

# Decolourization and COD removal from reactive dye-containing wastewater using sonophotocatalytic technology

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**Abstract:** Decolourization and COD removal from synthetic wastewater containing Reactive Brilliant Orange K-R (RBOKR) dye using sonophotocatalytic technology was investigated. Experimental results showed that this hybrid technology could efficiently remove the colour and reduce COD from the synthetic dye-containing wastewater, and that both processes followed pseudo first-order kinetics. At the condition of  $0.1 \text{ m}^3 \text{ h}^{-1}$  airflow,  $0.75 \text{ g dm}^{-3}$  titanium dioxide and  $0.5 \text{ mmol dm}^{-3}$  RBOKR solution, the rate constants of decolourization and COD removal were  $0.0750$  and  $0.0143 \text{ min}^{-1}$  respectively for the sonophotocatalytic process;  $0.0197$  and  $0.0046 \text{ min}^{-1}$  respectively for the photocatalytic process and  $0.0005$  and  $0.0001 \text{ min}^{-1}$  respectively for the sonochemical process. The rate constants of sonophotocatalysis were greater than that of both the photocatalytic and sonochemical processes either in isolation or as a sum of the individual process, indicating an apparent synergetic effect between the photo- and sono-processes.

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**Keywords:** sonophotocatalysis; photocatalysis; ultrasound; dye decolourization; COD removal; synergetic effect

## 1 INTRODUCTION

In the United States alone, more than  $3 \times 10^{11}$  kg of dyes are produced annually, and in the processes of their manufacturing and utilization, a variety of dyes-containing wastewaters are produced which are released into external water systems. Considering both the volume and chemical composition of the discharged effluent, dyes pose a potential environmental hazard.<sup>1</sup> Hence, from the environmental point of view, treatment of the dye-containing wastewater is of great concern.<sup>2</sup>

The treatment of dye-containing wastewater by conventional methods, such as flocculation, air sparging and activated carbon adsorption are quite ineffective in decolourization of wastewater since dyestuffs are recalcitrant<sup>3</sup> and difficult to remove by these processes due to their low molecular weight and high water solubility.<sup>1</sup> Moreover, these chemical treatment options merely transfer the pollutants from water to another phase. Alternative biological treatment is difficult to control in order to achieve the desired degree of removal.<sup>4,5</sup> Over the last few decades, there has been a growing interest in

the photocatalytic degradation of organic pollutants using  $\text{TiO}_2$  as catalyst.  $\text{TiO}_2$  may completely mineralize a variety of aliphatic and aromatic compounds under suitable conditions,<sup>6</sup> however, the development of a practical water treatment system based on photocatalytic oxidation has not yet been successfully achieved because of low photocatalytic efficiency.<sup>7</sup>

Several attempts have been made to increase the photocatalytic efficiency of titanium dioxide.<sup>8–13</sup> Ultrasonically-assisted photocatalysis is one alternative means by which the introduction of ultrasound into a photocatalytic reaction system might not only enhance the mass transport but also improve the activity of the photocatalyst.<sup>14</sup> However, there are only a few reports concerning ultrasonic effects on photocatalytic reactions. These research studies largely focused on the dechlorination and oxidation of chlorophenol and its derivatives with the exception of 2-propanol and phenyltrifluoromethylketone.<sup>13</sup> Few reports are available where the combination of ultrasound with photocatalysis, so called sonophotocatalysis, has been used in the degradation of dyes.<sup>15</sup>

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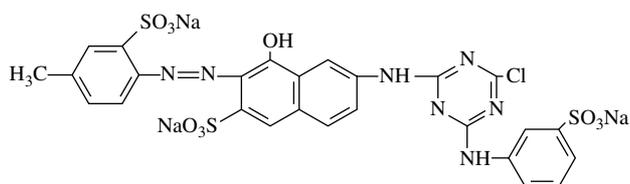


Figure 1. Structure of reactive brilliant orange K-R.

The aim of this study was to investigate the application of sonophotocatalysis to treating dye-containing wastewater. A reactive dye, Reactive Brilliant Orange K-R (RBOKR) (Fig 1) was used as a model pollutant. Particular attention was paid to the effect of operating conditions on sonophotocatalytic decolourization, COD removal kinetics and the synergistic effect existing in a hybrid process of ultrasound and photocatalytic oxidation.<sup>16</sup>

## 2 EXPERIMENTAL

### 2.1 Materials

The photocatalyst was titanium dioxide Degussa P25, mainly anatase (*c* 70%), from Degussa in the form of non-porous polyhedral particles of *c* 30 nm mean size with a surface area of 50 m<sup>2</sup> g<sup>-1</sup>. RBOKR was a commercial grade reagent, and the solutions were prepared with deionized water in the concentration of 0.5 mmol dm<sup>-3</sup> (COD: *c* 133 ppm, pH: 5.8).

### 2.2 Apparatus

Absorption spectra of RBOKR were recorded with a mode UV-PC2501 spectrophotometer (Shimadzu, Japan). A Branson 1200 mode ultrasonic cleaner (Branson Ultrasonic Corporation, USA) operating at a frequency of 47 kHz and an output power of 30 W was used as the ultrasonic source.

### 2.3 Sonophotocatalytic reactor

The experimental apparatus consisted of a batch slurry reactor, as shown in Fig 2, containing a double-walled quartz U-tube and an outer rectangular ultrasonic bath (length = 150 mm; width = 120 mm; height = 100 mm) fitted with a gas distributor at the base. A 500 W U-shape high-pressure mercury lamp was suspended vertically in the double-walled tube within a 10.0 mm thick cooling water jacket (800 cm<sup>3</sup> min<sup>-1</sup>) to maintain reaction isothermality. The circulating water also ensured infrared filtering of the incident

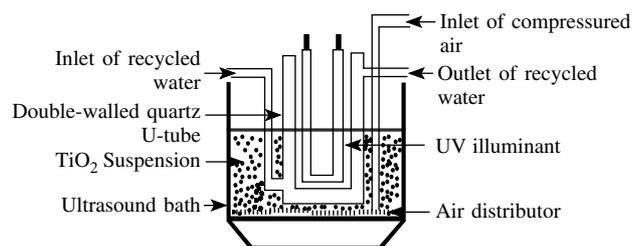


Figure 2. Schematic of reactor set-up.

ray.<sup>17</sup> The slurry solution containing titania particles was enclosed between the annulus of the quartz U-tube and the bath wall, the average distance between the two being 20 mm. Compressed air was bubbled from the bottom of the cell in all experiments.

### 2.4 Analysis

Millipore membrane (0.45 μm) was used to remove particulate mass from the colloid solution before the colour and COD analysis. Colour was measured and calculated according to the literature.<sup>18,19</sup> The COD was measured with potassium dichromate.<sup>20</sup>

### 2.5 Recommended procedure

A 700.0 cm<sup>3</sup> sample of a solution of RBOKR containing a known mass of titanium dioxide was fed into the sonophotocatalytic reactor. The experiment was timed as starting when the ultrasound power, illumination and compressed air supply were switched on. The colloid solution was sampled, separated by centrifugation and filtered through a Millipore membrane (0.45 μm) before COD, colour and optical absorption analysis at each 30 min interval. Except as indicated, normal experimental conditions were 0.1 m<sup>3</sup> h<sup>-1</sup> airflow, 0.75 g dm<sup>-3</sup> titanium dioxide, 0.5 mmol dm<sup>-3</sup> RBOKR solution, and 150 min treatment time.

## 3 RESULTS AND DISCUSSION

### 3.1 Kinetics of decolourization and COD removal

Compared with general organic pollutants, dyes also colour receiving waters. Hence both the decolourization and COD removal using a sonophotocatalytic process were investigated.

The changes of UV spectra at various reaction intervals are presented in Fig 3. It can be seen from the figure that all absorption peaks initially decreased rapidly and after 90.0 min the peaks at visible wavelengths completely disappeared, showing that the sonophotocatalytic process could effectively remove the colour from the RBOKR-containing solution.

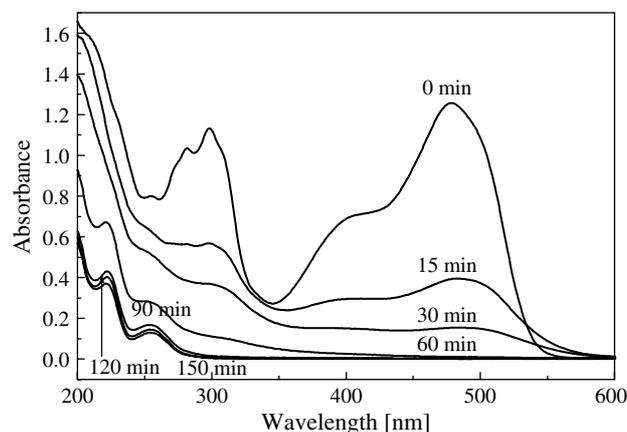
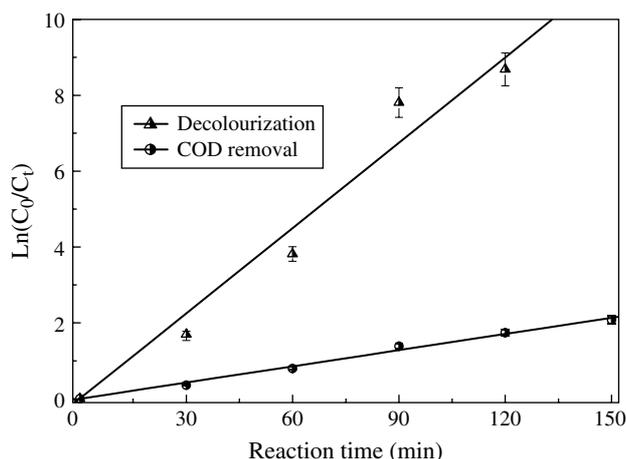


Figure 3. Change of UV spectra of RBOKR.



**Figure 4.** Kinetic curves of decolourization and COD removal. ( $C$  denotes colour or COD concentration;  $0.1 \text{ m}^3 \text{ h}^{-1}$  airflow,  $0.75 \text{ g dm}^{-3}$   $\text{TiO}_2$ ,  $0.5 \text{ mmol dm}^{-3}$  RBOKR solution, and 150 min treatment time).

Further, the peak at visible wavelengths appeared to shift from 478 nm towards 484 nm, simultaneous with the decrease in absorbance. This bathochromic shift indicates the presence of azo-hydrazone tautomerism in the sonophotocatalytic reaction.<sup>21</sup>

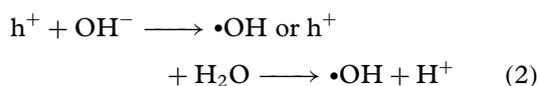
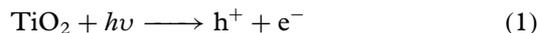
It has been recognized that photocatalytic<sup>6,9,17,22</sup> and ultrasonic degradation<sup>23–25</sup> of many organic pollutants accord with pseudo first-order kinetics. In this sonophotocatalytic decolourization and COD removal process, pseudo first-order kinetics were also confirmed by the linear transforms  $\ln(C_0/C_t) = f(t)$  (where  $C$  denotes colour or COD), as shown in Fig 4.

Dyes are not instantaneously oxidized to  $\text{CO}_2$ , and the oxidation presumably proceeds via a number of intermediates. Therefore, the decrease in optical absorption is not an infallible indicator of the concentration of organic solutes since intermediate decomposition products may have no absorption at the absorption wavelength for the original dye. The COD removal rate constant ( $0.0143 \text{ min}^{-1}$ ) was much less than that of the decolourization process ( $0.0750 \text{ min}^{-1}$ ) at the same conditions. The differences in the rate constants can be explained by the formation of more stable intermediates in the process of decolourization<sup>21</sup> and the difference between the photocatalytic mechanisms of decolourization and COD removal. RBOKR is a reactive dye with an azo chromophore. The decolouring mechanism might proceed predominantly through the destruction of the azo group by oxidation of positive holes etc, and by reduction of conduction band electrons, in a manner similar to that of decolourization of other azo dyes in photocatalytic processes,<sup>26</sup> while COD was removed only by the oxidation.

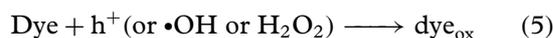
### 3.2 Reaction mechanism

Many research groups have studied the reaction mechanism for the photocatalytic degradation of dyes. The reaction mechanism can be summarized as following three processes:<sup>26–28</sup>

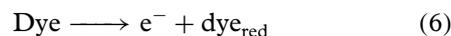
#### Initiation of photocatalytic reaction (Process 1)



#### Oxidation by positive hole, etc (Process 2)



#### Reduction by the electron of conduction band (Process 3)



where  $\text{h}^+$  and  $\text{e}^-$  are the positive hole in the valence band and electron in the conduction band, respectively, and subscripts 'red' and 'ox' denote reduced and oxidized forms, respectively.

It can be seen from process 1 that oxygen can scavenge the conduction band electron, effectively preventing electron–hole recombination and prolonging the lifetime of the hole. Parallel with the scavenging process, superoxide anion ( $\text{O}_2^-$ ) and  $\text{H}_2\text{O}_2$  are also generated, which can oxidize the dye directly. Water on the surface of photoexcited  $\text{TiO}_2$  can also be oxidized to hydroxyl radicals by the photo-generated holes (reaction 2). As a result, the oxidation of the dye is mediated mainly by the three species,  $\text{h}^+$ ,  $\bullet\text{OH}$  and  $\text{H}_2\text{O}_2$ . The dye can also be reduced by the conduction band electron through process 3. Although the reduction process increases COD in the reaction solution, it can enhance the decolouring of the dye. This is one explanation for the COD removal rate being much less than that for the decolouring reaction.

The reaction mechanism for ultrasonical degradation of organic pollutants has been studied in detail by many researchers.<sup>29,30</sup> They believed that during the cavitation bubble collapse  $\text{H}_2\text{O}$  underwent thermal dissociation within the vapour phase to give hydroxyl radical and hydrogen atoms. Many of the reactions observed during ultrasonication have been attributed to the secondary effects of  $\bullet\text{OH}$  and  $\bullet\text{H}$  atom production.



It is believed that the sonophotocatalytic reaction mechanism is the sum of those of photocatalytic and ultrasonic processes in addition to the effect of the enhanced mass transfer by ultrasound. In other words, coupling the ultrasound with photocatalysis may increase the concentration of the  $\bullet\text{OH}$  in the solution through reaction(7). The increase of  $\bullet\text{OH}$  may be the reason why the rate constants of sonophotocatalysis are greater than that of the photocatalytic or the sonochemical processes alone.

### 3.3 Effect of operating conditions on rate constant

The apparent rate constants of decolourization and COD removal are both dependent on the initial dye concentration rather than being constant values. As shown in Fig 5, the apparent rate constants first increase slightly and then decrease significantly with increases in the initial dye concentration. Wei<sup>31</sup> explained similar phenomena observed in photocatalytic degradation of phenol in terms of the competitive adsorption between  $\text{OH}^-$  and  $\text{ArO}^-$ . More recently Leng *et al.*<sup>32</sup> interpreted the decrease in the apparent rate constant with the concentration of substrate, aniline, by assuming that photoproducts competed with aniline for the site on the  $\text{TiO}_2$  surface. The increase in rate constant observed in our experiments can be simply ascribed to the increase in utilization of  $\text{TiO}_2$  active sites. Before saturation of the  $\text{TiO}_2$  surface is achieved, with increasing dye concentration, more  $\text{TiO}_2$  active sites can be used in the solution, resulting in an increase in the rate constant. The reduction of rate constant, in addition to the above two reasons mentioned by Wei<sup>31</sup> and Leng *et al.*,<sup>32</sup> may be due to the transparency of the dye solution being dramatically reduced so that the transmission intensity of ultraviolet light is greatly diminished when the dye concentration is increased, similar to the observations in the pure photocatalytic process.<sup>1</sup>

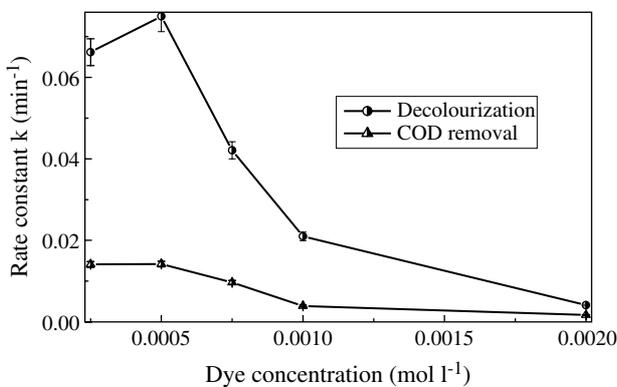


Figure 5. Effect of initial dye concentration.

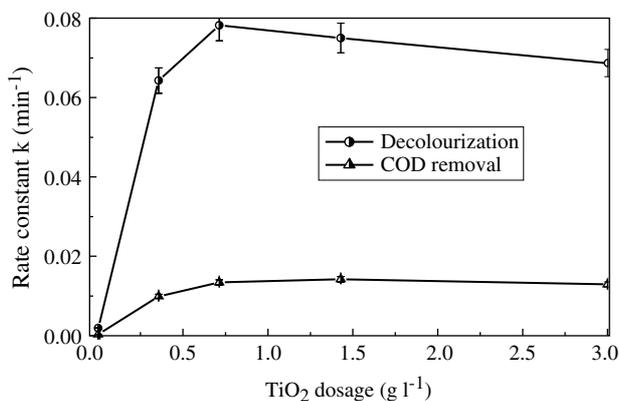


Figure 6. Effect of photocatalyst dosage.

For photocatalytic reactors, the optimal concentration of titanium dioxide loading has to be determined since it is strongly dependent on the geometry of the photoreactor and the incident flux as well as on the mean optical pathway within the suspension.<sup>1</sup> With respect to the sonophotocatalytic reactor, apparent rate constants are also strongly dependent on the dosage of  $\text{TiO}_2$ , as shown in Fig 6. Moreover, both rate constants for the processes of COD removal and decolourization have similar change trends. They increased greatly with the initial increase of  $\text{TiO}_2$  concentration, and then levelled off when the dosage of  $\text{TiO}_2$  exceeded  $0.75 \text{ g dm}^{-3}$ . The observation can be explained as follows: when the amount of  $\text{TiO}_2$  is increased, more active sites are presented so that the photocatalytic rate is increased. However, the photocatalytic rate is not improved because of the increase of scattering of the ultraviolet light with increasing  $\text{TiO}_2$  concentration. Therefore, it is essential to select a suitable dosage of  $\text{TiO}_2$  in the sonophotocatalytic process. In our experiments, a dosage of  $0.75 \text{ g dm}^{-3}$  was chosen as an optimal dosage.

It is well known that for charged substrates, pH value has a significant effect on the photocatalytic degradation of organic pollutants although the change in photocatalytic rate is rather insignificant for neutral substrates.<sup>1</sup> In this sonophotocatalytic experiment, decolouring was found to be strongly dependent on the initial pH value. As shown in Fig 7, the rate constants apparently decreased when the initial pH value exceeded 6. This trend is similar to that reported by Arslan *et al.*<sup>1</sup> but different from observations made by Zhang *et al.*<sup>21</sup> in photocatalytic experiments. The reduction in rate constant can be interpreted as a combination of the surface charge of  $\text{TiO}_2$ , and the nature of the dye. The adsorption of dye onto  $\text{TiO}_2$  is the first step in the process of sonophotocatalysis. At low pH values, RBOKR, being an anionic dye with a negative charge, can be adsorbed onto the surface of positively charged  $\text{TiO}_2$ . However, above pH 6, the surface of  $\text{TiO}_2$  gradually becomes more negatively charged, and the adsorption of the dye onto  $\text{TiO}_2$  becomes difficult due to the repulsion effect between the two species, and the rate constant of decolourization decreases.

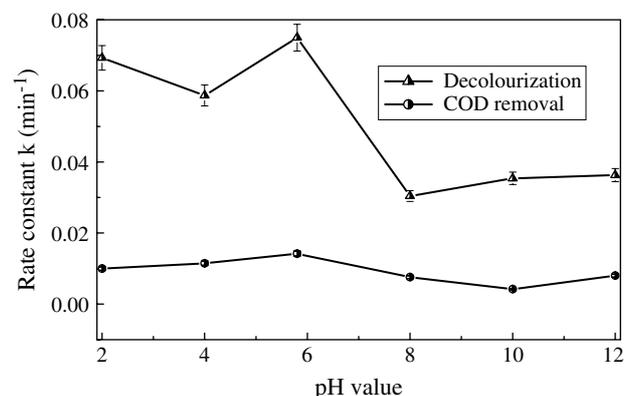


Figure 7. Effect of initial pH value.

In addition, although the generation of hydroxyl radical main reactive species can be favoured at high concentrations of adsorbed hydroxyl groups at high pH values,<sup>33</sup> main photoproducts at high pH (the bicarbonate/carbonate), can effectively scavenge the hydroxyl radicals.<sup>1</sup> The scavenging effect may be another factor reducing reaction rates. For COD removal, the rate constant also seems to be dependent on pH value, but is not as sensitive as decolourization.

With respect to a single photocatalytic process, it is well known that the sparged air serves two roles. One is to supply the essential oxygen to capture photogenerated electrons, reducing the combination of photogenerated-electron and—hole,<sup>34</sup> and generating many active species, such as,  $\bullet\text{OH}$ , superoxide anion ( $\text{O}_2^-$ ) and  $\text{H}_2\text{O}_2$ , that can oxidize the dye. The other is to agitate the solution in order to increase mass transfer.<sup>16</sup> In this study, the influence of sparged air on the rate constants of decolourization and COD removal have been plotted and are shown in Fig 8. From the figure, it is obvious that the rate constants first increase with increase in the airflow, exhibiting a maximum at about  $0.10 \text{ m}^3 \text{ h}^{-1}$ , and then decrease slightly. Further experiments showed that sparged oxygen has a more pronounced effect than the sparged air, as shown in Fig 9, while sparged nitrogen had no significant impact compared with the situation without any sparged gas. The observation indicated that, for the sonophotocatalytic process, the sparged air increased the decolouring rate only by the photoelectron capture role of oxygen rather than by

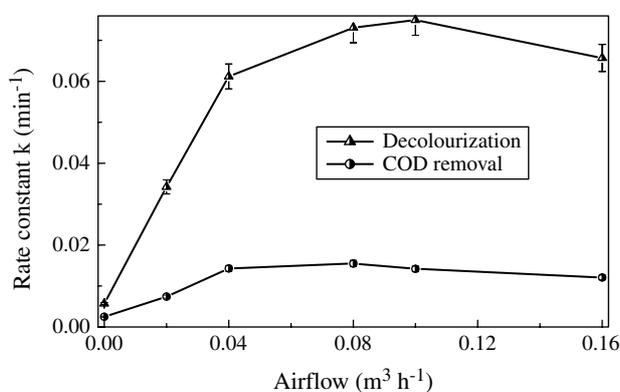


Figure 8. Effect of airflow.

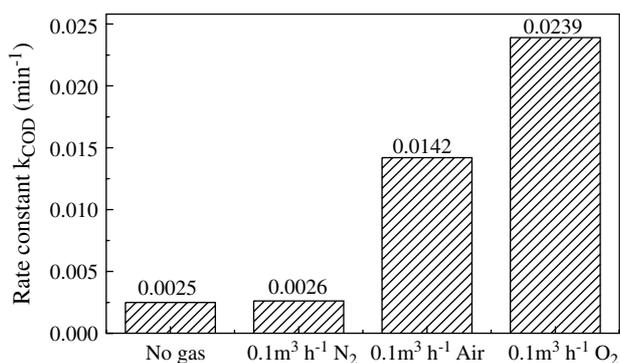


Figure 9. Effect of various gases.

increasing agitation. This is different from the pure photocatalytic process.<sup>35</sup> According to Vinodgopal and Kamat,<sup>13</sup> ultrasound increases mass transfer. Therefore, the discrepancy between photocatalytic and sonophotocatalytic processes may be attributed to ultrasound—promoted mass transfer being so effective as to negate the agitation role of sparged air in the sonophotocatalytic reactor. With regard to the slight decrease in the rate constant for COD removal after about  $0.08 \text{ m}^3 \text{ h}^{-1}$ , we presume tentatively that the result was due to the reduction of  $\text{O}_2$  residence time at the  $\text{TiO}_2$  surface at increased airflow. Further work is needed to verify this theory. However, it is certain at this moment that a suitable airflow can be selected to obtain higher rates of decolourization or COD removal in the sonophotocatalytic process.

### 3.4 Observation of synergetic effect

For any hybrid technology, it is frequently sought that the efficiency of the hybrid system (AB) should, at least theoretically, be higher than the sum of the efficiencies of the two single technologies (A and B) comprising the hybrid technology, that is,  $AB > A + B$ . Such synergetic effects in the interaction between single technologies are not uncommon.<sup>16,36–39</sup> Recently, we have proposed a simple formula to estimate the synergetic effect in the process of photoelectrocatalysis.<sup>40</sup> In this paper, a similar formula was used to evaluate the synergetic effect in the process of sonophotocatalysis:

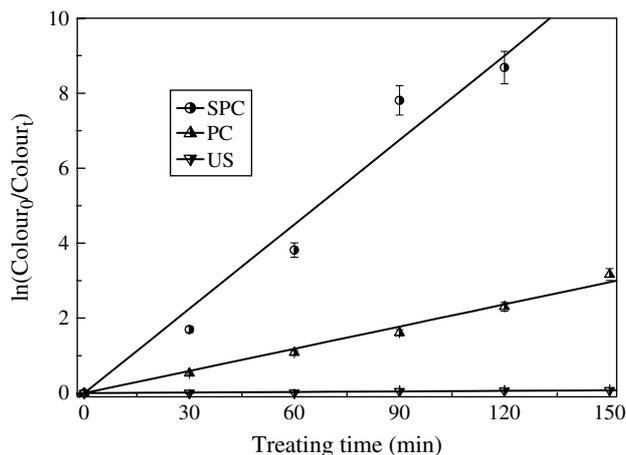
$$\text{SF} = R_{\text{spc}} - (R_{\text{pc}} + R_{\text{us}}) \quad (8)$$

where  $R_{\text{spc}}$ ,  $R_{\text{pc}}$  and  $R_{\text{us}}$  are the kinetic constants of decolourization and COD removal for sonophotocatalytic, photocatalytic and ultrasound processes, respectively, and SF is the synergetic factor. If  $\text{SF} > 0$ , the process combining photocatalysis with ultrasound has a synergetic effect. The greater the value of the SF, the stronger the synergetic effect. Conversely, if  $\text{SF} \leq 0$ , the processes have no synergetic interaction.

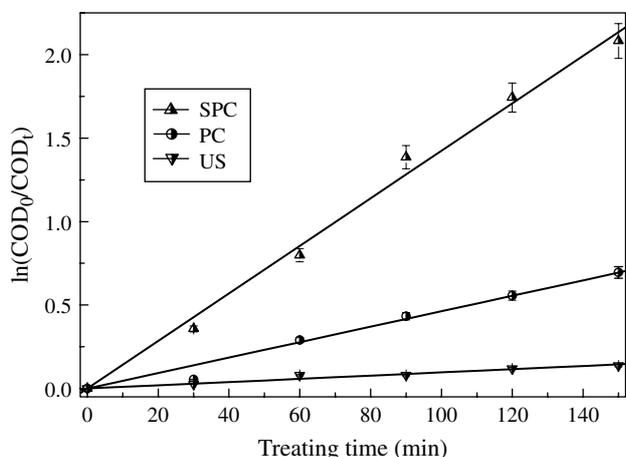
For sonophotocatalytic processes, there are only two reports in which the synergetic effect between sonochemical and photocatalytic technologies has been mentioned to date. In one, the synergetic effect was observed at 30 kHz but not at 514 kHz,<sup>39</sup> in the other, the synergetic effect was expected but not observed.<sup>16</sup>

In this work, photocatalytic, sonochemical and combined sonophotocatalytic processes followed pseudo first-order kinetics for decolouring and COD removal as confirmed by the linear transforms  $\ln(C_0/C_t) = f(t)$  (where  $C$  denotes colour or COD), as shown in Figs 10 and 11, and for which kinetic constants and their ratios are listed in Table 1. The SF values of decolourization and COD removal were 0.0548 and 0.0096  $\text{min}^{-1}$ , respectively, revealing that an apparent synergetic effect exists in both the decolouring and COD removal processes. Moreover, the synergetic effect is more apparent for decolouring than

for COD removal. The synergetic effect can be simply explained by the following three arguments. First, ultrasound can increase the overall surface area of the solid particles used as catalyst and prevent deactivation by continuously cleaning the catalyst surface.<sup>16</sup> Secondly, promotion of mass transfer of the substrate to the surface of TiO<sub>2</sub> from the bulk solution by ultrasonication can accelerate the sonophotocatalytic reaction.<sup>14</sup> Finally, additional hydroxyl radicals can be generated in the photocatalytic process from the hydrogen peroxide produced by ultrasound.<sup>39</sup>



**Figure 10.** Decolourization kinetics for sonochemical, photocatalytic and sonophotocatalytic processes.



**Figure 11.** COD removal kinetics for sonochemical, photocatalytic and sonophotocatalytic processes.

**Table 1.** Rate constants and SF for decolouring and COD removal processes

Rate constant/SF	Decolourization	COD removal
$k_{\text{SPC}}$ (min <sup>-1</sup> )	0.0750	0.0143
$k_{\text{PC}}$ (min <sup>-1</sup> )	0.0197	0.0046
$k_{\text{SU}}$ (min <sup>-1</sup> )	0.0005	0.0001
$k_{\text{SPC}}/k_{\text{PC}}$	3.8	3.1
$k_{\text{SPC}}/k_{\text{SU}}$	150	47.7
SF (min <sup>-1</sup> )	0.0548	0.0096

## 4 CONCLUSIONS

The following conclusions can be drawn:

1. Sonophotocatalytic technology could efficiently remove colour and COD from RBOKR-containing solution. Decolourization is much more easily achieved than COD removal.
2. Both decolouring and COD removal conformed to pseudo first-order kinetics. These rate constants are operating condition-dependent.
3. The rate constants of sonophotocatalysis were greater than that of both photocatalytic and sonochemical processes either in isolation or as a sum of individual processes, indicating an apparent synergetic effect between photo- and sono-processes.

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