Improved dark ambient degradation of organic pollutants by cerium strontium cobalt perovskite

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Abstract
This work investigates the effect of cerium substitution into strontium cobalt perovskites (CeSrCoO) for the oxidative degradation of Orange II (OII) in dark ambient conditions without the aid of any external stimulants such as light, heating or chemical additives. The OII degradation rate by CeSrCoO reached 65% in the first hour, whilst for the blank sample without cerium (SrCoO) took over 2 hr to reach the same level of OII degradation. Hence, the cerium substitution improved the catalytic activity of the perovskite material, mainly associated with the Ce0.1Sr0.9CoO3 perovskite phase. Upon contacting CeSrCoO, the –N=N–azo bonds of the OII molecules broke down resulting in electron donation and the formation of by-products. The electrons are injected into the CeSrCoO and resulted in a redox pair of Co3+/Co2+, establishing a bridge for the electron transfer between OII and the catalysts. Concomitantly, the electrons also formed reactive species (–OH) responsible for OII degradation as evidenced by radical trapping experiment. Reactive species were formed via the reaction between O2 and donated electrons from OII with the aid of cobalt redox pair. As the prepared materials dispensed with the need for light irradiation and additional oxidants, it opens a window of environmental applications for treating contaminated wastewaters.

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Introduction
Our society is facing a growing demand for products resulting in environmental pollution associated with industrial chemicals and textiles (Ong et al., 2008; Chan et al., 2001; Brillas and Martínez-Huitle, 2015), pharmaceuticals (Murray et al., 2017; Foureaux et al., 2019), personal care products (Langdon et al., 2011), pesticides (Derralah et al., 2019; Aimer et al., 2019) and food additives such as coffee (Buerge et al.,

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A common global concern associated with product demand is the discharge of industrial water and sewage to natural receiving water bodies (Lapworth et al., 2012). One of the strategies used to tackle this environmental problem is by imposing strict regulations to reduce discharge limits of the environmental pollutants. To achieve these discharge limits, technologies driven by advanced oxidation process (AOP) such as photocatalysis (Kashif and Ouyang, 2009; Zubir et al., 2016; Wang et al., 2017; Didli et al., 2018), Fenton reaction (Ohja et al., 2017; Zhang et al., 2017a), catalytic wet air oxidation (Heimbuch and Wilhelmi, 1985; Zerjav et al., 2018) and electrochemical oxidation (Klidi et al., 2019; Abbas and Abbas, 2019), have been developed. Novel and more interesting AOP technology are dark ambient catalysis which dispenses the requirement of any external stimulant such as irradiation, heat, high pressure and chemical additives such as \( \text{H}_2\text{O}_2 \).

Dark ambient catalysis has recently been reported for perovskite materials (Chen et al., 2018a) for the degradation of organic pollutants. Perovskites are ceramic crystalline materials following the general formula \( \text{ABO}_3 \), where A and B are sites in the crystal structure. Perovskite ceramics have been widely used for the production of oxygen from air (Cruz et al., 2014; Leo et al., 2017), where the A and B sites can be manipulated by doping other cations (A’ or B’) of different sizes and valences, such as rare earth or alkaline elements. As a result, a new perovskite compound is created following the general formula \( \text{A}_x\text{A’}_1\text{B}_y\text{B’}_1\text{O}_{3-x} \). Therefore, the physicochemical properties of perovskite compounds associated with dark ambient catalyses can also be manipulated by rationally choosing A/B site cations, thus opening opportunities to expand perovskite catalysts and to correlate solid-state chemistry to catalytic properties in the field of wastewater processing.

In the perovskite crystal structures, the B-site cations are in the outer region whilst the A-site cations occupy the centre of the cubic structure (Zhang et al., 2017b). The B-site cations dominate the electronic properties and therefore significantly influence the redox properties of the perovskite based catalysts (Shalla et al., 2000; Hwang et al., 2017; Wang et al., 2018). The B-site is crucial to the activity of perovskite catalysts and various transition metal ions have been investigated as B-site cations for use in dark ambient catalysis. Very recently, Chen et al. (2018a) prepared a series of Cu(B site)-based perovskites with varied A-site composition that demonstrated excellent Orange II (OII) degradation activity. Ni was also used as the B site in \( \text{La}_x\text{Ni}_y\text{O}_{3.10} \) (Lapworth et al., 2012) and \( \text{La}_x\text{NiO}_4 \) (Wang et al., 2017) compounds for photocatalytic reactions. Recently, Chen et al. (2018b) reported that calcium nickel strontium oxide \( \text{CaSrNiO} \) was very effective for the degradation of OII dyes under dark ambient conditions. Iron based perovskites such as \( \text{BaFeO} \) (Sun et al., 2010a), \( \text{SrFeO} \) (Leiw et al., 2013), and Ce-doped \( \text{SrFeO} \) (Tummino et al., 2017) are also reported to have dark ambient catalytic activity in the field of wastewater processing.

Co is another important cation for B-site substitution. \( \text{Co}^{3+} \) in \( \text{LaCoO}_3 \) have shown dark catalysis for Methyl Orange (Sun et al., 2010b) and phenolic compounds (Li et al., 2012). The replacement of La in \( \text{LaCoO}_3 \) by Sr gave rise to \( \text{SrCoO}_3 \) perovskites, which exhibited enhanced OII catalytic performance under dark ambient conditions. The study also found substituting Sr by equimolar Ba, Ca and Mg in \( \text{SrCoO}_3 \), further increased the surface stability and cycling performance (Chen et al., 2018c). As cerium is an outstanding element in dark catalysis (Tummino et al., 2017; Chen et al., 2018b), it is of interest to probe the partial substitution effect of Ce for Sr in \( \text{SrCoO}_3 \), particularly because currently there is a limited number of papers reporting dark catalysis of dyes.

Therefore, this work investigates B-site Co-based perovskite by partially substituting Ce in the A-site, thus forming \( \text{Ce}_{x-\text{Sr}}\text{CoO}_3 \) perovskites. The dark catalytic behaviour was evaluated using OII as a model organic pollutant. Surface properties of resultant materials were systematically investigated using a wide range of characterization techniques such X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), thermal analysis (TGA) and Fourier transformed infrared spectroscopy (FTIR). The structure-function relationship of the perovskite was correlated to the OII degradation profile, thus allowing a proposed degradation mechanism.

### 1. Materials and methods

Chemical reagents used in this study were of analytical grade and used as received. They were purchased from Merck DABCO (1,4-diazabicyclo [2.2.2]octane (>99%)), Chem-supply Pty Ltd., (KI (>99%)), and Alfa Aesar (\( \text{Sr(NO}_3\text{)}_2 \) (98%), \( \text{Co(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \) (98%)) and (Ce(NO_3)_3 \cdot 6\text{H}_2\text{O} (99%)) and Chem-Supply Pty Ltd (ethylenediamine tetraacetic acid (EDTA, 98%), ammonia solution in water (30 wt.%) and citric acid monohydrate (99.5%)). Deionized water was used throughout the experimental processes. Materials were synthesized via an EDTA-citric acid complexation method, as reported elsewhere. For a typical synthesis, metal salts, EDTA, citric acid, and ammonium solution with a fixed stoichiometric ratio of 1:1:1.2:10 were mixed together to obtain a transparent solution. The dissolution process was followed by preheating (160°C, 6 hr), pre-calcination (450°C, 4 hr) and sintering (1000°C, 4 hr) in the air to allow for solvent evaporation, organics removal and metal oxide crystallization. The obtained samples were ground with a mortar and pestle for further use. A field-emission scanning electron microscope (FESEM) (JSM-7001 F, JEOL, Japan) operating at 5 kV and at a working distance of 10 mm was employed to observe the morphology of pristine and spent samples. A X-ray diffractometer (SmartLab with HyPix 3000 detector, Rigaku, Japan) equipped with 9 kW rotating \( \text{Cu} \) anode X-ray generator operating at 45 kV and 200 mA was used for the crystal phase analysis of the samples. The X-ray diffraction (XRD) patterns were used to identify and match the crystal phases with previously-published powder diffraction file data. The elemental composition and the oxidation state of the samples were determined by an X-ray photoelectron spectrometer (Axis ULTRA, Kratos, Japan). The binding energies were calibrated to the adventitious C 1s peak at 284.8 eV. Thermogravimetric analysis of the samples was carried out using a thermal analysis apparatus (TGA-DSC 1; Mettler Toledo, Switzerland). Fourier transform infrared (FTIR) analysis was carried out using an infrared spectrometer equipped with an attenuated total reflection (ATR) (IRAffinity-1, Shimadzu, Japan) over a wavenumber range of 600–4000 cm^{-1}. 

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2003; Motuzas et al., 2018).
The catalytic performance of the as-synthesized catalysts was evaluated using Orange II (OII) as a target organic pollutant as this compound is one of the stable and toxic organic pollutants widely observed in wastewaters, particularly in the textile industry. All experiments were conducted with continuous magnetic stirring in the dark without external additives at 20 °C and atmospheric pressure. For a typical batch run, 0.2 g catalyst was added to 200 mL OII solution (20 mg/L) to initiate the reaction which was contained in a conical flask (250 mL) covered with aluminium foil to maintain the dark environment. Aliquots were withdrawn regularly at given time intervals and filtered (0.22 μm, Millex Syringe Filter, Merck, Germany) to obtain transparent filtrates before recording the ultraviolet-visible (UV-Vis) spectra on a UV–Vis spectrophotometer (Evolution 220, Thermo Fisher Scientific, USA). For the cycling experiment, a stock OII solution was added to the reaction system to compensate the consumed OII and to maintain the volume of reaction system (200 mL). High performance liquid chromatography (HPLC, UltiMate 3000, UHPLC + focused, Thermo Scientific, USA) system was also employed to separate compounds in the solution after catalysis and study the degradation kinetics. Total organic carbon (TOC) of liquid samples was measured using a TOC-VGSH analyser (TOC-VGSH, Shimadzu Co. Japan).

2. Results and discussion

The pristine and spent samples were analysed by X-ray diffraction (XRD) and patterns are displayed in Fig. 1. The sharp peaks for both materials revealed a high degree of crystallinity. Notably, the XRD pattern of spent material showed negligible shift in comparison with that of the pristine counterpart, indicating the high stability of as-prepared catalysts after catalysis. The peaks at 2θ values of 28.52, 33.0, 47.4, 56.3, 58.78, 69.4, 76.7 and 78.6° are attributed to cubic CeO2 (Powder Diffraction File™ (PDF) #00-034-0394). The characteristic peaks of cubic Co3O4 (PDF#00-043-1003) are also observed at 31.2, 36.8, 44.6, 59.3 and 65.2°. The peaks at 32.9, 40.6, 47.3, 58.2 and 69.0° can be indexed to tetragonal SrCoO2.77 (PDF#04-006-6078) or cubic Sr0.9Ce0.1CoO3 (PDF#04-020-1798). Overall, as-prepared materials in this study composed of metal oxides (CeO2/Co3O4) and perovskites (Sr0.9Ce0.1CoO3/SrCoO2.77). To simplify the nomenclature for this mixed metal oxide phase material, the nomenclature CeSrCoO is used indicating that the samples contain cerium (Ce), strontium (Sr), cobalt (Co) and oxygen (O).

FESEM was employed to investigate the size and morphology of as-fabricated CeSrCoO before and after catalysis. The images for both pristine (Fig. 2a) and spent (Fig. 2b) CeSrCoO samples consist of particles of different sizes ranging from nanometre to micrometre. Both samples show the irregular formation of particles with smaller particles aggregated on the surface of larger particles. After catalysis, the aggregated particles on the surface became smaller suggesting a structural re-arrangement of the aggregated particles during catalysis.

The catalytic activity of CeSrCoO and the non-substitute A-site sample without Ce (blank SrCoO) were initially tested for comparison purposes. Fig. 3 shows that the catalytic activity of CeSrCoO was consistently higher than that of SrCoO. For instance, OII degradation rate for MeSrCoO reached 65% in the first hour whilst SrCoO took over 2 hr to reach the same level of degradation. Based on XRD results (Fig. 1), as-prepared CeSrCoO is a mixture of CeO2, Co3O4 and SrCoO2.77 and/or Sr0.9Ce0.1CoO3. Previous reports showed that CeO2 (Chen et al., 2018c) and Co3O4 (Chen et al., 2018b) had negligible catalytic activity toward OII under identical conditions with this study. Therefore, the improved catalytically active phases in CeSrCoO over the blank sample are attributed to Ce0.1Sr0.9CoO3. This provides a clue that Ce0.1Sr0.9CoO3 was one of the active phases (if there are many) in CeSrCoO catalysts.

The evolution of OII degradation as a function of time was measured using UV-Vis for the CeSrCoO sample. Fig. 4 displays the characteristic peaks of OII at 229, 430 and 485 nm, associated to benzene ring, azo form (-N=N-) and hydrazone form (-N=N-) of OII, respectively (Li et al., 2017). It is observed a significant decrease in these peaks after 8 hr of catalysis, indicating that OII molecules were decomposed by the CeSrCoO catalyst. However, the peaks at 258 and 308 nm still exist, suggesting that organic compounds remained in the treated OII solutions. TOC measurement of the treated solutions showed that negligible TOC was removed after reaction, consistent with UV-Vis results in Fig. 4. The negligible TOC removal also demonstrated that the decrease in OII concentration after reaction was due to degradation rather than adsorption on catalyst surface. Further, FTIR analyses of CeSrCoO (spent) CeSrCoO (blank) and CeSrCoO (leached CeSrCoO in water) was carried out as shown in Appendix A Fig. S1. All spectra resembled each other, and none of them, in particular the spent sample, matched the featured peaks for OII. Therefore, these results further confirm that adsorption was not significant. Overall, CeSrCoO can destroy OII molecules into smaller molecular weight species.

The kinetics of OII degradation by CeSrCoO was monitored using HPLC. The characteristic peak of OII solution was found at the retention time of 1.8 min (Fig. 5a). The intensity of the characteristic peak gradually decreased with time with two new peaks emerging at retention times of 1.1 and 1.4 min, which could be attributed to the formation
of by-products such as 1,2-dihydroxynaphthalene, 4-hydroxybenzenesulfonate and 4-nitrosobenzenesulfonate (Zhang et al., 2013; Calza et al., 2016). These two additional observed peaks are for newly formed products whose UV-Vis spectra are shown in Fig. 5b. It can be seen that the UV-Vis spectra of formed products are distinct from that of OII with respect to peak numbers, peak intensities, and peak positions, clearly indicating the degradation of OII. This result is in line with UV-Vis results and TOC results that organic carbon retained after catalysis. The evolution of the peak at the retention time at 1.1 min is significant from the initial time of reaction \( t = 0 \) min to \( t = 1 \) hr, with a slight increase in the peak at \( t = 2 \) hr. These results correlate well with CeSrCoO catalytic activity in Fig. 3, where 65% OII degradation occurred within the first hour and reaching 80% at the second hour. From there on, there are no more significant changes in peak intensity (Fig. 5) and no more significant OII degradation (Fig. 3). The peak changes at retention time 1.4 min are not significant, indicating that there is a minor formation of by-product.

X-ray photoelectron spectroscopy (XPS) was employed to examine the surface composition and chemical environment of pristine and spent CeSrCoO materials. The wide scan XPS spectra (Fig. 6a) show the characteristic photoelectron lines attributed to Ce 3d, Co 2p, Sr 3d, O 1s and C 1s in both pristine and spent CeSrCoO. The deconvolution of high-resolution XPS spectra of Ce 3d (Fig. 6b) demonstrates the presence of a mixed valence state (Ce\(^{3+}\) and Ce\(^{4+}\)) (Burroughs et al., 1976; Cai et al., 2010; Paparazzo et al., 1991), where v and u refer to 3d_{5/2} and 3d_{3/2} spin-orbit component of Ce ions, respectively. The two
pairs of spin-orbit doublets \( ((v_0, u_0), (v', u')) \) represent the presence of Ce\(^{3+}\). The other three pairs \( ((v, u), (v_0, u_0), (v'', u'')) \) are characteristic peaks for Ce\(^{4+}\). The relative content of Ce\(^{3+}\) was calculated based on the integrated areas using Eq. (1) (Korsvik et al., 2007). The relative content of Ce\(^{3+}\) remained practically the same before (24.27 atomic%) and after (26.84 atomic%) catalysis, suggesting the stable nature of Ce ions in the catalysis.

\[
[\text{Ce}^{3+}] = \frac{A_{v_0} + A_{v'} + A_{u_0} + A_u}{A_{v_0} + A_{v'} + A_{u_0} + A_u + A_{v''} + A_{u'} + A_u + A_{u'} + A_{u''}}
\]

where, \( A \) is area of peaks corresponding to different 3d\(^{5/2}\) and 3d\(^{3/2}\) spin-orbit component of Ce\(^{3+}\) and Ce\(^{4+}\) in XPS spectrum.

The high-resolution XPS for Sr in Fig. 6c shows that Sr in CeSrCoO was chemically affected in the reaction. The double peaks at the binding energies of 134.8 and 132.9 eV are the featured spin-orbit coupling of Sr\(^{2+}\) in the perovskite (Sr\(_{0.9}\)Ce\(_{0.1}\)CoO\(_2\))/SrCoO\(_{2.77}\) structure (Tabata et al., 1987; Zhao et al., 2008). After catalysis, a new doublet shown in blue line appeared, which can be assigned to SrCoO\(_3\) (Sr 3d 5/2–133.9 eV) (Seitz et al., 2016). In the case of Co, the high-resolution XPS spectra of Co 2p (Fig. 6d) in pristine CeSrCoO clearly indicate the coexistence of Co\(^{2+}\) (781.1 eV) and Co\(^{3+}\) (780.0 eV). After catalysis, the intensity attributed to Co\(^{2+}\) was reduced with respective to that associated to Co\(^{3+}\), indicating part of Co\(^{3+}\) was reduced to Co\(^{2+}\). These results suggest that Co played an active role in OII degradation.

In order to understand the degradation process of OII in this study, radical trapping experiments were performed. Fig. 7 shows that the addition of KI (a hydroxyl radical quencher) and 1,4-diazabicyclo[2.2.2]octane (DABCO, a single oxygen quencher) dramatically suppressed OII degradation, particularly in the initial stage of reaction. This inhibition effect suggests the probable involvement of hydroxyl radicals (\(\cdot\text{OH}\)) in OII dark ambient catalytic degradation. Furthermore, the bubbling of air (O\(_2\) supplier) enhanced OII degradation, which demonstrates that oxygen-rich environment accelerated the catalytic degradation of OII. This indirectly confirms that OII was losing electrons and was oxidized after reaction, which can be further supported by the boosted catalytic activity due to the presence of electron acceptor AgNO\(_3\). The facilitated oxidation degradation with the aid of air/AgNO\(_3\) was also reported elsewhere for Methyl Orange degradation under dark ambient conditions when using La\(_4\)Ni\(_3\)O\(_{10}\) as the catalyst (Wu and Wen, 2010).

The performance of the CeSrCoO catalyst was further assessed by testing under a series of reaction cycles. Fig. 8 shows that the OII degradation underwent a gradual loss of activity from cycle 1 to 10. For instance, OII degradation reduced from 0.92 (92%) at the first cycle to 0.56 (65%) at the fifth cycle and 0.45 (45%) at the last tested cycle. The loss of activity is common in iron oxide Fenton-like catalysts which
tend to be fully inactive at the fifth cycle due to the passivation of active sites (Bokare et al., 2008; Zubir et al., 2015), though the CeSrCoO catalyst proved to more stable in this work. Some mixed oxide catalysts delivered higher loss of activity at the fifth cycle such as CeSrCuO (37%) (Chen et al., 2018d). Thus replacing Cu with Co as in this work improved the stability of the tested catalyst. Nevertheless, the loss of activity displayed in Fig. 8 is attributed to surface passivation of the catalyst, in particular to the reduction of the active Co$^{3+}$ sites to Co$^{2+}$ as observed in Fig. 6.

Based on the experimental results in this study, it is proposed that the degradation mechanism of OII follows (Eqs. (2)–(12)). The primary step of this reaction in the dark starts with OII contacting the CeSrCoO surface (Eq. (2)), followed by the electron injection from OII to CeSrCoO, resulting in the generation of OII$^+$ and trapped electrons (e$^-$) in CeSrCoO (Eq. (3)). Trapped electrons would further react with electron acceptors O$_2$ to successively yield diverse catalytically reactive species like O$_2^-$, HO$_2$, H$_2$O$_2$, ·OH (Eqs. (4)–(10)), among which ·OH is responsible for the degradation of OII/OII$^+$ (Eq. (11)) as confirmed by radical trapping experiment (Fig. 7). Charge migration is vital in catalytic reaction and Co$^{3+}$ in CeSrCoO is
proposed as the electron acceptor by accepting an electron from OII to become reduced Co\(^{2+}\), followed by the electron stripping process from trapped site (Co\(^{2+}\)) to oxygen molecules with the simultaneous regeneration of Co\(^{3+}\) (Eq. (4)). This cyclic process of gaining and losing electrons within cobalt redox pair (Co\(^{3+}/Co^{2+}\)) is widely reported in heterogeneous catalysis for wastewater treatment (Burroughs et al., 1976).

Eq. (12) shows the reduction of Co\(^{3+}\) to Co\(^{2+}\) after catalysis, supported by the XPS results (Fig. 6d).

\[
\text{OII} + \text{CeSrCoO} \rightarrow \text{CeSrCoO(OII)} \quad (2)
\]

\[
\text{CeSrCoO(OII)} \rightarrow \text{CeSrCoO} + \text{OII}^- + e^- \quad (3)
\]

\[
e^- + O_2 \rightarrow O_2^- \quad (4)
\]

\[
O_2^- + H^+ \rightarrow HO_2^- \quad (5)
\]

\[
2HO_2^- \rightarrow O_2 + H_2O_2 \quad (6)
\]

\[
H_2O_2 + e^- \rightarrow \bullet OH + \bullet OH^- \quad (7)
\]

\[
O_2^- + \bullet OH \rightarrow O_2 + OH^- \quad (8)
\]

\[
HO_2^- + O_2^- \rightarrow O_2 + HOO^- \quad (9)
\]

\[
2HO_2^- \rightarrow O_2 + H_2O_2 \quad (10)
\]

\[
\bullet OH / O_2 + \text{OII}/OII^- \rightarrow ... \rightarrow \text{byproducts} \quad (11)
\]

\[
\text{CeSrCo(III)O} + e^- \rightarrow \text{CeSrCo(II)O} \quad (12)
\]

Fig. 9 illustrates an idealised schematic representing the OII degradation in this work under dark conditions only, where there is no energy nor chemical additives to supplement the catalytic reaction. In step 1, OII molecules contact the surface of CeSrCoO resulting in the breakage of the \(-N=\text{N-}\) azo bonds and the production of electrons. This is confirmed by the UV-Vis results in Fig. 4 as the peak intensity at 430 and 485 nm decreased dramatically. This is further supported by the discoloration of degraded OII solution (very light yellow) in Appendix A Fig. S2 as compared to the dark orange colour of the initial OII solution. The \(-N=\text{N-}\) azo bonds in the OII molecules

Fig. 8 – Cycling performance of as-prepared CeSrCoO. Experimental conditions: \([C_0] = 20 \text{ mg/L}, [\text{catalyst}] = 1 \text{ g/L}, \) and temperature \((T) = 20 ^\circ \text{C}, \) in the dark and under magnetic stirring.

Fig. 9 – Schematic illustration of OII degradation mechanism by CeSrCoO catalyst under dark ambient conditions. ROS: reactive oxygen species.
are the most vulnerable chemical bonds under oxidative attack (Barros et al., 2016). As perovskites are electron conductor materials (Kharton and Marques, 2002), this allows for electrons to diffuse through the perovskite structure. Hence, in step 2 and upon contact of oxygen in water with CeSrCoO, radicals are generated. In a similar fashion, there is the step 2 and upon contact of oxygen in water with CeSrCoO, radicals are generated. Hence, in step 3 radicals are responsible for the degradation of the OII molecules. This is evidenced by the formation of byproducts in Fig. 5.

3. Conclusions

This work shows that cobalt perovskites containing Ce can be used as heterogeneous catalyst to degrade organic pollutant OII at atmospheric temperature and pressure and without extra energy input or additional chemical additives. Fast degradation kinetics was achieved especially in the first 1 hr reaction with 65% OII degradation. This degradation rate was twice as fast as compared to blank samples SrCoO, without cerium. Therefore, by substituting Ce into the A-site of perovskite, the resultant compound CeSrCoO became catalytic more active. The mechanism of degradation followed OII contacting the surface of the CeSrCoO perovskite particle, resulting in the breakdown of –N=N- azo bonds of the OII molecule. This reaction resulted in the generation of electrons and by-products. The electrons reacted with CeSrCoO and resulted in a redox pair of Co3+/Co2+, leading to the reduction of Co3+ to Co2+ and conversely the oxidation of Co2+ to Co3+. At the same time, the electrons also formed reactive species (·OH) responsible for OII degradation as confirmed by radical trapping experiments.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.jes.2019.11.013

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