



Microwave induced catalytic degradation of crystal violet in nano-nickel dioxide suspensions

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ABSTRACT

Nickel oxide catalyst was obtained by precipitation–oxidation method with the assistance of microwave irradiation. The samples were characterized by X-ray diffraction, Raman spectrophotometer, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, surface area and porosity analyzer. On the basis of the results, the as-prepared product was nano-NiO₂ with OH group and active oxygen. The catalytic activity of the as-prepared product might be attributed to its microwave absorbing property and the role of active oxygen, OH group under microwave irradiation. The microwave induced catalytic degradation process (MICD) with as-prepared product was further applied to degrade triphenylmethane dye crystal violet (CV). 97% of a 100 mg L⁻¹ sample of CV was rapidly degraded in 5 min with the corresponding 81% TOC removal. The main intermediates were separated and identified by LC–ESI–MS and GC–MS techniques. The LC–ESI–MS analytical results demonstrated that a series of *N*-de-methylation products were obtained in a stepwise manner, namely mono-, di-, tri-, tetra-, penta-, and hexa-de-methylated CV species. Nine organic acids with benzene ring and four low molecular acids were yielded with the assistance of GC–MS. The proposed degradation pathways were discussed in this study. The degradation processes might include *N*-de-methylation, destruction of conjugated structure and opening-benzene ring. MICD, as a potential technique with wide application perspective, can be used to purify triphenylmethane dye wastewater with nanosized nickel dioxide.

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1. Introduction

Environmental pollution is an increasing serious challenge for the whole world. Being one of the important subclasses of pollutants, dyes have attracted many attentions for their removal from effluents. Crystal violet (CV) is a typical triphenylmethane dye, which has been extensively used as a biological stain, dermatological agent, veterinary medicine, additive to poultry feed to inhibit propagation of harmful bacteria and a commercial textile dye. However, CV is toxic to mammalian cells and also a mutagen and mitotic poison [1]. The wastewater containing CV not only causes colouration of water, but also harms to aquatic life [2]; furthermore, its presence in drinking water poses a potential threat to human health. Therefore, there are both environmental and health concerns on this particular dye and this causes a need for the development of efficient, energy-saving and inexpensive dye wastewater treatment processes.

In the past decade, different approaches have been utilized to remove or degrade the wastewater containing CV including biological decolouration [3–5], adsorption [6–9], and some advanced

oxidation processes (AOPs) such as photo-Fenton reaction [10–12], TiO₂-mediated photocatalytic degradation using visible light irradiation [13] and UV irradiation [14,15], and TiO₂ photocatalytic degradation using microwave powered electrodeless discharge lamps [16–19]. However, each technology has its own limitations. Biological method could not eliminate the CV solution completely because CV is a recalcitrant molecule [20]. Adsorption method cannot degrade pollutants but just transfer their phase [21]. The application of AOPs is also limited due to the related expensive operating costs and high energy requirements.

The microwave induced catalytic degradation process (MICD) is a promising technology that provides a perspective alternative in purifying wastewater containing CV. This technology, which integrated microwave irradiation with some suitable strong microwave absorbent catalysts, has proved to be an efficient method for degradation of organic pollutants including 2-tert-butylphenol [22], acid orange 7 [23], phenol [24], congo red [25], 4-chlorophenol [26] and rhodamine B [27]. The strong microwave absorbent could be absorber, semiconductor, ferromagnetic metal and transition metal oxide. Among them, transition metal oxide nickel oxide appears to be especially efficient. Christoskova and Stoyanova studied the degradation of phenolic wastewater over Ni-oxide under low-temperature liquid-phase catalytic oxidation [28]. Lai et al. evaluated the microwave-enhanced catalytic degradation of 4-

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chlorophenol and phenol over Ni-oxide [24,26]. Different synthesis and treatment methods make a significant difference in the composition and structure of nickel oxide which determines the activity of the products, such as the oxidation state of nickel, the existence of active oxygen and the morphology of the products.

Recently, we synthesized a kind of nanosized nickel oxide through precipitation–oxidation method with the assistance of microwave irradiation. This nanosized nickel oxide seemed to be a higher valence state nickel dioxide with OH group and active oxygen in its structure. As a strong microwave absorbent together with the existence of active oxygen and OH group in its structure, nickel dioxide introduced to MICD process has the feasibility for purifying organic pollutants. The principle aim of this study is to investigate the possible application of the synthesized and characterized nanosized nickel dioxide for removing CV dye wastewater in MICD process, as well as the degradation mechanism.

2. Materials and methods

2.1. Materials

The target dye crystal violet (CV, laser-grade) was obtained from Alfa Aesar Chemical Company. Stock solutions containing 100 mg L^{-1} of CV in aqueous solution were prepared, protected from light, and stored at 4°C . NaOH, NaClO, and NiCl_2 were obtained from Nanjing Chemical Company. HPLC-grade ammonium acetate, acetate acid and methanol were purchased from Tedia Company and used without further purification. Milli-Q water was used throughout this study.

2.2. Preparation and characterization of nickel oxide

Nickel oxide was prepared by a modification of previously described method [29]. Precipitation–oxidation method with the assistance of microwave irradiation was employed in this study. Nickel oxide was obtained from nickel chloride with sodium hypochlorite in the sodium hydroxide solution. The black precipitate was then filtered, washed with deionized distilled water and irradiated with 2450 MHz microwave for 10 min at 100 W, dried in a muffle furnace at 110°C for 24 h. The dried product was ground to fine powders and stored in a desiccator. The as-prepared sample was separately calcined at different temperatures for 3 h.

The crystallinity of the nickel oxide samples was determined by X-ray diffraction (XRD) using a diffractometer with $\text{Cu K}\alpha$ radiation over the scan range $30\text{--}80^\circ$ (Model, Shimadzu LabX XRD-6000). Measurement of BET surface area and pore distribution were performed using N_2 adsorption/desorption isotherms on a Micromeritics ASAP 2020. X-ray photoelectron spectroscopy (XPS) measurement was done on an ESC ALB MK-II XPS system with a monochromatic $\text{Al K}\alpha$ source and a charge neutralizer; all the binding energies were referenced to the C 1s peak at 284.6 eV of the surface adventitious carbon. The FT-IR spectra were recorded by a NEXUS 870 FT-IR, made in USA NICOLET Company in a wavenumber range of $4000\text{--}400 \text{ cm}^{-1}$. Raman spectra were obtained by JY HR 800 Laser Raman spectrometer (JY Company, France).

2.3. Microwave induced catalytic degradation experiment

The microwave induced catalytic degradation process (MICD) was conducted in a house microwave setup that was same as referred to our previous study [16]. Two processes were conducted during the degradation experiments. For the process of microwave alone (MW), only 50 mL CV ($C_0 = 100 \text{ mg L}^{-1}$, pH 9.01) was put into the reactor vessel. In MICD process, 50 mL CV ($C_0 = 100 \text{ mg L}^{-1}$, pH 9.01) solution and 0.040 g nickel oxide was added together to the reactor vessel. All the experiment was carried out with the

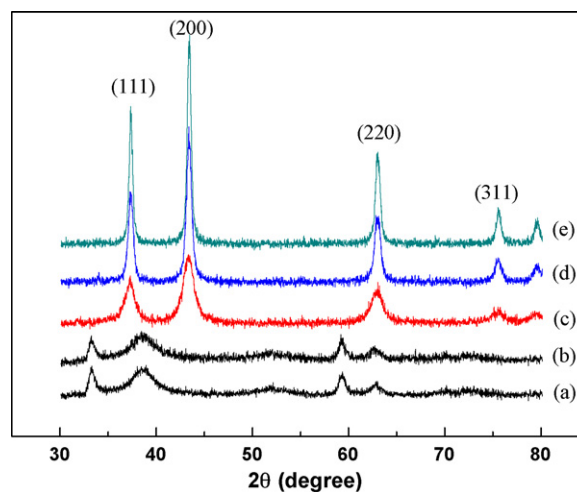


Fig. 1. XRD patterns of as-prepared nanosized nickel oxide samples: (a) before use, (b) after use and the products calcined at (c) 300°C , (d) 400°C , and (e) 500°C .

microwave oven at 750 W. Samples were collected at regular interval after the reaction and were immediately centrifuged to remove catalyst particles for analysis if needed.

2.4. Analytical methods

The samples after reaction were centrifuged for 15 min at 10,000 rpm, and then filtered with $0.22 \mu\text{m}$ Millipore to remove catalyst particles. The solution pH was measured with pH meter (PHS-2C, China). The total organic carbon (TOC) was determined with Shimadzu TOC-5000 analyzer. The determination of CV concentration was performed by HPLC (Agilent 1200, USA) using a Gemini C18 column ($150 \text{ mm} \times 4.6 \text{ mm i.d.}$, $5 \mu\text{m}$, Phenomenex, USA). The HPLC evaluation was carried out using an ammonium acetate buffer solution (10 mM) and methanol as mobile phase with a flow rate of 1 mL min^{-1} and a diode array detector (DAD, detection wavelength 580 nm).

The reaction intermediates were detected by LC/MS (Thermo, Finnigen, USA) equipped with electrospray ionization (ESI). The samples were chromatographically separated using a Gemini C18 column at a flow rate of 0.2 mL min^{-1} , and the mobile phase was methanol–ammonium acetate buffer solution ($60:40$, v/v). The identification of intermediates was also conducted by a Thermo

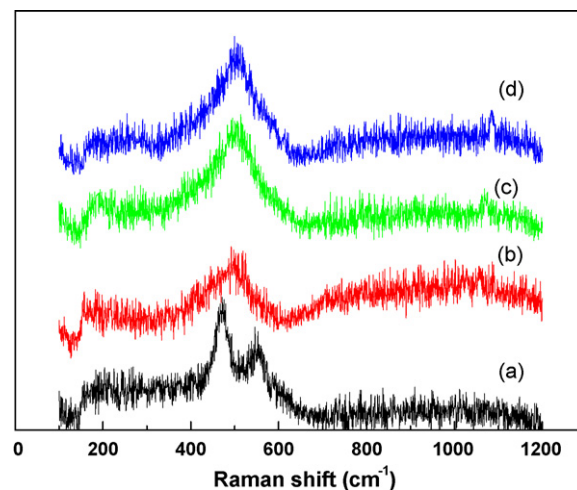


Fig. 2. Raman spectra of nanosized nickel oxide samples: (a) as-prepared and the products calcined at (b) 300°C , (c) 400°C , and (d) 500°C .

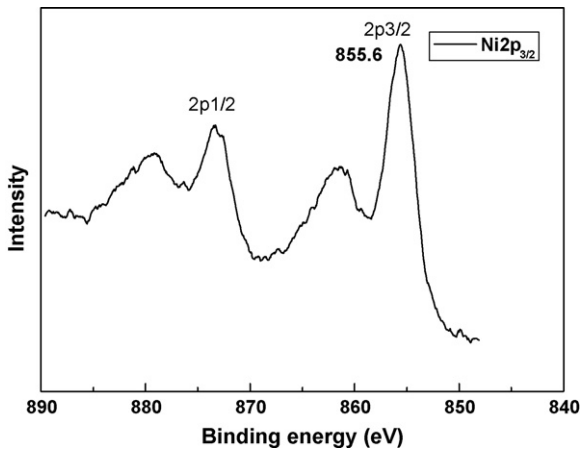


Fig. 3. Ni 2p X-ray photoelectron spectrum of as-prepared nano-structured NiO samples.

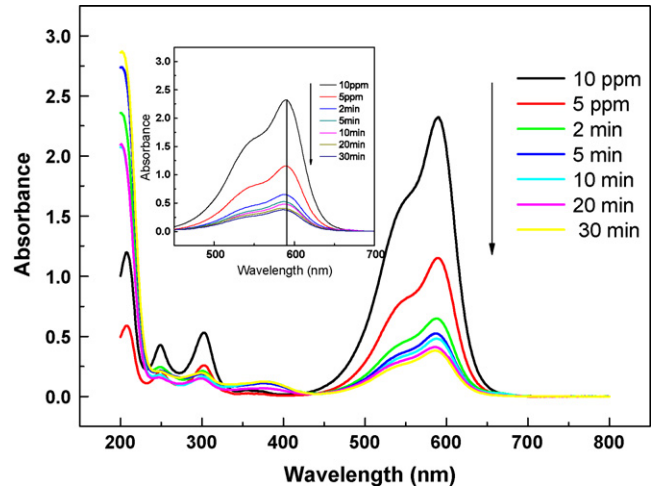


Fig. 6. UV-vis spectra changes of CV degraded.

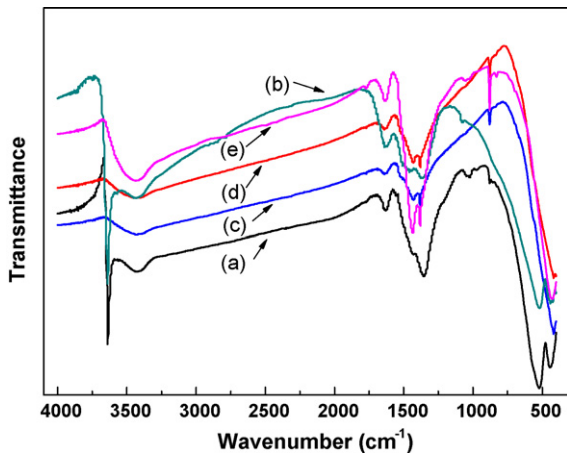


Fig. 4. FT-IR spectra of the as-prepared nanosized nickel oxide samples: (a) before use, (b) after use and the products calcined at (c) 300 °C, (d) 400 °C, and (e) 500 °C.

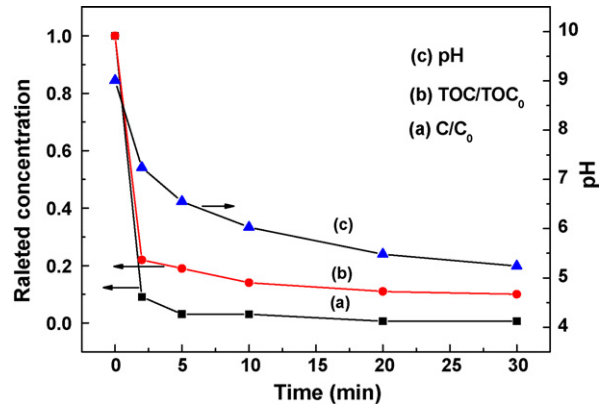


Fig. 7. The variation of CV concentration, TOC and pH in MW-induced process.

Finnigan Trace gas chromatography interfaced with a Polaris Q ion trap mass spectrometer (GC/MS, Thermo, Finnigen, USA) equipped with DB-5 fused-silica capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The pre-treatment process was according to previous method [17] as follows: 15 mL filtered solution was extracted with 25 mL n-hexane for three times, and the extracted

solution was dehydrated using anhydrous sodium sulphate. Afterward, the dehydrated solution was concentrated to 1 mL and blown drying with Nitrogen Evaporator. Before GC-MS analysis, trimethylsilylation was carried out at 50 °C for 30 min using 0.5 mL bis(trimethylsilyl)trifluoroacetamide (BSTFA). The final sample (2.0 μl) was automatically injected into GC with DB-5 column with splitless mode. The oven temperature was programmed as follows:

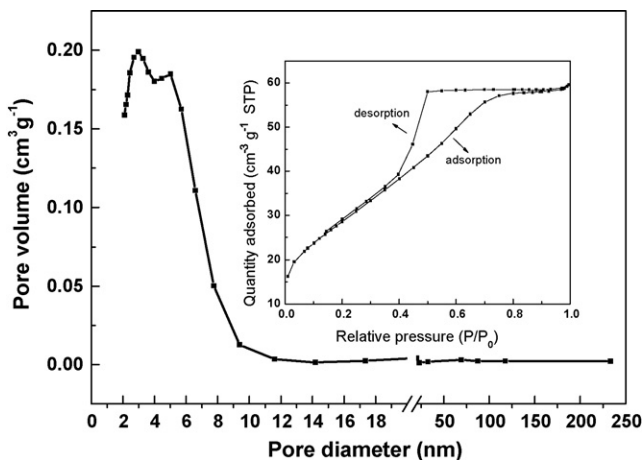


Fig. 5. N₂ isotherms and pore size distribution of as-prepared nanosized nickel oxide samples.

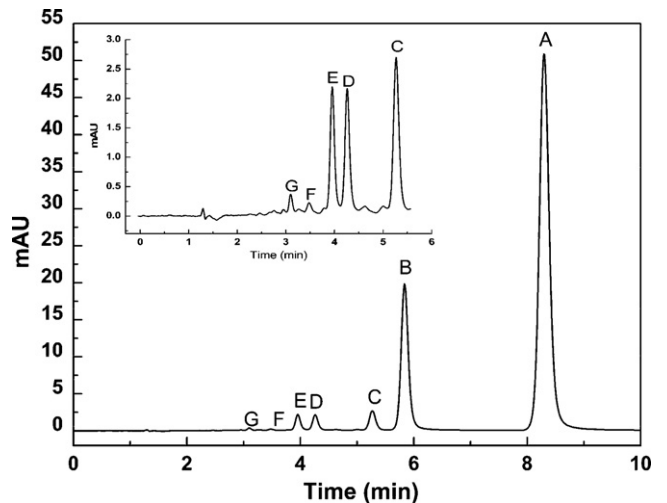


Fig. 8. HPLC chromatogram of the reaction intermediates recorded at 580 nm.

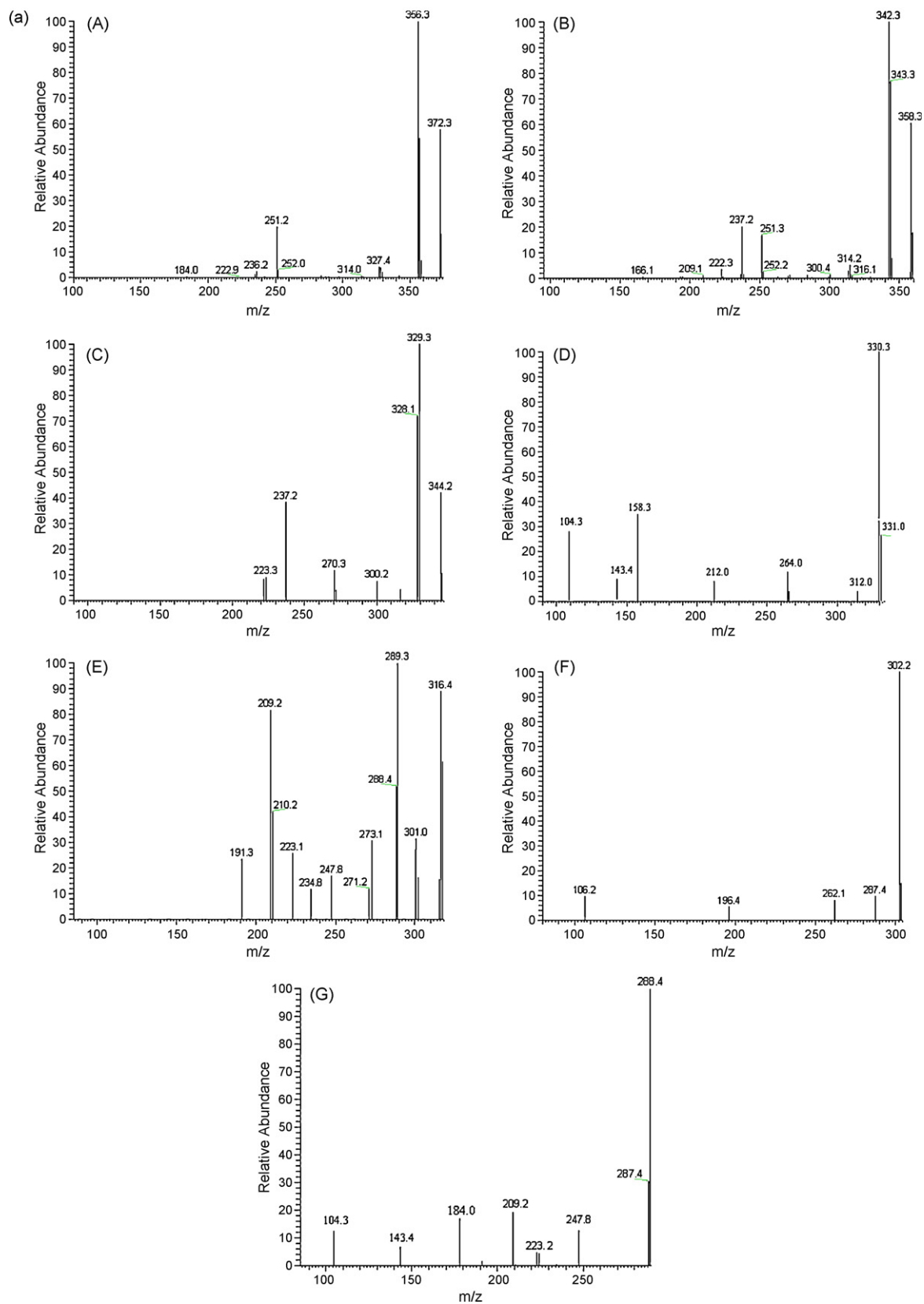


Fig. 9. ESI mass spectra of *N*-de-methylated intermediates from the degradation of CV by LC/MS: (a) ionic spectra for specific mass and (b) SIM for specific mass.

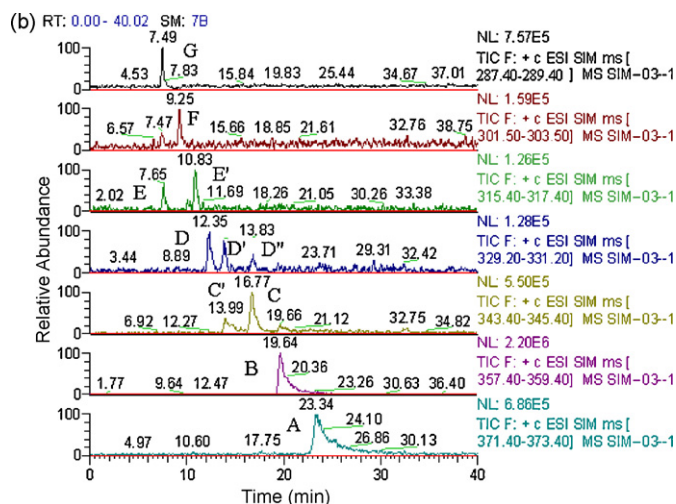


Fig. 9. (Continued).

the initial temperature was 60 °C, then 60–250 °C at ramp rate of 5 °C min⁻¹, held 2 min, 250–280 °C at ramp rate of 10 °C min⁻¹, held 2 min. The MS was operated with 70 eV electron impact (EI) mode and positive ion mode.

3. Results and discussion

3.1. Characterization

The XRD and Raman spectra of the as-prepared sample and calcined samples at 300, 400, and 500 °C are shown in Figs. 1 and 2, respectively. As can be seen in Fig. 1, similarity of the patterns for three calcined samples (Fig. 1c–e) is quite evident. In Fig. 1c–e, the peaks at 37°, 43°, 63°, 75°, and 79° correspond to cubic phase pure NiO [30]. Along with the increase of the calcining temperature, the peaks become narrow and sharp which indicated that the crystallinity and the grain size of the calcined products increased. The average crystalline size can be roughly calculated using a diffraction peak from Scheerer's formula. The average size of the samples obtained at different calcining temperature (300, 400 and 500 °C) was 5.4, 7.2 and 10.5 nm, respectively. Originally, nickel oxide obtained before microwave irradiation is an amorphous black powder, insoluble in organic solvents and water other than acidic solvents [31]. Then with the irradiation of microwave, there is obvious crystal phase of the as-prepared product (Fig. 1a). Meanwhile, the XRD spectrum of as-prepared product was different from that of calcined pure NiO, which indicated that the as-prepared product was another pattern of nickel oxide. The average size of the as-prepared product was 3.0 nm.

In addition, the Raman spectra shown in Fig. 2 present the similar results to the case of XRD. As the calcining temperature increased, the peaks become narrow and sharp; moreover, the symmetry of the peaks increases gradually. The spectral features of the as-prepared nickel oxide are about at 470 and 550 cm⁻¹ (Fig. 2a) which is different to the calcined products NiO but similar to that of commercial NiO₂ [32]. The Raman spectra indicated that the as-prepared nickel oxide may be a higher oxide NiO₂.

To understand the structure of the as-prepared nickel oxide better, the Ni 2p XPS was shown in Fig. 3. A peak at 855.6 eV was observed, which illustrated that the surface of the as-prepared product was in an oxidation valence higher than 2+ [33]. The binding energy of 855.6 eV is higher than that typical of Ni²⁺ in NiO which is 854.6 eV [34,35]. According to the literatures [32,36], and combination of the data of Raman and XRD, there should be a Ni⁴⁺ in the as-prepared nickel oxide, which further demonstrated that

the as-prepared product was NiO₂. The results of element analysis showed that the atomic percentage O:Ni is 2.80:1 indicating that there is other oxygen-bonded species.

The FT-IR spectra of the as-prepared and calcined at 300, 400 and 500 °C samples are given in Fig. 4. Comparison of the spectra shows that two absorption bands at 517 and 3640 cm⁻¹ exist in the spectrum of as-prepared product, which are absent from the spectra of the products calcined at different temperatures. The band at 517 cm⁻¹ may be attributed to the structural fragment, which is the active oxygen according to the literature [33]. The band at 3640 cm⁻¹ is a characteristic absorption band for OH group, indicating the existence of OH group in the as-prepared product. That was corresponding to the atomic percentage O:Ni (2.80:1) where O atom was excessive to Ni.

The nitrogen adsorption–desorption isotherm and pore volume distribution of the as-prepared product was also carried out and the results were presented in Fig. 5. The pore volume distributions are in the range 2–10 nm. The specific surface area of the as-prepared product is 105 m² g⁻¹. The as-prepared product has large specific surface area which could increase the active sites on the surface of particles.

On the basis of the results obtained above, it is inferred that the as-prepared product was a nanosized nickel dioxide (NiO₂) with an OH group and active oxygen in its structure. As NiO₂ is a strong microwave absorbent, meanwhile OH group and active oxygen can generate •OH radical under microwave irradiation, we have reasons to consider that the as-prepared product may be a good catalyst in MICD process.

3.2. Recovery of the nickel oxide

The used as-prepared product was collected and then filtrated, washed, and dried at 110 °C for 24 h. The spectra changes between the as-prepared product before and after use were characterized by XRD and FT-IR. From Fig. 1a and b, the sharpness and position of reflections peaks of the two spectra were almost the same. The FT-IR spectra shown in Fig. 4a and b indicated that the recovered product was in conformity with the product before use. The spectra analysis demonstrated that the recovered product had catalytic activity as well as the properties of the product before use.

3.3. Microwave-induced degradation of CV

Initially, experiments were carried out in the presence of either MW or as-prepared nickel oxide alone; neither of these treatments had a notable effect on the characteristic absorption band of the dye and imparted no decolouration. However, in the presence of as-prepared nickel oxide, the CV dye in aqueous solution can be degraded efficiently under microwave irradiation (2450 MHz). However, in the presence of calcined products at 300, 400 and 500 °C, the CV dyes in aqueous solutions were not degraded apparently under the same condition. The reason may be that the calcined products were pure NiO with larger particle and smaller surface area than that of as-prepared product. So the as-prepared product was used as catalyst in the further investigation. The variation of absorption spectra of CV in different treatment time under MICD process is shown in Fig. 6. As can be seen in the spectra, the absorbance intensity rapidly decreased, which indicated that CV was degraded gradually as time prolonged. Furthermore, the absorption maximum peak of the degraded solution exhibited slight hypsochromic shifts (590–586 nm), which might result from the formation of a series of *N-de*-methylated intermediates.

Fig. 7 shows the removal of CV solution and the variation of TOC and pH in MICD process. The curve (a) is the variation of concentration of CV. It can be seen that, 90.9% of CV dye was degraded in 2 min. 5 min later, the CV was almost degraded completely; the

removal reached 97%. However, similar removal of CV (0.18 mM) in TiO₂-mediated photocatalytic degradation using visible light irradiation needed 90 min [14], whereas in the study of literature [15] it needed 16 h to degrade 50 mg L⁻¹ CV under TiO₂-assisted photodegradation with UV irradiation. So microwave induced catalytic degradation process is a more efficient technology for degradation of CV.

It also can be seen that TOC decreased gradually as the irradiation time prolonged, indicating that CV was mineralized continuously. The removal efficiency of TOC was 81% in 5 min, and 90% in 30 min. Furthermore, it could be observed that the decrease of TOC took more time than the degradation of CV because of the organic intermediates generated during the degradation of target dye. Meanwhile, the pH of the solution decreased as the irradiation time prolonged with the changing range from 9.01 to 5.24 in 30 min, which probably because some organic acids with low molecular weight might be produced after the CV and its intermediates were degraded.

3.4. Identification of the intermediates and final products

Analysis of the reaction intermediates and final products may reveal some details of the reaction process. The intermediates of CV in MW-induced process were identified by HPLC, LC/MS and GC/MS. Fig. 8 is the HPLC chromatograms of the reaction intermediates recorded by a diode array detector (at 580 nm). The peak A was parent CV with retention time (*t_R*) at 8.30 min, and the other six peaks from B to G with the *t_R*s at 5.83, 5.27, 4.26, 3.95, 3.47 and 3.10 min were some reaction intermediates (C–G shown in Fig. 8 inset). On the basis of the fact that the absorption maximum peak of the CV solution exhibited slight hypsochromic shifts (590–586 nm) (shown in Fig. 6), it could be inferred that these intermediates were *N*-*de*-methylated intermediates.

To further identify the intermediates, LC/MS technique was employed. As shown in Fig. 9(a), seven different *m/z* peaks were detected. They were 372.3, 358.3, 344.2, 330.3, 316.4, 302.2 and 288.4, respectively. According to the results of mass spectral analysis, shown in Fig. 9(b), the components *m/z* 372.3, 358.3, 344.2, 330.3, 316.4, 302.2 and 288.4 were parent CV, mono-, di-, tri-, tetra-, penta-, and hexa-*N*-*de*-methylated intermediates, respectively, corresponding to A–G shown in Fig. 10. These *N*-*de*-methylated intermediates were corresponding to the A–G.

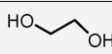
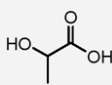
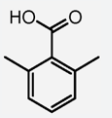
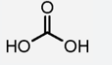
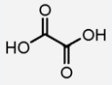
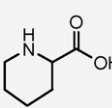
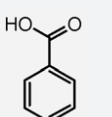
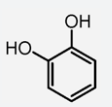
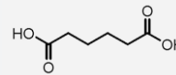
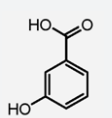
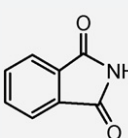
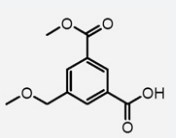
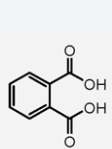
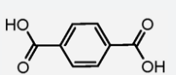
It is well-known that the combination of LC/MS and GC/MS information might be more effective in getting more information about degradation products. To obtain more information about low molecular intermediates, the degradation products were further analyzed by a GC/MS technique. The major reaction intermediates detected were listed in Table 1. They were mainly organic acids, such as oxalic acid, terephthalic acid, phthalic acid, benzoic acid and 3-hydroxybenzoic acid and so on, were most likely the low molecular intermediates resulting from the cleavage of the triphenylmethane ring in CV structure.

3.5. Proposed degradation pathways

The catalyst used in the MICD was nanosized NiO₂ with OH group and active oxygen in its structure. As a charge transfer transition metal oxide, the as-prepared product NiO₂ was a strong microwave absorbent that can strongly absorb and transfer microwave energy. Meanwhile, with the assistance of microwave energy, the OH group and active oxygen in its structure would finally transform into •OH radical which can oxidize all kinds of organic substances. On the basis of the analysis above, catalytic degradation of CV may easily take place in MICD process.

On the basis of the reaction intermediates identified by LC/MS technique, *N*-*de*-methylation process was in a stepwise manner.

Table 1
Main products of the catalytic degradation of CV detected by GC/MS.

<i>m/z</i>	Identified intermediates	Structural formula
62	Ethane-1,2-diol	
90	2-Hydroxypropanoic acid	
150	2,6-Dimethylbenzoic acid	
62	Carbonic acid	
90	Oxalic acid	
129	Piperidine-2-carboxylic acid	
122	Benzoic acid	
110	Pyrocatechol	
146	Adipic acid	
138	3-Hydroxybenzoic acid	
147	Isoindoline-1,3-dione	
224	3-(Methoxycarbonyl)-5-(methoxymethyl)benzoic acid	
166	Phthalic acid	
166	Terephthalic acid	

As shown in Fig. 9(b), there also had some isomeric intermediates of *N-de*-methylated products. There were two isomeric intermediates for di-*N-de*-methylated product, three for tri-*N-de*-methylated product, and two for tetra-*N-de*-methylated product, respectively. Furthermore, the GC/MS results also provided solid evidence for the destruction of the conjugated triphenylmethane structure of CV and opening-benzene ring. It is well-known that the CV degradation occurs via two processes: one is stepwise *N-de*-methylation, and the other is the destruction of the conjugated structure [14]. However, there are three degradation processes in this study such as *N-de*-methylation, destruction of conjugated structure and opening-benzene ring.

Corresponding to the LC/MS and GC/MS identification, the possible microwave-induced catalytic degradation pathway of CV with NiO₂ was proposed, as shown in Fig. 10.

4. Conclusions

The nanosized as-prepared product was successfully synthesized by precipitation–oxidation method with the assistance of microwave irradiation. The as-prepared product was a higher oxide nickel dioxide with OH group and active oxygen in its structure which displayed large specific area with 105 m² g⁻¹ and the nanosized average size with 3 nm. It is demonstrated that the as-prepared product could serve as an efficient catalyst in MICD process. The catalytic activity of the as-prepared product might be attributed to its strong microwave absorbing property and the role of active oxygen, OH group under microwave irradiation. MICD process with the as-prepared product could catalytically degrade CV efficiently and the removal was about 97% in 5 min. Three degradation processes such as *N-de*-methylation, destruction of conjugated structure and opening-benzene ring occurred in MICD with nanosized nickel dioxide. All six *N-de*-methylated intermediates were confirmed by LC/MS in this study. With the assistance of GC/MS, fourteen organic acids, such as oxalic acid, terephthalic acid, phthalic acid, benzoic acid and 3-hydroxybenzoic acid, etc., were identified. Based on the efficient degradation of CV and the reaction mechanisms, MICD process with nanosized nickel dioxide catalyst could be a potential promising technology to remove organic pollutants from waters.

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