Accepted Manuscript

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PII: DOI: Reference:	S1350-4177(14)00184-9 http://dx.doi.org/10.1016/j.ultsonch.2014.05.025 ULTSON 2621
To appear in:	Ultrasonics Sonochemistry
Received Date:	17 February 2014
Revised Date:	27 May 2014
Accepted Date:	27 May 2014



Please cite this article as: P. Li, Y. Song, S. Wang, Z. Tao, S. Yu, Y. Liu, Enhanced decolorization of methyl orange using zero-valent copper nanoparticles under assistance of hydrodynamic cavitation, *Ultrasonics Sonochemistry* (2014), doi: http://dx.doi.org/10.1016/j.ultsonch.2014.05.025

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1	Enhanced decolorization of methyl orange using zero-valent copper
2	nanoparticles under assistance of hydrodynamic cavitation
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24 ABSTRACT

25 The rate of reduction reactions of zero-valent metal nanoparticles is restricted by 26 their agglomeration. Hydrodynamic cavitation was used to overcome the disadvantage Experiments for decolorization of methyl orange azo dye by 27 in this study. 28 zero-valent copper nanoparticles were carried out in aqueous solution with and 29 without hydrodynamic cavitation. The results showed that hydrodynamic cavitation 30 greatly accelerated the decolorization rate of methyl orange. The size of nanoparticles 31 was decreased after hydrodynamic cavitation treatment. The effects of important operating parameters such as discharge pressure, initial solution pH, and copper 32 nanoparticle concentration on the degradation rates were studied. It was observed that 33 34 there was an optimum discharge pressure to get best decolorization performance. Lower solution pH were favorable for the decolorization. The pseudo-first-order 35 36 kinetic constant for the degradation of methyl orange increased linearly with the copper dose. UV-vis spectroscopic and Fourier transform infrared (FT-IR) analyses 37 38 confirmed that many degradation intermediates were formed. The results indicated 39 hydroxyl radicals played a key role in the decolorization process. Therefore, the 40 enhancement of decolorization by hydrodynamic cavitation could due to the deagglomeration of nanoparticles as well as the oxidation by the in situ generated 41 42 hydroxyl radicals. These findings greatly increase the potential of the Cu^{0} /hydrodynamic cavitation technique for use in the field of treatment of wastewater 43 44 containing hazardous materials.



45 Keywords: Zero-valent copper, nanoparticle, hydrodynamic cavitation, hydroxyl

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46 radicals, agglomeration, azo dye

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47 1. Introduction

48 Over 100,000 commercially available dyes are extensively used in different 49 industries, and more than 0.7 million tons of synthetic dyes are produced annually worldwide [1, 2]. During the dyeing process, approximately 15% of the dye is lost 50 51 and is released through industrial effluents [2, 3]. Azo dyes which are characterized 52 by the presence of nitrogen double bonds (-N=N-) represent the largest class of 53 synthetic dyes used in the textile processing, paper making, printing and cosmetic 54 industries [3, 4]. The release of azo dyes into the environment through colored dye 55 effluents creates serious environmental pollution problems due to their intense color, toxicity, carcinogenicity and mutagenicity [5]. Hence, the treatment of azo dye 56 57 wastewaters is becoming a matter of great concern. Azo dye wastewaters with high 58 concentration are difficult to treat using conventional activated sludge treatment 59 methods because of their synthetic origins and complex aromatic molecular structures [6]. Treatment though physical separation processes such as adsorption, coagulation, 60 membrane filtration, etc., is basically contaminants transfer from wastewater to 61 62 another waste. Advanced oxidation processes (AOPs), such as ozonation, Fenton's 63 oxidation, photocatalytic oxidation, sonolysis appear to be more appropriate for 64 treating wastewaters that containing azo dyes [7-10]. This is because hydroxyl 65 radicals generated in AOPs are very strong and non-selective oxidants with the ability to rapidly decompose many dissolved compounds in water matrix. But at the present 66 67 level of their development, the AOPs have not been widely employed in large-scale 68 industries because of their high cost and complex system.

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69 In recent years, metal-containing micro/nano particles, especially zero-valent iron 70 (ZVI), have drawn considerable attention for the remediation of contaminated land, 71 surface and groundwater. Zero-valent metals are efficient reducing agents and they have been proven effective in reducing azo dyes [11, 12]. The mechanism is well 72 known as the reductive cleavage of the azo group as shown in Scheme 1 [11, 12]. 73 74 Zero-valent metals, such as iron and copper are good electron donors. The azo dye 75 molecules accept electrons from the metals and transform into transitional products 76 when combining with H^+ . ≛ (CH₃)₂N SO₃ Na Methyl orange (MO) CH₃)₂N NH, 77 Scheme 1 78

The degradation reaction of azo dyes using zero-valent iron is found to occur on the 79 surface of ion metal. The mass transfer of dye chemicals to the iron surface is the 80 81 controlling step of the heterogeneous reaction [12, 13]. Therefore, the degradation rate can be increased by decreasing particle size to nano-scale. However, commercial 82 83 grade zero-valent metal nanoparticles are always agglomerates rather than single primary nanoparticles, which results in loss of the reactivity of surface site[14]. Many 84 85 attempts were taken to improve the efficiency of zero-valent metal reducing system. 86 Acoustic cavitation appears to deagglomerate particles and improve mass transfer 87 through the collapse of cavities or microbubbles [15-17].

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88 Hydrodynamic cavitation is known as a kind of cavitation which usually induced 89 by pressure differentials in a flowing liquid by introducing constrictions in the flow 90 [18-20]. Cavities can be generated due to the large pressure decrease. These bubble 91 cavities subsequently collapse when the pressure suddenly recovers. As cavities 92 collapse, a given bubble can reach temperatures as high as 5000K and pressures as high as 100 MPa (so-called "hot spots"). The drastic environmental change triggers 93 94 high-speed micro-jets and free radical generation due to decomposing water vapor 95 and noncondensable gases inside the bubble [21-23]. As compared to acoustic cavitation, hydrodynamic cavitation is more energy efficient and more suitable to 96 large scale application [18, 22, 24]. Recently, water jet cavitation is reported to be an 97 98 efficient method to modify the surface properties at the nano levels[25]. The use of 99 hydrodynamic cavitation in combination with Fenton process results in a good 100 synergistic effect in degradation of refractory contaminants [26-29]. We previously 101 reported that free-radicals could be generated by the collapse of microbubbles [30, 102 31].

In the current study, the combination of zero-valent copper nanoparticles with hydrodynamic cavitation for the decolorization of azo dye was investigated. Copper is known to be a mild hydrogenation catalyst and it is also widely used as a catalyst in other AOPs, such as wet-air oxidation. Accordingly it was selected in the study. The decolorization of methyl orange, used here as a model azo dye, was investigated under various conditions. The purpose of this study is to determine possible

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109 enhancement of decolorization of azo dye by the combined process, with the aim of 110 advancing the technical application of the zero-valent metal reduction technique. Material and methods 111 2. 112 2.1 Reagents Cu⁰ was obtained from Shanghai Chao Wei Nano Technology Co., Ltd, China. 113 Morphological and elemental analyses of the Cu⁰ nanoparticles were performed using 114 115 scanning electron microscope (SEM) (S-360, Cambridge, UK) with а energy-dispersive X-ray (EDX) at 20 kV. Particle size was analyzed with Malvern 116 117 Mastersizer 3000 particle analyzer (Malvern Instruments Ltd., United Kingdom). It was found that the Cu⁰ nanoparticles were agglomerated without pretreatment and 118 119 they had an average diameter of approximately 18 µm (Fig. 1). The SEM-EDX 120 spectrum showed that copper was the major species, accounting for 97.7% of the mass of the sample (Fig. 2). 121

Methyl orange, methanol, hydrochloric acid and sodium hydroxide were purchased from Sinopharm Chemical Teagent Co., Ltd., China. All chemicals used were analytical grade or higher.

125 2.2 Hydrodynamic cavitation reactor

Figure 3 shows a schematic diagram of the hydrodynamic cavitation reactor used in the current study. The system consists of a water tank with a 10 L capacity, a centrifugal pump (0.37 kW, 20NPD04S, Shanghai Nikuni Pumps co., Ltd., China) and an adjustable orifice valve acting as a cavitation device. The sectional area of flow at the valve is variable. The intake side of the pump was connected to the bottom of the

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131 water tank while the discharge side of the pump was connected to the bottom of the 132 water tank, forming a closed loop circuit. Pressure gauges were provided at 133 appropriate places to measure the pressures. The temperature was maintained constant 134 by a heat-exchanger coil inside the water tank. 135 2.3 Decolorization experiments For the decolorization experiment, 5 L of aqueous solution of 10 mg L^{-1} methyl 136 137 orange was prepared in the water tank. Hydrodynamic cavitation began by switching 138 on the pump and controlling the valves. After switching on the pump, water could be 139 sucked in by the pump and then discharged through the orifice valve at a pressure of 140 0.2-0.5 MPa. The solution was circulated at a flow rate of 5.8-14 L min⁻¹. The 141 decolorization experiments were initiated after the addition of the desired amount of 142 Cu⁰ nanoparticles to the water tank. The dye solution was periodically sampled by pipettes (5 mL), and the total sampling volume did not exceed 5% of the total solution 143 volume. Membrane filtration (pore size of $0.22 \ \mu m$) and solution pH adjustment to 144 pH=6.5 were conducted immediately after sampling to terminate the reaction. The 145 liquid temperature in the tank was maintained at 293 ± 1 K using a chiller. The initial 146 pH of the solution was adjusted using diluted sodium hydroxide solution (5.0 mol L^{-1} 147 NaOH) or diluted hydrochloric acid solution (5.0 mol L^{-1} HCl) and was measured by 148 149 a pH meter (SevenEasy S20, Mettler-Toledo International Inc., China). The dosage of Cu^0 nanoparticles was varied between 20 mg L⁻¹ and 200 mg L⁻¹. 150

151 2.4 Analysis



The concentration of methyl orange in the treated dye solution was determined

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153	based on the constructed calibration curve at the absorption wavelength of 460 nm
154	and expressed as the molar ratio to the initial concentration. The UV-vis spectrum
155	during the dye degradation was measured at 200-800 nm using a UV-vis spectrometer
156	(UV765, Shanghai Precision & Scientific Instrument Co., LTD, China). The
157	intermediates formed during the degradation of methyl orange were analyzed using
158	FT-IR (Nicolet 5700, Thermo Electron Scientific Instruments Co., Ltd., UK).
159	2.5 Kinetic analysis
160	Colored dye degradation by zero valent metals is generally assumed to be a
161	first-order reaction. Therefore, the reaction kinetics of methyl orange degradation was
162	modeled using a pseudo-first-order rate equation, Eq. (1):
163	$C = C_0 \times e^{-k_{obs}t} \tag{1}$
164	where k_{obs} denotes the observed first-order reaction rate constant, t the reaction time,
165	C_0 the initial concentration of methyl orange, and C the concentration of methyl
165 166	C_0 the initial concentration of methyl orange, and <i>C</i> the concentration of methyl orange at time <i>t</i> . When the reaction occurs in the water/bubble/Cu ⁰ interphase, the
165 166 167	C_0 the initial concentration of methyl orange, and <i>C</i> the concentration of methyl orange at time <i>t</i> . When the reaction occurs in the water/bubble/Cu ⁰ interphase, the phase transfer is limited, which makes it difficult to reach 100% degradation
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165 166 167 168 169 170	C_0 the initial concentration of methyl orange, and <i>C</i> the concentration of methyl orange at time <i>t</i> . When the reaction occurs in the water/bubble/Cu ⁰ interphase, the phase transfer is limited, which makes it difficult to reach 100% degradation efficiency. Thus, the residual dye concentration is modified as Eq. (2): $C - C_{\min} = (C_0 - C_{\min}) \times \alpha \times e^{-k_{obs}t} \qquad (2)$ where C_{\min} is the ultimate residual methyl orange concentration after treatment and
 165 166 167 168 169 170 171 	C_0 the initial concentration of methyl orange, and <i>C</i> the concentration of methyl orange at time <i>t</i> . When the reaction occurs in the water/bubble/Cu ⁰ interphase, the phase transfer is limited, which makes it difficult to reach 100% degradation efficiency. Thus, the residual dye concentration is modified as Eq. (2): $C - C_{\min} = (C_0 - C_{\min}) \times \alpha \times e^{-k_{obs}t} \qquad (2)$ where C_{\min} is the ultimate residual methyl orange concentration after treatment and α is the variation coefficient for the ideal first-order kinetics (1.0 denotes ideal
 165 166 167 168 169 170 171 172 	C_0 the initial concentration of methyl orange, and <i>C</i> the concentration of methyl orange at time <i>t</i> . When the reaction occurs in the water/bubble/Cu ⁰ interphase, the phase transfer is limited, which makes it difficult to reach 100% degradation efficiency. Thus, the residual dye concentration is modified as Eq. (2): $C - C_{min} = (C_0 - C_{min}) \times \alpha \times e^{-k_{obs}t}$ (2) where C_{min} is the ultimate residual methyl orange concentration after treatment and α is the variation coefficient for the ideal first-order kinetics (1.0 denotes ideal first-order kinetics; a larger deviation from 1.0 indicates less fit with the first-order
 165 166 167 168 169 170 171 172 173 	C_0 the initial concentration of methyl orange, and <i>C</i> the concentration of methyl orange at time <i>t</i> . When the reaction occurs in the water/bubble/Cu ⁰ interphase, the phase transfer is limited, which makes it difficult to reach 100% degradation efficiency. Thus, the residual dye concentration is modified as Eq. (2): $C - C_{\min} = (C_0 - C_{\min}) \times \alpha \times e^{-k_{obs}t}$ (2) where C_{\min} is the ultimate residual methyl orange concentration after treatment and α is the variation coefficient for the ideal first-order kinetics (1.0 denotes ideal first-order kinetics; a larger deviation from 1.0 indicates less fit with the first-order kinetics). C_{\min} and k_{obs} can be obtained by non-linear regression.

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175 3.1 Decolorization of methyl orange with and without hydrodynamic cavitation in the
 176 presence of Cu⁰ nanoparticles

Methyl orange was treated by hydrodynamic cavitation alone, Cu⁰ nanoparticle 177 alone and Cu⁰ nanoparticle reduction coupled with hydrodynamic cavitation. The 178 degradation efficiency was illustrated in Fig. 4. The dosage of Cu⁰ nanoparticle was 179 40 mg L^{-1} , the initial pH of solution was 3.0, and the pump discharge pressure was 0.4 180 181 MPa. Only 6.8% of methyl orange removal was obtained using hydrodynamic 182 cavitation alone. It has been known that hydrodynamic cavitation can produce 'OH 183 radicals due to the creation of hotspots (local areas of high temperature and pressure) 184 [31]. But the quantities of 'OH generated by hydrodynamic cavitation only were too low to be of practical use in decolorization. 185

186 Cu^0 nanoparticle alone test was conducted under mechanical stirring. Cu^0 187 nanoparticles were added to 1 L of 10 mg L⁻¹ methyl orange solution at varying 188 mixing rates (100, 500 and 1000 rpm) in a 2-L beaker without hydrodynamic 189 cavitation exposure. Only 20% of the methyl orange was decolorized during the 190 20-min test period (Fig.4), and no apparent difference in degradation rate was 191 observed at the varied mixing rates. It suggested that only mechanical stirring hardly 192 deagglomerated metal nanoparticles.

Figure 4 shows that the degradation efficiency was increased sharply to 83%when introducing hydrodynamic cavitation to Cu⁰ nanoparticle treatment (Cu⁰/HC). This means that the degradation of the dye by Cu⁰ was elevated by approximately 3.15 times, showing the synergistic effect compared to the individual Cu⁰ reduction

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and hydrodynamic cavitation. The synergistic coefficient (R) was defined as

$$R = \frac{k_{obs,Cu^0}}{k_{obs,Cu^0/HC}}$$

(3)

where k_{obs,Cu^0} and $k_{obs,Cu^0/HC}$ are the pseudo-first-order reaction constants for the degradation reaction with Cu⁰ and Cu⁰/HC, respectively. The synergistic coefficient was 4.25, which indicates good synergistic effect between hydrodynamic cavitation and Cu⁰ nanoparticle.

We also determined whether methyl orange could be removed through physical adsorption by Cu^0 nanoparticles. The dye solution (1 L) was filtered using a 0.22-µm membrane after the decolorization treatment by the Cu^0 /HC process. Acidification with 1 mol L⁻¹ HCl was performed to dissolve any particles left on the membrane. The UV-vis spectrum of the acidic solution was measured at 200-650 nm. Neither UV nor visible absorption was observed for the acidic solution, which suggested that methyl orange was not removed by Cu^0 nanoparticle adsorption.

The SEM picture of Cu^0 samples after hydrodynamic cavitation was shown in Fig 1. The size of Cu^0 nanoparticles was apparently reduced after hydrodynamic cavitation after 20-min of continuous treatment. We also measured zeta potential of Cu^0 samples, which is an important factor in understanding dispersion stability of nanoparticles in water. The zeta potential of Cu^0 samples decreased from -13.0 mV to -17.6 mV after cavitation treatment. Consequently, it is suggested that hydrodynamic cavitation could effectively promote the dispersion of Cu^0 nanoparticles in water.

217 3.2 Effects of solution pH on the decolorization

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To identify the optimum operational conditions, we performed experiments in

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219	which the pH of the dye solution was varied from alkaline to strongly acidic. The
220	changes in the concentration of methyl orange with time are illustrated in Fig. 5. The
221	Cu^0 nanoparticle dosage was 40 mg L^{-1} and the pump discharge pressure was 0.4
222	MPa. No perceptible changes in methyl orange concentration occurred when the pH
223	was not adjusted (pH= 6) or when NaOH solution was added (pH= 10 and 12).
224	However, obvious decolorization was observed when HCl was added to the solution,
225	and the methyl orange was degraded at a greater rate when the pH was decreased
226	from 4.0 to 3.0, which suggested that the decolorization process favors acidic
227	conditions and the lower solution pH contributes to a higher degradation rate. This
228	supports the fact that H^+ ions in the solution are directly involved in the reduction
229	reaction [12, 32]. When azo dye molecules collision with zero valent copper at lower
230	pH, Cu^0 accepts electrons oxidizing to Cu^{2+} . At the same time, azo molecules combine
231	with H^+ and turn into unstable transitional compounds (Scheme 1). Consequently, the
232	change of pH strongly influences the decolorization of the azo dye.
233	3.3 Effects of pump discharge pressure on the decolorization

The pump discharge pressure was changed from 0.2 MPa to 0.5 MPa and the effect on decoloriaztion are depicted in Fig. 6. The dosage of Cu^0 nanoparticle and the initial pH of solution was kept constant at 40 mg L⁻¹ and 3.0, respectively. It was found that the extent of decolorization increased with an increase in the pressure from 0.2 MPa to 0.4 MPa and then decreased. The maximum reaction rate constant was observed at 0.4 MPa discharge pressure.

240 Bubble dynamics studies have indicated that cavitational intensity generated at

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241	the collapse of the bubble increases with higher discharge pressure of the system. The
242	condition of cavitation can be evaluated by a dimensionless number, namely,
243	cavitation number which is calculated as follows:
244	$C_{v} = \frac{P - P_{v}}{\frac{1}{2}\rho v_{0}^{2}} $ (4)
245	where P is the recovered downstream pressure (N/m ²), P_{ν} is the vapor pressure of the
246	liquid at the operating temperature (N/m ²), v_0 is the velocity of the liquid at the orifice
247	valve (m/s), and ρ (g/m ³)is the density of the liquid. The cavitation number decreased
248	from 1.3 to 0.55 when the discharge pressure increased from 0.2 MPa to 0.5MPa in
249	the present system. The decrease in the cavitation number results in the increase of the
250	number of cavities formed. But excess cavities at high pressures are liable to coalesce
251	resulting in large bubbles which could decrease cavitational intensity [19]. Similar
252	results have been reported in optimizing the operation parameters for hydrodynamic
253	cavitation reactors [19, 33]. Mishra and Gogate [26] investigated the degradation of
254	Rhodamine B using orifice and venturi cavitation reactors and observed the reaction
255	rate reached maximum at the inlet pressure of 4.8 atm. Gogate and Pandit [34] have
256	modified the mathematical modeling of hydrodynamic cavitation and demonstrated
257	that there is at an optimum pressure at which the cavitation intensity could reach
258	maximum.

259 3.4 Effects of catalyst dosage on the decolorization

We next investigated the effects of Cu^0 nanoparticle dosage on methyl orange decolorization by the Cu^0/HC process under acidic pH conditions (pH= 3). The pump discharge pressure was kept at 0.4 MPa. The color removal efficiency significantly

263	increased with the Cu^0 nanoparticle dosage in the methyl orange solution (Fig. 7). The
264	Cu ⁰ doses were 10, 40, 60, 140 and 200 mg L ⁻¹ , which corresponded to rate constants
265	(k_{obs}) of 0.0906, 0.344, 0.859, 1.49 and 1.08 min ⁻¹ , respectively. A regression analysis
266	indicated that the observed first-order rate constant and the Cu ⁰ nanoparticle dose had
267	a nicely linear relationship ($R^2 = 0.95$) (Fig. 7). As the degradation of methyl orange
268	by Cu ⁰ /HC occurs on the surface, it is anticipated that the heterogeneous reaction rate
269	would increase with the increase of copper surface active sites. Accordingly, the
270	observed first-order rate constant linearly increases with the increase of copper dosage.
271	Nevertheless, they did not show a linear relationship when the Cu ⁰ dosage was
272	excessive (over 140 mg L^{-1}). It is supposed that the active surface area of unit mass
273	copper decreased due to the aggregation or overlapping of copper particles[35].
274	3.5 Discussion on the reaction pathways
275	3.5.1 UV-vis spectra change during treatment
276	The UV-vis spectra analysis was conducted to investigate the dye degradation
277	and evolution of intermediates during the Cu ⁰ /HC treatment. Figure 8 illustrates the
278	UV-vis spectrum changes of the dye solution as a function of reaction time. As can be
279	observed from these spectra, before the degradation, the absorption spectrum of
280	methyl orange in water was characterized by one main band in the visible region, with
281	a maximum absorption at 465 nm, and by another band in the ultraviolet region
282	located at 273 nm. The peak at 273 nm was associated with "benzene-like" structures
283	in the molecule [36], and that at 465 nm originated from an extended chromophore
284	comprising both aromatic rings connected through the azo bond (-N=N-). During

285	the first 10 min of Cu ⁰ /HC treatment, the absorption of the visible band at 465 nm
286	decreased rapidly, while the absorption at 273 nm increased and reached a peak at 10
287	min. During the next 20 min, the absorption at 273 nm decreased gradually. The decay
288	of the absorbance at 273 nm was considered to be evidence of aromatic fragment
289	degradation in the dye molecule and its intermediates [36].
290	3.5.2 FT-IR spectra changes after treatment
291	The methyl orange degradation and formation of intermediates was also
292	evidenced by changes in the FT-IR spectra. Figure 9 illustrates the typical FT-IR
293	spectra in the region of 500-4000 cm ⁻¹ for the dye at the initial conditions and after 1
294	h of treatment (pH: 3.0, pump pressure: 0.4 MPa, dosage: 40 mg L ⁻¹). The
295	characteristic peaks of the azo bond ($-N=N-$, at 1440 and 1519 cm ⁻¹) and the benzene
296	ring (at 1400-1600 cm ⁻¹) of methyl orange disappeared, and the antisymmetric and
297	symmetric stretching vibrations of $-CH_3$ (three peaks at 2800-3000 cm ⁻¹) clearly
298	disappeared. The characteristic peaks at 1197 and 1038 cm ⁻¹ , attributed to the
299	asymmetric stretching vibration of the -SO ₃ Na group [37], also clearly decreased.
300	The results indicated that the azo bond and the benzene ring were broken and that
301	desulfuration and demethylation occurred with the decolorization of methyl orange.
302	The breakage of chromophore band in methyl orange could form anilines and
303	benzenesulfonic acids. Meanwhile, several new peaks at 1417, 1585 and 1720
304	cm ⁻¹ were generated after 1 h of Cu ⁰ /HC treatment, which were attributed to the
305	antisymmetric and symmetric stretching vibrations of the $C - O$ groups in the salts of
306	carboxylic acids. Further oxidation of the aromatic intermediates could produce

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307 carboxylic acids, such as acetic acid and formic acid.

308 3.5.3 Effects of •OH scavenging on decolorization

The degradation experiment was performed in the presence of methyl alcohol, 309 a type of •OH scavenger, to investigate the role of •OH. Methyl alcohol is capable of 310 311 deactivating •OH and its derivatives. Methanol reacts with •OH and, to a lesser extent, with hydrogen radicals (•H) with the second-order rate constants $9.7 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$ 312 and $2.6 \times 10^6 \text{ mol}^{-1} \text{ s}^{-1}$, respectively [38]. Methanol was added to the methyl orange 313 solution during the decolorization treatment by the Cu⁰/HC process. The 314 concentration of methanol was varied in the range of 0.1 to 1.0 mL L⁻¹, while the Cu⁰ 315 nanoparticle dose and the initial solution pH were maintained at 40 mg L⁻¹ and 3, 316 respectively. It was found that the decolorization rate decreased significantly with the 317 318 addition of methanol (Fig. 10). When methanol concentration was 1 mL L^{-1} , the degradation efficiency only achieved 18% during a 20-min treatment period. It is 319 notable that the degradation efficiency after adding enough •OH scavenger decreased 320 to a level as low as that obtained during only Cu⁰ treatment. These results indicated 321 322 that \cdot OH was mainly responsible for the dye degradation process by Cu⁰/HC.

The degradation reaction of azo dyes using ZVI is well known to be a hydrogenation reaction occurring on the surface of metal iron. Therefore, the chromophore (-N=N-) in the methyl orange molecule may convert to anilines when they are absorbed on copper surface (Eq. (5)). Meanwhile, hydroxyl radicals are generated by the extremely high temperature caused by the adiabatic compression of cavities in association with hydrodynamic cavitation. Copper may enhance the

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329	generation of free radicals (Eq. (6)). The \cdot OH could attack the chromophore (–N=N–)
330	in the methyl orange molecule through the addition of electrons and transfer reactions
331	that yielded hydroxylated products (Eq. (7)).
332	$R_1 - N = N - R_2 + H^+ \xrightarrow{Cu^0} R_1 - NH_2 + R_2 - NH_2 $ (5)
333	$H_2 O \xrightarrow{Cu^0, Hydrodynamic cavitation} \cdot OH $ (6)
334	$Dye + \cdot OH \rightarrow dye - OH \tag{7}$
335	4. Conclusions
336	The degradation of methyl orange by copper nanoparticles was investigated in
337	the presence and absence of hydrodynamic cavitation. It was shown that the
338	decolorization efficiency of the process was markedly enhanced by the exposure of
339	hydrodynamic cavitation. We investigated that hydrodynamic cavitation could
340	effectively promote the dispersion of nano Cu ⁰ . The decolorization process was
341	greatly affected by the solution pH, the discharge pressure and the copper dose. The
342	decolorization rate increased when the pH of the dye solution was decreased from 4 to
343	3. The pseudo-first-order kinetic constant for the degradation of methyl orange
344	increased linearly with the copper dose. UV-vis spectroscopic and Fourier transform
345	infrared (FT-IR) analyses confirmed that many degradation intermediates were
346	formed. It is testified that hydroxyl radicals played an important role in the
347	decolorization process by Cu ⁰ /HC. Our results provide valuable information for the
348	treatment of azo dye wastewaters.

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350 Acknowledgments

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351 This work was supported by the National Natural Science Foundation of China

- 352 (51208366), the Foundation of the Science and Technology Commission of Shanghai
- Municipality, China (12ZR1451000) and the Foundation of the State Key Laboratory 353
- Acception 354 of Pollution Control and Resource Reuse, China (PCRRY12001).

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Figure 1. Size change and SEM images of Cu⁰ nanoparticles (a) before and (b) after hydrodynamic cavitation treatment



particles



Figure 3. Schematic of the hydrodynamic cavitation system



Figure 4. Decolorization of methyl orange by nano Cu⁰ with and without hydrodynamic cavitation





Figure 6. Effect of pump discharge pressure on the decolorization of methyl orange by Cu⁰/HC



Figure 7. Effect of Cu^0 nanoparticle dosage on the decolorization of methyl orange by Cu^0/HC



Figure 8. UV-visible absorption spectral changes of methyl orange during Cu⁰/HC treatment



Figure 9. FTIR analysis of (A) methyl orange and (B) metabolites obtained after the decolorization of methyl orange



Figure 10. Decolorization of methyl orange with and without methanol during Cu⁰/HC treatment

	Highlights
•	HC could greatly enhance the decolorization of methyl orange by nano Cu^0 .
	Higher inlet pressure and lower solution pH were favorable for Cu ⁰ /HC
57 treatment.	
	We investigated that HC could effectively promote the dispersion of nano Cu^0 .
	We testified that the enhanced degradation should be ascribed to 'OH oxidation.
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