [9]. Nevertheless, there are two major factors that have limited the use of CUR as a photosensitizer in those applications: (i) the low solubility of CUR in neutral and acidic media and (ii) the instability in basic and neutral condition [10]. Concerns have recently been raised about the stability of CUR and their properties under *in vivo* and *in vitro* assay conditions [11]. Therefore, increasing the stability of the compound using biocompatible systems, may be a viable alternative for those concerns.

Several approaches have been explored in order to stabilize the CUR molecule, such as binding CUR into proteins, as human and bovine serum albumin [12–15] or nanoparticles-based technologies, including encapsulation in liposomes, phospholipid complexes and starch nanocomposite [16–20].

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**Scheme 1.** Keto–enol tautomeric equilibrium of Curcumin.

An attractive material which can be employed as a support to stabilize ions and organic molecules are the clay minerals [21,22]. Clay minerals are a low-cost abundant material which can be characterized by some properties such as the possibility of surface modification (adsorption, ion exchange or grafting) [23]. The incorporation of the dyes into these clay minerals may improve not only the stability but also their photophysical and chemical and biological properties such as fluorescence, triplet and singlet oxygen quantum yield, solubility and biological activities [24–28]. The formation of anthocyanin/clay hybrid increased the stabilization against alkaline conditions compared to the solutions without clay [25]. Hybrid materials composed by clay and methylene blue exhibited an enhancement in the singlet oxygen generation [29] and antimicrobial activity [30].

In present paper, we report the effect of two clay minerals, Lap and SWy-2 montmorillonite, on the CUR properties in a neutral environment. The aim of this study is to provide an insight into the role of clays on the CUR stabilization in the presence and absence of light.

## 2. Experimental section

CUR was purchased from Sigma-Aldrich and used it was received. A natural montmorillonite Na<sup>+</sup>-SWy-2 (Source Clays Repository of the Clay Minerals Society, University of Missouri, Columbia, Missouri) and synthetic nanoclay Laponite RD (Lap, Laporte Ind) were used in this work. The clays were purified as described earlier [31]. Stock suspensions of clays (2.8 g L<sup>-1</sup>) were prepared in deionized water (Millipore water) and stirred at 25 °C for 18 h. Afterward, a second clay suspension with a concentration of 0.11 g L<sup>-1</sup> was prepared from the former. A stock solution of CUR (2.7 × 10<sup>-3</sup> mol L<sup>-1</sup>, log ε<sub>422 nm</sub> = 4.76) was prepared in ethanol and stored in the dark at low temperature. This ethanolic solution was diluted in aqueous solutions (99:1 v/v) with pH = 1 and pH = 7 and with suspensions of SWy-2 (0.11 g L<sup>-1</sup>) and Lap (0.11 g L<sup>-1</sup>). All the characterizations were performed right after the addition of CUR in the aqueous solution and clay suspensions since it was known that CUR degrades as a function of time.

UV–vis absorption spectra were recorded on a Shimadzu UV-2550 Spectrophotometer in the range of 200–700 nm. The CUR concentration of the samples employed for absorption studies was 2.5 × 10<sup>-5</sup> mol L<sup>-1</sup>. To avoid interference due to light scattering by the clays particles, reference samples were prepared in the same experimental condition of the CUR/clay samples.

Fluorescence quantum yield (Φ<sub>F</sub>) were determined at λ<sub>exc</sub> = 450 nm using riboflavin in ethanol (Φ<sub>F</sub> = 0.30) [32] as standard from Equation (1):

$$\Phi_F = \Phi_F^S \frac{F_C \times A_S \times \eta_C^2}{F_S \times A_C \times \eta_S^2} \quad (1)$$

where *F* is the integrated area under the fluorescence emission spectrum, *A* is the absorbance of the solutions at the excitation

wavelength and the subscripts S and C refer to the standard and the CUR, respectively. Fluorescence measurements were performed on spectrofluorometer Hitachi F-4500 at room temperature.

Dynamic light scattering (DLS) analyses were performed using a Zetasizer Nano ZS analyzer (Malvern Instruments).

The light source used for the photodegradation was a blue LED with emission centered at 455 nm (*I* = 34 mW cm<sup>-2</sup>, THORLAB). The samples were irradiated at 25 °C for 180 min, which totalizes a light dose of 22 kJ.

The singlet oxygen quantum yield (Φ<sub>Δ</sub>) was determined by an indirect method, using 1,3-diphenylisobenzofuran (DPBF) as singlet oxygen quencher. CUR solutions with optical density 0.2 at 455 nm were prepared in water or clays and mixed to an equal volume of 2.0 × 10<sup>-4</sup> mol L<sup>-1</sup> DPBF solution in the same solvent. The samples were placed in a quartz cuvette and irradiated for 15s, using the above mentioned LED. Absorption spectra was recorded every 0.5s in a Shimadzu Multispec-1501 spectrophotometer and the absorbance of the solution at 424 nm was used to calculate the pseudo-first order rate of DPBF decomposition. The singlet oxygen quantum yields were obtained using riboflavin in water (Φ<sub>F</sub> = 0.49) [33] as standard from Equation (2):

$$\Phi_{\Delta} = \frac{k_C \times (1 - 10^{A_S}) \times \eta_S^2}{k_S \times (1 - 10^{A_C}) \times \eta_C^2} \Phi_{\Delta S} \quad (2)$$

which *k* is the rate of DPBF photodecomposition, *η* is the refractive index of the solvent, *A* is the dye absorption at 455 nm and the subscripts S and C are the standard and CUR samples, respectively.

## 3. Results and discussion

### 3.1. Absorption and fluorescence spectra of CUR with and without presence of the clay minerals

The initial absorption spectrum of CUR in neutral aqueous solution (pH = 7) consisted in two bands at 265 and 418 nm (Fig. 1a). These peaks can be attributed to the n-π\* and π-π\* transitions, respectively [34]. The absorption spectrum of CUR in acidic medium consists of a broad (with maximum absorption around 429 nm) and weaker band compared to neutral aqueous solution. We ascribe this observed behavior may due to (i) an overlap between the diketo form and enol form in acidic aqueous solution; and (ii) aggregation of undissociated CUR molecules [35]. In addition, the diketo and enol forms also can be seen in the fluorescence spectrum of CUR in acidic aqueous solution (Fig. 1b). Because the goal of this work was a new approach to CUR stabilization, most of the following discussion will be focused on the clay suspensions samples.

The π-π\* transition of CUR in the presence of clays dispersions showed a significantly blue shift (406 nm), compared to that one observed in aqueous solution. It has been proposed that the π-electrons of the dye can interact with the hybridized orbitals of the surface oxygen atoms of the clay, leading to a stabilization of the π-

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