FeNiCeOₓ ternary catalyst prepared by ultrasonic impregnation method for diclofenac removal in Fenton-like system
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ABSTRACT
FeNiCeOₓ was firstly prepared by ultrasonic impregnation method and used to remove diclofenac in a Fenton-like system. The catalytic activity was improved successfully by doping Ni into FeCeOₓ. The diclofenac removal efficiency reached 97.9% after 30 min reaction. The surface morphology and properties of FeNiCeOₓ were characterized by Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), Raman and X-ray photoelectron spectroscopy (XPS) analyses. FeNiCeOₓ in this paper had larger specific surface area than those prepared by other methods, which was attributed to the cavitation effect and hot-spot effect during the ultrasonic synthesis process. Low crystallinity of Fe₂O₃ and NiO showed by characterization could lead to high interaction of Fe and Ni ions with support of CeO₂. They substituted Ce in CeO₂, caused lattice contraction and formed more oxygen vacancies, which favoured the catalytic reaction. Meanwhile, Fe and Ce ions both had redox cycles of Fe³⁺/Fe²⁺ and Ce⁴⁺/Ce³⁺, which facilitated the electron transfer in the reaction. The synergistic effect among Fe, Ni and Ce might lead to better catalytic performance of FeNiCeOₓ than any binary metal oxides constituted from the above three elements. Finally, the potential mechanism of diclofenac removal in FeNiCeOₓ-H₂O₂ system is proposed.

Key words | diclofenac, FeCeOₓ, Fenton-like, oxygen vacancy, ultrasonic impregnation

INTRODUCTION
Pharmaceutical wastewater, an emerging contaminant, contains many harmful refractory organic compounds that cannot be removed efficiently by conventional biological methods (Salmani et al. 2017), so advanced oxidation processes (AOPs) have received considerable attention for handling this wastewater. Commonly used AOPs are classic Fenton and Fe⁰-based heterogeneous Fenton-like processes, but both methods have severe drawbacks. The classic Fenton process needs low pH, high H₂O₂ dosage and generates high amount of iron sludge (Blanco et al. 2016). Fe⁰ materials agglomerate easily into larger particles for their high surface energy and intrinsic magnetic interaction, which is unfavorable to the catalytic performance and the recovery of catalyst (Zha & Wang 2016).

Therefore, the novel heterogeneous Fenton-like process has attracted more attention for the benefits of high efficiency, mild operation conditions, easy separation and so on (Nidheesh 2015). The essential factor of the heterogeneous Fenton-like process is an effective catalyst. Combination of Fe with Ce has shown good catalytic activity in both Fenton-like and photocatalytic systems. Previous research showed that the highest diclofenac removal efficiency reached 84% in the FeCeOₓ·H₂O₂ system within 40 min (Chong et al. 2017). The removal efficiency of 4-chlorophenol was about 78% using a Fe₃O₄/CeO₂ composite as the heterogeneous Fenton-like catalyst (Xu & Wang 2015).

To further improve the catalytic property of Fe-Ce material, nickel was considered to be doped into it. This Fe-Ni-Ce ternary composite has shown great catalytic potential in various areas. Inoishi et al. (2015) found that Ni-FeCe/(Mn)O₂ was an excellent cement-based anode for rechargeable Fe-air batteries. Allaedini et al. (2016) reported that the photocatalyst Fe-Ni-Ce showed superior activity in refractory organics degradation of methylene blue dye.

Herein, FeNiCeOₓ was synthesized by the ultrasonic impregnation method. The prepared catalyst was
characterized by Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), Raman and X-ray photoelectron spectroscopy (XPS) analyses. Its catalytic performance was examined in a Fenton-like system to remove diclofenac, a typical anti-inflammatory drug. Finally, the potential reaction mechanism is discussed. The aim was to use an improved method to develop a novel catalyst, FeNiCeOx, and explore how its peculiar characteristics act for the effective diclofenac removal in a Fenton-like system.

MATERIALS AND METHODS

Reagents and materials

All reagents and materials used in this study were analytical grade. Fe(NO3)3·9H2O and NiCl2·6H2O were purchased from Xilong Scientific Co., Ltd (China). Ce(NO3)3·6H2O was obtained from Tianjin Guangfu Fine Chemical Research Institute (China). H2O2 (30%) was purchased from Beijing Chemical Works (China). Diclofenac sodium was purchased from Tokyo Chemical Industry Co. Ltd (Japan). C4K2O9Ti·2H2O was purchased from Shanghai Macklin Biochemical Co. Ltd (China). NaCl was obtained from National Pharmaceutical Group Corporation (China).

Synthesis of FeNiCeOx

FeNiCeOx was prepared by an improved ultrasonic impregnation method. 2 g CeO2 powder prepared by the precipitation method was impregnated in a 100 ml beaker with 20 ml 1 mol/L Fe(NO3)3 and 1 mol/L NiCl2 mixed solution. Then, the beaker was placed in an ultrasonic wave cleaner (AORAN FB-1500, Aoran Technology Limited, ultrasonic frequency 40 KHz, ultrasonic power 1,500 W) with 5 L deionized water (i.e. ultrasonic density was 0.3 W/cm³). After 0.3 W/cm³ ultrasonic irradiation for 30 min, the solid was filtered by 0.45 μm filter membrane and calcined for 3 h at 450 °C. Finally, FeNiCeOx catalyst was obtained by grinding to powder form.

Characterization of FeNiCeOx

The nitrogen adsorption/desorption isotherm was characterized by the BeiShiDe 3H-2000PS2 instrument. The SEM analysis was recorded by Hitachi S 4,700 scanning electron microscope analyzer. The XRD analysis was carried out by Rigaku D/max-rc diffractometer. The HRTEM measurement was investigated by the JEOL JEM-2010 instrument. Raman spectra were recorded by a Via+ Reflex Raman spectrometer with 514 nm excitation light. The XPS was performed by an EScalab250Xi spectrometer.

Determination of diclofenac removal process

50 mL diclofenac solution (20 mg/L) was added to a 150 mL beaker and the pH adjusted to 5 with dilute NaOH and H2SO4 solution. Then, a certain dosage of catalyst and H2O2 was put into the solution with magnetic stirring. At a certain time, a 1.0 mL sample was taken out and filtrated with a 0.45 μm membrane filter.

The diclofenac concentration of the filtrate was measured by a Waters e2695 HPLC instrument with a C18 reversed phase column (4.6 mm × 150 mm I.D.). Operation conditions: flowing phase (acetonitrile: 0.2% acetic acid solution = 70: 30, v/v), flow rate (1 mL/min), injection volume (10 μL), and λmax (275 nm). H2O2 concentration was measured by titanium oxalate spectrophotometry at λ = 400 nm (Monteagudo et al. 2018).

RESULTS AND DISCUSSION

Characterization of FeNiCeOx

BET analysis

The BET analysis results are shown in Figure 1. The N2 adsorption-desorption isotherm of FeNiCeOx belonged to
FeNiCeOx was 71.5 m²/g, which was much larger than that made by other methods. Allaedini et al. (2016) prepared Fe-Ni-Ce by impregnation and co-precipitation methods, the specific surface area being 39.3 and 30.4 m²/g, respectively. Odedairo et al. (2013) prepared Fe-Ni/CeO₂ by the co-impregnation method with 45.6 m²/g specific surface area. Large specific surface area could provide more reaction sites for H₂O₂ and diclofenac, hence an improved catalytic property. The large specific surface area of FeNiCeOx in this study was due to the ultrasonic impregnation method. The cavitation effect and shock waves of ultrasound decreased aggregation of iron and nickel oxides on CeO₂, then these oxides dispersed uniformly on CeO₂.

The hysteresis loop belonging to H₄, with a sudden increase in the adsorption capacity at about P/P₀ = 0.4–0.9, demonstrated that a capillary condensation phenomenon took place in the mesoporous structure of FeNiCeOₓ. The pore size distribution was shown in the inset of Figure 1. The pore volume and pore diameter of FeNiCeOₓ were 0.1125 mL/g and 6.298 nm, respectively. The pore diameter of FeNiCeOₓ was smaller than that of CeO₂ (9.86 nm) in our previous study (Chong et al. 2016). This might because the loaded of FeOₓ and NiO on the surface of CeO₂ took up part of the pore space.

SEM analysis

The morphology of FeNiCeOₓ was characterized by SEM. Different from the flat surface of CeO₂ (Zhang et al. 2018), the rough surface of FeNiCeOₓ formed with many small particles dispersed on the bulk, as observed in Figure 2(a) and 2(b), which implied that Fe and Ni loaded on CeO₂. The element distribution maps of FeNiCeOₓ (Figure 2(c)–2(f)) showed that Fe, Ni, Ce and O were all highly dispersed in the catalyst, which was attributed to the excellent dispersion effect of the ultrasonic impregnation process. The rough surface and highly dispersed elements could afford uniform active sites, which improved the activity of the catalyst. EDS analysis confirmed that the atomic percentages of Fe, Ni, Ce and O were 3.8%, 2.3%, 31.9% and 61.2%, respectively.

XRD analysis

The XRD pattern of FeNiCeOₓ is shown in Figure 3. The X-ray diffraction peaks of FeNiCeOₓ are clear and matched well with the JCPDS standard cards of Fe₂O₃, NiO and CeO₂, and there were no impurity peaks which are corresponding to other phases. This demonstrated that FeNiCeOₓ was successfully prepared. Compared with CeO₂, the diffraction peaks of FeNiCeOₓ shifted slightly towards higher diffraction angles and the peaks were also slightly broadened. This result was ascribed to the asymmetry of the crystal structure caused by the substitution of Ce by Ni and Fe with smaller ionic radii inside the CeO₂ lattice. The difference in the ionic radii of the host and dopant ions led to reduction of the crystallite size and lattice contraction (Abbas et al. 2015).

Moreover, reflection peaks assigned to Fe₂O₃ and NiO were weak, demonstrating that Fe₂O₃ and NiO were dispersed finely over CeO₂ by the ultrasonic impregnation method. Low crystallinity of Fe₂O₃ and NiO particles could result in high interaction of Fe and Ni active phases with CeO₂ support (Yosefi et al. 2015). It can thus be concluded that the ultrasonic impregnation method provided a suitable condition (transient, localized hot spots) for Fe and Ni ions doped into CeO₂ and substituted Ce ions, thereby possibly forming oxygen vacancy, an advantageous defect for the catalytic property of Ce-based catalyst by offering a relatively high electron transfer rate in the catalytic reaction (Chong et al. 2016).

HRTEM analysis

The HRTEM images of FeNiCeOₓ are shown in Figure 4. The general view in Figure 4(a) indicates that the particle size of FeNiCeOₓ was roughly uniform and the catalyst particles were highly dispersed. The lattice fringe in Figure 4(b) spaced at 0.314 nm was slightly wider than the lattice fringe spacing (0.312 nm) corresponding to the (111) plane of CeO₂. This result further confirmed that lattice contraction occurred in the structure of FeNiCeOₓ, which was in agreement with the XRD results.

Raman analysis

The micro-structural property of FeNiCeOₓ was analyzed by Raman spectroscopy (Figure 5), which was very sensitive to a minute amount of impurities and structural defects such as oxygen vacancies (Abbas et al. 2015). As is well known, the strong band at 462 cm⁻¹ of CeO₂ belongs to the vibration mode of the F2g symmetry in the cubic fluorite CeO₂ lattice. The peak around 593 cm⁻¹ is known to be associated to the oxygen vacancies in the CeO₂ lattice. The peak intensity of FeNiCeOₓ around 593 cm⁻¹ was much higher than CeO₂, indicating that more oxygen vacancies were generated with the doping of Fe and Ni. This phenomenon confirmed the XRD results showing that Fe and Ni ions substituted...
some Ce ions in CeO$_2$. The presence of more oxygen vacancies signified that there was more Ce in the reduction state, which could effectively activate H$_2$O$_2$ (Chen et al. 2014). Then, the catalytic activity of FeNiCeO$_x$ could be significantly enhanced.

**XPS analysis**

The valence states of Fe, Ni, Ce and O in FeNiCeO$_x$ were characterized by XPS. As shown in Figure 6(a), the peaks at binding energy (BE) of 710.8, 714.0 and 719.0 eV were the signal of Fe(II). The peak at 725.0 eV was ascribed to Fe(III) in FeNiCeO$_x$. 733.4 and 716.3 eV were the satellite peaks position of Fe(III) (Wang et al. 2014). Thus, the Fe element in FeNiCeO$_x$ was stated with $^{+2}$ and $^{+3}$.

The peaks at 856.3 and 873.9 eV in Figure 6(b) belonged to Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$, respectively. The other two peaks, 862.4 and 883.8 eV, were the satellite peaks of Ni. These peaks demonstrated that the Ni element in FeNiCeO$_x$ was stated with $^{+2}$.

The Ce 3d spectrum of FeNiCeO$_x$ (Figure 6(c)) showed several doublets of peaks referring to Ce 3d$_{5/2}$ (lower BE) and Ce 3d$_{3/2}$ (higher BE). The double peaks at 883.0/900.2, 889.4/908.8, and 898.9/918.1 eV were assigned to Ce(IV).
The double peaks at 884.1/908.8 eV corresponded to Ce(III) (Cai et al. 2010). Thus, Ce(III) and Ce(IV) both existed in FeNiCeOx.

The BE peaks of O 1s are shown in Figure 6(d). The peak at 529.8 eV was ascribed to the lattice oxygen of FeNiCeOx and the peak at 531.4 eV corresponded to the chemisorbed oxygen (Chen et al. 2017). The chemisorbed oxygen was the most active oxygen in the structure of the catalyst, thus it played an important role in the oxidation reaction.

Fe and Ce ions both coexisted with two valences in dynamic equilibrium, giving the redox cycles of Fe$^{3+}$/Fe$^{2+}$ and Ce$^{4+}$/Ce$^{3+}$, which facilitated the electron transfer in the reaction. Meanwhile, it was beneficial to form oxygen vacancy defects and improve the oxygen storage capacity (Bai et al. 2017), which were favoured the redox reaction of Fenton-like system (Ge et al. 2014).

**Catalytic performance of FeNiCeO$_x$ in Fenton-like system**

FeNiCeO$_x$, H$_2$O$_2$ and FeNiCeO$_x$-H$_2$O$_2$ were used to treat diclofenac. Figure 7(a) shows clearly the diclofenac removal in the FeNiCeO$_x$-H$_2$O$_2$ system was much higher than that in single FeNiCeO$_x$ and single H$_2$O$_2$ systems, demonstrating the good catalytic ability of FeNiCeO$_x$, 97.9% diclofenac was removed after 30 min in the FeNiCeO$_x$-H$_2$O$_2$ system, which was 72.8% and 96.9% higher than that in single FeNiCeO$_x$ and single H$_2$O$_2$. 

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**Figure 3** | XRD pattern of FeNiCeO$_x$.

**Figure 4** | HRTEM images: (a) general view; (b) diffraction fringes.

**Figure 5** | Raman spectra of CeO$_2$ and FeNiCeO$_x$. 

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systems, respectively. Chong et al. (2016) used FeCeO\textsubscript{x} to treat diclofenac in a Fenton-like system and 85% diclofenac was removed in 30 min. Xu et al. (2016) degraded diclofenac via a visible light/\alpha-(Fe, Cu)OOH/H\textsubscript{2}O\textsubscript{2} system, and about 72% diclofenac was removed in 30 min. In comparison, FeNiCeO\textsubscript{x} was a highly efficient Fenton-like catalyst for diclofenac removal.

The diclofenac removal of the FeNiCeO\textsubscript{x}-H\textsubscript{2}O\textsubscript{2} system from 0 to 30 min in the insert graph of Figure 7(a) shows a ‘2 regions model’ which involved a fast adsorption followed by a relatively slow zero order reaction. A similar pattern was observed in other studies on Fenton system, such as Frontistis et al. (2011), who found a fast 17\alpha-ethynylestradiol removal in photo-Fenton oxidation during the first few minutes followed by a slower removal rate. In this FeNiCeO\textsubscript{x}-H\textsubscript{2}O\textsubscript{2} system, a rapid removal of 42.5% diclofenac in 1 min suggested an adsorption-dominated stage in which a lot of diclofenac was adsorbed on the surface of FeNiCeO\textsubscript{x}. Then, the slower approximate linearity in the insert graph of Figure 7(a) indicated a zero order reaction. This result might be due to the degradation rate of diclofenac being limited to the surface area and active sites of the catalyst (which often occurs in surface catalytic reactions). Only when diclofenac is adsorbed on the catalyst can the degradation occur. At the initial stage of reaction, the surface of the catalyst was filled with adsorbed diclofenac. In the process of degradation, diclofenac was constantly adsorbed from the solution while being decomposed, thus showing a zero order reaction. A similar trend was also observed in the kinetics of H\textsubscript{2}O\textsubscript{2} decomposition (Figure 7(b)). H\textsubscript{2}O\textsubscript{2} was quickly adsorbed on the catalyst, then a zero order decomposition reaction occurred, catalyzed by FeNiCeO\textsubscript{x}. The above phenomenon implied that the diclofenac removal in FeNiCeO\textsubscript{x}-H\textsubscript{2}O\textsubscript{2} system should be a heterogeneous process, the adsorption of diclofenac and
H₂O₂ by the catalyst was an important step in the removal process.

Studies of different reaction conditions, i.e. solution pH (4, 5, 6, 7, 8), FeNiCeOₓ dosage (0.6, 0.8, 1.0, 1.2, 1.4 g/L) and H₂O₂ dosage (2.0, 4.9, 9.8, 14.7 mmol/L), indicated that when the pH went from 4 to 5, the removal of diclofenac increased. The result might be due to it being beneficial to diclofenac dissociation for the pH to be higher than the pKa of diclofenac (4.2); thus, the electrostatic attraction between diclofenac and the catalyst would facilitate the adsorption and degradation (Chong et al. 2017; Salmani et al. 2017). When the pH continued to rise beyond the pHpzc of FeNiCeOₓ (about 5.98, measured by the solid addition method (Mitrogiannis et al. 2017)), the surface of the catalyst was negatively charged, which was unfavorable to diclofenac adsorption (Xu et al. 2016). Meanwhile, with increasing pH, Fe³⁺ would combine with -OH via deprotonation, forming FeOH²⁺, Fe(OH)₂ adsorbed on the catalyst, lowering FeNiCeOₓ catalytic activity (Li et al. 2017; Tang et al. 2017; Wei et al. 2017). Moreover, because the reaction occurred on the interface between FeNiCeOₓ and the solution, the more catalyst added, the more adsorption and active sites were available. But the removal of diclofenac showed no significant increase when the FeNiCeOₓ dosage was beyond 1 g/L, which might be ascribed to the sufficient reaction sites for H₂O₂ and the consumption of ·OH by the excess Fe²⁺ (Xu & Wang 2012; Chong et al. 2017). Similarly, a lack of H₂O₂ (less than 9.8 mmol/L) led to a decrease of radicals. Conversely, the scavenging of ·OH by excessive H₂O₂ would form ·OOH and ·O₂⁻ with a relatively weaker oxidizability (Monteagudo et al. 2011), which was not good for diclofenac removal. Finally, pH = 5, FeNiCeOₓ dosage = 1 g/L, H₂O₂ dosage = 9.8 mmol/L, were used as the optimal operating parameters in subsequent studies.

To confirm the main active component of FeNiCeOₓ in a Fenton-like system, FeCeOₓ, NiCeOₓ and FeNiCeOₓ were all used to remove diclofenac (Figure 8(a)). The removal efficiency of diclofenac with NiCeOₓ-H₂O₂ was low. The difference in diclofenac removal between FeCeOₓ-H₂O₂ and FeNiCeOₓ-H₂O₂ gradually increased with reaction time. The removal efficiency of diclofenac with FeNiCeOₓ-H₂O₂ was 20.9% higher than that with FeCeOₓ-H₂O₂ after 30 min reaction. Thus, compared with FeCeOₓ, the diclofenac removal of FeNiCeOₓ over a longer reaction time was obviously enhanced by the presence of Ni. However, Costa et al. (2006) found that the presence of Ni in Feₓ₋₃NiₓO₄ inhibited the activation of H₂O₂. In summary, the catalytic property of FeNiCeOₓ was better than that of bimetallic metal oxides (Fe-Ce, Ni-Ce and Fe-Ni), indicating that the ternary metal oxide (combination of Fe, Ni, and Ce) was beneficial to the enhancement of catalytic removal of diclofenac in a Fenton-like system.

The reuse of FeNiCeOₓ in a Fenton-like system was performed to evaluate the stability of the catalyst. After each run, the catalyst was collected and washed with ethyl alcohol and deionized water followed by drying for the next run. As shown in Figure 8(b), after four runs, the diclofenac removal efficiency was still maintained at over 80%, which indicated that the catalyst had good stability.

Potential reaction mechanism of FeNiCeOₓ-H₂O₂ system

It is well known that Fe is an excellent active metal to activate H₂O₂ (Equation (1)). Ce and Ni also can
decompose H$_2$O$_2$ to form ·OH (Chong et al. 2011; Zhao et al. 2012), as shown in Equations (2) and (3). Besides, H$_2$O$_2$ would react with ·OH to generate other radicals like ·OOH and ·O$_2$/C0, which have been proved to be kinds of main oxidative intermediate species in AOPs and were detected in the FeCeO$_x$ catalyzed Fenton-like system (Monteagudo et al. 2011; Chong et al. 2011). These implied that ·OOH and ·O$_2$/C0 were also two of the important active species to attack organics in the FeNiCeO$_x$-H$_2$O$_2$ system.

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\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ & \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{H}_2\text{O} \quad (1) \\
\text{Ce}^{3+} + \text{H}_2\text{O}_2 + \text{H}^+ & \rightarrow \text{Ce}^{4+} + \cdot \text{OH} + \text{H}_2\text{O} \quad (2) \\
\text{Ni}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ & \rightarrow \text{Ni}^{3+} + \cdot \text{OH} + \text{H}_2\text{O} \quad (3)
\end{align*}
\]

In addition, owing to the standard redox potential of Fe$^{3+}$/Fe$^{2+}$ (0.77 V) being lower than that of Ce$^{4+}$/Ce$^{3+}$ (1.44 V), Ce$^{4+}$ could be reduced to Ce$^{3+}$ according to Equation (4) (Xu & Wang 2011). Meanwhile, Fe$^{2+}$ could be regenerated via Fe$^{3+}$ reduction by accepting electrons from Ni$^{2+}$ (Equation (5)) (Guan et al. 2018). Sequentially, the regenerated low valent metals could continue to catalyze H$_2$O$_2$ to produce reactive oxygen species, which would promote diclofenac removal. Thus, the synergistic effect based on the interaction among Fe, Ni and Ce might be an important reason for the excellent catalytic activity of FeNiCeO$_x$.

\[
\begin{align*}
\text{Fe}^{2+} + \text{Ce}^{4+} & \rightarrow \text{Fe}^{3+} + \text{Ce}^{3+} \quad (4) \\
\text{Fe}^{3+} + \text{Ni}^{2+} & \rightarrow \text{Fe}^{2+} + \text{Ni}^{3+} \quad (5)
\end{align*}
\]

Fe and Ni changed the cation distribution of FeNiCeO$_x$ by replacing Ce and generating oxygen vacancies for different atomic diameter and valence states. More oxygen vacancies led to stronger adsorption of diclofenac and higher catalytic activity (Jauhar & Singhal 2014); furthermore, diclofenac could be oxidized by lattice oxygen (Theofanidis et al. 2016).

It can be deduced from the above, the potential mechanism of good catalytic ability of FeNiCeO$_x$ to H$_2$O$_2$ for diclofenac removal depends on several factors, such as the favorable activation of H$_2$O$_2$ by various active metals, the synergistic effect among Fe, Ni, Ce, as well as the strong adsorption and rapid electron transfer caused by abundant oxygen vacancies due to the effective doping of Fe and Ni into CeO$_2$ by ultrasonic impregnation.

**CONCLUSIONS**

FeNiCeO$_x$ prepared by the ultrasonic impregnation method was an efficient Fenton-like catalyst. 97.9% diclofenac was removed in 30 min with an FeNiCeO$_x$ catalyzed Fenton-like system. The catalytic activity was greatly improved by doping Ni into FeCeO$_x$. FeNiCeO$_x$ had a larger specific surface area than Fe-Ni-Ce catalyst prepared by other methods, which was attributed to the cavitation effect and hot spot effect during the ultrasonic synthesis process. Ultrasonic impregnation did not destroy the CeO$_2$ structure, but promoted the substitution of Ce by Fe and Ni with high interaction, hence causing lattice contraction and forming more oxygen vacancies. Diclofenac might be mainly removed by free radicals (·OH, ·OOH and ·O$_2$) generated.
from H₂O₂ decomposition by Fe, Ni, Ce with synergistic effect. More oxygen vacancies enhanced the catalytic performance of the catalyst by improving the electron transfer rate and strengthening adsorption of diclofenac and product molecules.

ACKNOWLEDGEMENTS

Authors thank financial supports from Open Project Program of State Key Laboratory of Petroleum Pollution Control (PPC2017009) and Department of Science & Technology of Shandong province, China (2018CXGC1007).

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First received 4 January 2019; accepted in revised form 29 April 2019. Available online 10 May 2019