Catalysis Communications 84 (2016) 151–154

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Multicatalytic properties of nanoparticle CaO_2 synthesized by a novel, simple and economical method for wastewater treatment

Pongpen Kaewdee [a], Nopakarn Chandet [a], Gobwute Rujijanagul [b], Chamnan Randorn [a,*]

[a] *Department of Chemistry, Faculty of Science, Chiang Mai University, 50200, Thailand*
[b] *Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, 50200, Thailand*

ARTICLE INFO

Article history:
Received 7 April 2016
Received in revised form 12 June 2016
Accepted 29 June 2016
Available online 30 June 2016

Keywords:
Calcium peroxide
Oxygen release
Disinfection
Photocatalysts

ABSTRACT

The synergistic effect of oxygen releasing and oxidizing power of calcium peroxide (CaO_2) provides considerable advantages to environmental issues. In this research, a novel productive method to synthesize high-purity nanoparticle was reported. $Ca(NO_3)_2$ was used as an effective precursor under mild conditions. High-purity CaO_2 with nanosized spherical particle was observed. Disinfection effect of the CaO_2 powders was investigated using *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*). Surprisingly, photoactivity of CaO_2 was discovered. The CaO_2 exhibited intriguing photoactivity on dye oxidation and reduction under visible light. This method produces high-purity nanoparticulate CaO_2 for pilot-scale testing.

1. Introduction

Several industries have grown rapidly in developing countries, thereby increasing the pollutant waste. Regulations on management of pollutants before releasing them to lakes, streams, groundwater and rivers is therefore necessary for industries and even agricultural farms. In general, contaminant chemicals in groundwater and soil include polycyclic aromatic hydrocarbons [1], toluene [2], benzene, 2,4,6-trinitrotoluenes [3], trichloroethylene [4], total petroleum hydrocarbons [5], ethylbenzene, arsenic [6,7], α-methylnaphtalene [8] and endocrine-disrupting compounds in waste activated sludge [9]. Oxygen releasing materials, such as H_2O_2, MgO_2 [10] and CaO_2 [11–13], are among the most effective materials used in wastewater treatment. Oxidizing agents are also necessary for removal of some toxic chemicals. Moreover, antimicrobial activity and photoactive material might be helpful for complete treatment. As a result, materials that can release oxygen, act as an oxidizing agent, increase antimicrobial activity and be photoactive would be interesting.

Hydrogen peroxide is normally the oxygen source used in in situ chemical oxidation for bioremediation applications in soil [14,15] and ground water because oxygen will be generated during its decomposition. Hydrogen peroxide can also generate hydroxyl radicals when it is in the system that is thermodynamically favorable or under UV irradiation and plays an important role in chemical oxidation of pollutant removal as shown in Eq. (1) [16,17].

$$H_2O_2 + h\nu \rightarrow \cdot OH + \cdot OH \tag{1}$$

However, hydrogen peroxide has some drawbacks for practical utilization because it is decomposed and consumed in a short time. Recently, investigation on peroxo compounds that can release oxygen longer than hydrogen peroxide, has gained much attention.

CaO_2 is an alternative promising source to release oxygen because it can be biodegraded in soil and ground water [13]. H_2O_2 would slowly release from CaO_2 in the presence of moisture. CaO_2 has been extensively used in medicine, aquaculture and agriculture [18–22]. Disinfectant for water treatment has been validated recently. Prolonging disinfection is an advantageous property of CaO_2, which is an environmentally friendly material. However, its disinfection activity depends on the type of acid [21]. As mentioned above, the advantages of using CaO_2 as an oxygen releaser and disinfection material for environmentally friendly water remediation, as well as high-purity CaO_2 synthesis, will be revealed in this research using beneficial chemistry.

CaO_2 can be prepared by the addition of hydrogen peroxide to calcium compound precursors and later dried out. Possible calcium compound precursors, such as $Ca(OH)_2$ [2] and $CaCl_2$ [18,23], are normally chosen, as shown in Eq. (2).

$$Ca(OH)_2 + H_2O_2 \rightarrow CaO_2 + 2H_2O \tag{2}$$

However, the exothermic nature of this reaction creates difficulty for preparation. Moreover, the minor phases obtained along with the synthesis of CaO_2 are $Ca(OH)_2$, CaO and $CaCO_3$ [2,24]. Occasionally, high

---

* Corresponding author.
E-mail addresses: crandorn@gmail.com, chamnan.r@cmu.ac.th (C. Randorn).

http://dx.doi.org/10.1016/j.catcom.2016.06.031
1566-7367/

temperatures, approximately 500 °C, or very low temperatures, approximately 0–5 °C, are required for anhydrous CaO_2 [25]. When $Ca(OH)_2$ is used for the reaction, it is generally difficult to control the purity during precipitation with NH_4OH or NaOH because H_2O_2 reacts vigorously with $CaCl_2$ and $Ca(OH)_2$. This behavior increases the reaction temperature and may decrease the phases of $CaCO_3$ and $Ca(OH)_2$. Nanosized CaO_2 was obtained using $CaCl_2$ and H_2O_2 as precursors and polyethylene glycol (PEG 200) as a stabilizer. This finding demonstrated the effective oxidizing power on arsenic(III) removal [7]. The purpose of this research is to develop wet synthesis of CaO_2 using $Ca(NO_3)_2$ as a precursor, for the first time, to the best of our knowledge. $Ca(NO_3)_2$ can eliminate the difficulty of an exothermic reaction because the reaction between $Ca(NO_3)_2$ and H_2O_2 is an endothermic reaction. As a result, the simple but productive preparation of high-purity nanosized CaO_2 is suitable for use in large-scale production and will be explored in this study.

2. Experimental

2.1. Materials

Chemicals included ACS grade Calcium nitrate tetrahydrate (SIGMA-ALDRICH, 99%), aqueous Hydrogen peroxide solution (Merck, 30%), and Ammonium Hydroxide (J.T.BAKER 28.0–30.0%) 2.2 Preparation of CaO_2 powder.

Forty-eight grams of calcium nitrate tetrahydrate were dissolved in 50 mL distilled water, and 30 mL of 30% H_2O_2 was added while stirring at ambient temperature. The solution was adjusted to a pH of 10 using ammonia solution or NaOH, resulting in precipitation of pale yellow precipitates. The resultant precipitates were separated from the solution by filtering and washing several times with distilled water or ammonia solution. The powders then were dried at 80 °C or 200 °C for 2 h.

2.2. Characterization

XRD data were collected using a Rigaku Mini Flex II X-ray diffractometer. The specific surface area of the powder samples were measured by nitrogen adsorption at 77 K using the Brunauer–Emmett–Teller (BET) method (Micromeritics TriStar II). Scanning electron microscopy and transmission electron microscopy were obtained using a JEOL JSM-6335F and JEOL JEM-2010 electron microscope, respectively. A UV–visible spectrophotometer (UV–vis 2450, Shimadzu) was used to measure the diffuse reflectance spectra of the CaO_2 powders.

2.3. Evaluation of photocatalytic activity

2.3.1. Photocatalytic oxidation

With aeration created by an aquarium air pump, 0.05 g CaO_2 powder was suspended in 50 mL of 1×10^{-5} M MB solution. The solution was first kept in the dark for 30 mins to reach adsorption equilibrium at room temperature. Then, an visible LED (white) or UV LED lamps was switched on and a decrease in absorbance at 660 nm was monitored every 30 min using UV–Vis spectrophotometer.

2.3.2. Photocatalytic reduction

A resazurin (Rz) ink test was used for investigation of photoreduction activity of CaO_2 powders. Rz was dropped on CaO_2 before irradiation with visible or UV LED lamps. Color change from blue (resazurin) to pink (resorufin) would be observed and would indicate a photoreduced active sample.

2.4. Investigation of disinfection

The disinfection effect by the CaO_2 powders were investigated using *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*).

2.4.1. Antibacterial assay

The synthesized CaO_2 powders were put on four pathogenic bacteria using a zone of inhibition assay on NA. Each bacterial suspension, which is adjusted to a turbidity of 0.5 McFarland, was swabbed on an NA plate using a sterilized cotton bud. Next, one loop full of CaO_2 powder was placed on the surface of NA covered with a tested bacterial strain. NA plates were incubated at room temperature (27 ± 1 °C) for 24 h. Antibacterial activity was investigated by measuring the zone of inhibition (clear zone).

3. Results and discussion

3.1. Characterization of the CaO_2 powders

XRD patterns of the CaO_2 powders prepared using $Ca(NO_3)_2$ as a precursor after drying at 80 °C were shown in Fig. 1. It is clearly seen that phase and intensity of major peaks belong to CaO_2, which contained 4 main peaks at $2\theta = 30.2$, 35.6, 47.3, and 53.2 (JCPDS card number 00-003-0865). However, there are some minor peaks of $CaCO_3$ at $2\theta = 29.3°$, 39.4°, 43.2°, 47.3°, 48.6°; $Ca(OH)_2$ at $2\theta = 18.0°$, 34.1°, 47.1°, 50.8°; and CaH_2 at $2\theta = 27.9°$, 30.1°, 31.8°, 41.5°, 60.0°, which depends on the synthetic condition. Fig. 1a shows the spectrum of the CaO_2 powder that was received from rapid precipitation with ammonia followed by distilled water washing and drying at 80 °C. High crystallinity of CaO_2 phase with a small minor phase of $CaCO_3$ were obtained. It is noted that the rate of H_2O_2 addition significantly affects the CaO_2 phase. High-purity CaO_2 phase will be obtained if H_2O_2 was added to the $Ca(NO_3)_2$ solution rapidly, whereas, slowly adding H_2O_2 caused a $CaCO_3$(vaterite) phase as the major phase and CaO_2 will be a minor phase as shown in Fig. 1b. Moreover, washing the powders obtained by rapid precipitation with ammonia solution would help decrease the minor phase of $CaCO_3$ (Fig. 1c). Higher purity CaO_2 can be produced by a modified washing solution. As $CaCO_3$ was a minor phase, reaction between CO_2 and as prepared powders during heat treatment should be avoided. Use of ammonia solution instead of distilled water for washing was found to increase the purity of CaO_2. As a result, ammonia solution was used for washing throughout the synthesis. A NaOH precipitating agent was also investigated but the strong base NaOH created $CaOH_2$ as a major phase at $2\theta = 18.0°$, 34.1°, 47.1°, 50.8° instead of CaO_2 as shown in Fig. 1d. The advantage of using $Ca(NO_3)_2$ clearly showed that the high-purity CaO_2 can be obtained easily, rapidly, and economically and can be scaled up because it did not require close scrutiny when adding the H_2O_2, and there was minimal heat from the reaction

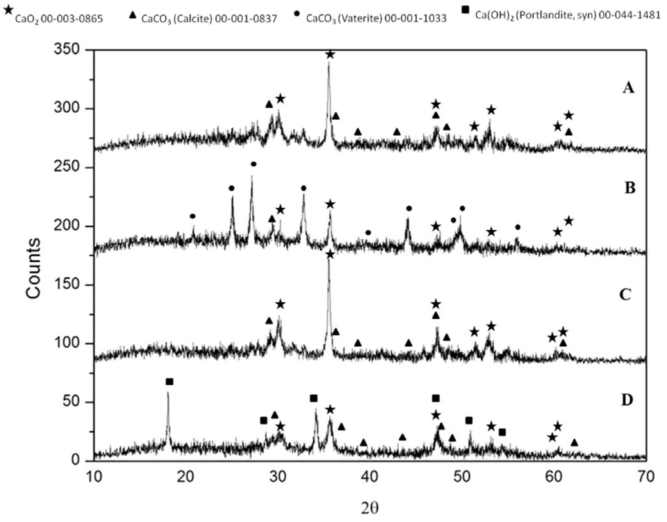

Fig. 1. XRD patterns of the products prepared using $Ca(NO_3)_2$ as a precursor under various conditions after drying at 80 °C.

between H_2O_2 and the calcium precursor. Moreover, it was found that the CaO_2 can be stable as a major phase up to 200 °C with same amount ratio of $CaCO_3$.

Fig. 2 Showed SEM image of the CaO_2 prepared by the $Ca(NO_3)_2$ precursor after drying at 80 °C. The SEM image revealed the nanosized particle CaO_2, measuring approximately 20–50 nm, with some agglomeration, probably due to the effect of the nanosize. Interestingly, the $Ca(NO_3)_2$ precursor can be used to prepare nanosized CaO_2 without any chelating agent or capping agent or stabilizer. Particle size of these powders was smaller than using some conventional precursors such as $CaCl_2$ [25] and $CaOH_2$ [8] and was close to the CaO_2 prepared using $CaCl_2$, but with PEG as a stabilizer [18]. Morphology of the particles was further studied by a TEM technique. It was found that spherical powders and a small amount of rod shapes were observed. The first assumption of the rod shape was expected to be a morphology of $CaCO_3$ minor phase, which might be correlated in terms of amount. However, atomic percentage from EDS of the rod shape shows similar mole ratios of Ca:O to spherical shape and correspond to the CaO_2 phase. This finding may confirm that the rod shape is the CaO_2 phase, as well.

A surface area of 13.16 m^2/g measured by BET method is consistent with the nanosized particle of CaO_2. The physical properties of nanosized, moderate surface area and high purity of the CaO_2 prepared using $Ca(NO_3)_2$ seems attractive for the applications. Disinfection and, especially, photoactivity have been validated.

3.2. Disinfection of CaO_2

CaO_2 has been shown to have some disinfecting properties in water which were examined at the bactericidal characteristics of the CaO_2 disinfectants [21]. In this research, an efficiency of removal for microorganisms was determined using *Staphylococcus aureus* and *Escherichia coli*. It was found that CaO_2 can inhibit growth of bacteria for both gram negative and gram positive as seen in Fig. 3. clear zone of approximately 6 mm was observed for CaO_2, whereas $CaCO_3$ did not show any disinfecting properties. It is noteworthy that the clear zone has still been retained for several weeks to date, implying that CaO_2 slowly releases H_2O_2 actively for an extended period.

3.3. Photocatalytic activity of CaO_2

Photoactivity of CaO_2 is rarely examined. To the best of our knowledge, this report might describe the first time that CaO_2 was investigated for photoactivity. Photobleaching of methylene blue was used to examine photooxidation activity of the CaO_2, while color changing of resazurin was used to explored photoreduction. Photoactivity was evaluated under UV and visible light from a homemade LED bulb reactor. In prior testing, control experiments confirmed that no bleaching of MB from the CaO_2 under dark conditions at ambient temperature and at 70 °C. $CaCO_3$ and H_2O_2 were also used for comparative materials. H_2O_2 can bleach MB under UV, as expected, because the hydroxyl radicals can be generated from a dissociation of H_2O_2 by UV. Next, hydroxyl radicals oxidize the MB solution. However, CaO_2 and $CaCO_3$ seem not to be photocatalysts because a very small amount of MB was bleached.

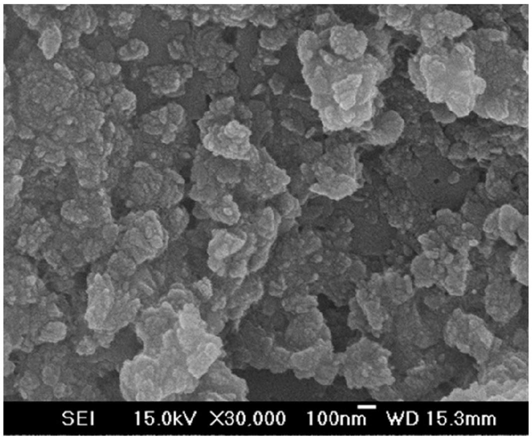

Fig. 2. SEM image of CaO_2 after drying at 80 °C.

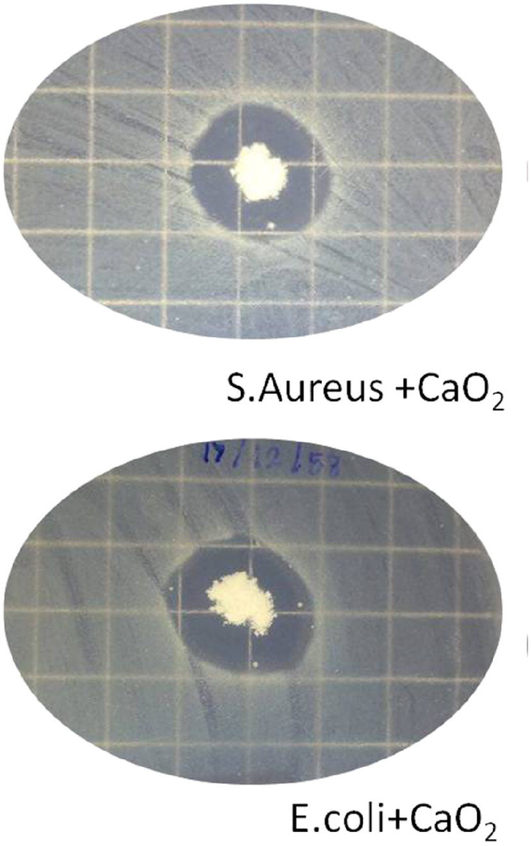

Fig. 3. Disinfection of *S. aureus* and *E. coli* by CaO_2.

Fig. 4 showed the photoactivity of CaO_2, H_2O_2 and $CaCO_3$ under visible light. Surprisingly, CaO_2 was highly active under visible light, whereas H_2O_2 and $CaCO_3$ were rather inactive. As a result, CaO_2 tends to be a photocatalyst under visible light, which will be good for wastewater treatment because sunlight can be used to activate CaO_2 to be photocatalyst.

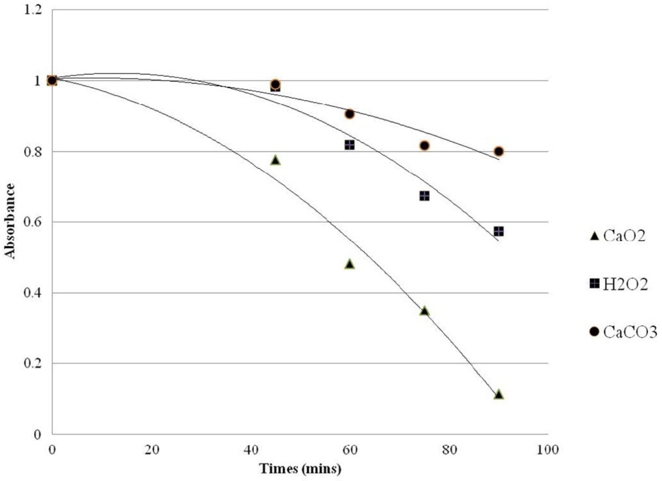

Fig. 4. Photooxidation activity of CaO_2 under visible light comparison between CaO_2, H_2O_2 and $CaCO_3$.

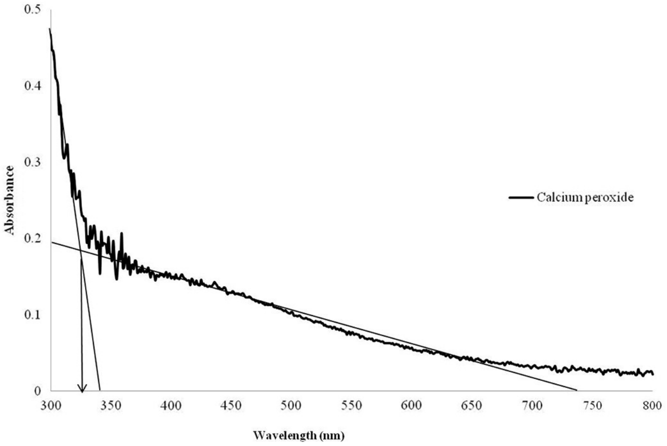

Fig. 5. UV–Vis diffuse reflectance spectrum of CaO_2.

The preliminary result of bleaching MB is consistent with the UV–Vis diffuse reflectance spectrum of the CaO_2, as shown in Fig. 5. A sharp absorption edge at approximately 330 nm or 3.75 eV and a broad absorption peak is approximately 400–550 nm or 3.1–2.25 eV can be observed. It can be confirmed that the CaO_2 can be a photocatalyst under visible light because of that broad absorption peak. Moreover, it may be assumed that the CaO_2 is an effective photocatalyst because the MB bleaching rate is fast despite the fact that the absorption peak under visible is rather broad, which means that small amounts of visible light were absorbed. Contrary, a sharp absorption edge at 330 nm might be too high for the UVA bulb, which gives off 365 nm radiation, resulting in no activity of CaO_2 under UVA. However, CaO_2 might be active under UVB bulb, which will be further investigated.

To obtain more data on photoactivity of CaO_2, photoreduction of resazurin was measured and compared to $CaCO_3$. It was found that the color of resazurin changed from blue to pink in the case of CaO_2 under visible light as shown in Fig. 6 but no color change from $CaCO_3$ under visible light. Furthermore, CaO_2 can be reused to reduce resazurin several times. $CaCO_3$ did not show any positive results under UV or visible or even with heating at 70 °C.

4. Conclusions

A new method for synthesis of calcium peroxide using $Ca(NO_3)_2$ as a precursor helps to improve the purity of calcium peroxide. This process is simple, low-cost and environmentally friendly. The results indicated that nanosized CaO_2, approximately 20–50 nm, can be prepared without any stabilizer or chelating agent. The CaO_2 exhibited promising properties on bacterial disinfection, photocatalytic oxidation and photocatalytic reduction.

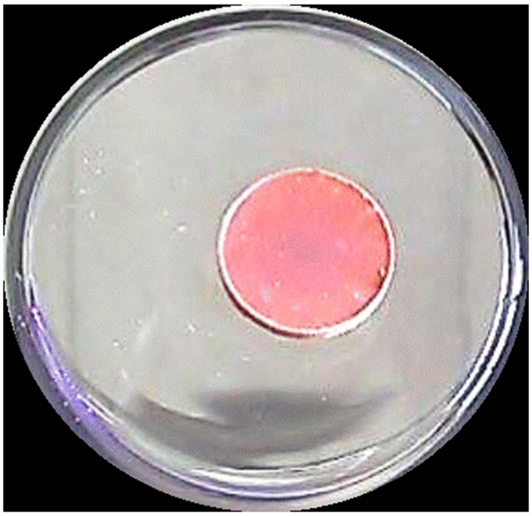

Fig. 6. Photoreduction of resazurin of CaO_2 under visible illumination.

Acknowledgments

The authors would like to acknowledge the Research and Researchers for Industries (RRi), the Thailand Research Fund (MSD58I0018), STP CHEM SOLUTIONS CO., Ltd. and the Center of Excellence for Environment and Biodiversity, Faculty of Science, Chiang Mai University for financial support.

References

[1] B.W. Bogan, V. Trbovic, J.R. Paterek, Inclusion of vegetable oils in Fenton's chemistry for remediation of PAH-contaminated soils, Chemosphere 50 (2003) 15–21.
[2] Y. Qian, X. Zhou, Y. Zhang, W. Zhang, J. Chen, Performance and properties of nanoscale calcium peroxide for toluene removal, Chemosphere 91 (2013) 717–723.
[3] M. Arienzo, Degradation of 2,4,6-trinitrotoluene in water and soil slurry utilizing a calcium peroxide compound, Chemosphere 40 (2000) 331–337.
[4] X. Zhang, X. Gu, S. Lu, Z. Miao, M. Xu, X. Fu, Z. Qiu, Q. Sui, Degradation of trichloroethylene in aqueous solution by calcium peroxide activated with ferrous ion, J. Hazard. Mater. 284 (2015) 253–260.
[5] A.C. Ndjou'ou, D. Cassidy, Surfactant production accompanying the modified Fenton oxidation of hydrocarbons in soil, Chemosphere 65 (2006) 1610–1615.
[6] L. Chuan-ping, L. Chun-ling, X. Xiang-hua, W. Chuang-an, L. Fang-bai, Z. Gan, Effects of calcium peroxide on arsenic uptake by celery (*Apium graveolens* L.) grown in arsenic contaminated soil, Chemosphere 86 (2012) 1106–1111.
[7] E. Olyaie, H. Banejad, A. Afkhami, A. Rahmani, J. Khodaveisi, Development of a cost-effective technique to remove the arsenic contamination from aqueous solutions by calcium peroxide nanoparticles, Sep. Purif. Technol. 95 (2012) 10–15.
[8] Y. Qian, X. Zhou, Y. Zhang, P. Sun, W. Zhang, J. Chen, X. Guo, X. Zhang, Performance of α-methylnaphthalene degradation by dual oxidant of persulfate/calcium peroxide: implication for ISCO, Chem. Eng. J. 279 (2015) 538–546.
[9] A. Zhang, J. Wang, Y. Li, Performance of calcium peroxide for removal of endocrine-disrupting compounds in waste activated sludge and promotion of sludge solubilization, Water Res. 71 (2015) 125–139.
[10] A. Goi, M. Viisimaa, M. Trapido, R. Munter, Polychlorinated biphenyls-containing electrical insulating oil contaminated soil treatment with calcium and magnesium peroxides, Chemosphere 82 (2011) 1196–1201.
[11] C.S. Lee, T.L. Thanh, E.J. Kim, J. Gong, Y.Y. Chang, Y.S. Chang, Fabrication of novel oxygen-releasing alginate beads as an efficient oxygen carrier for the enhancement of aerobic bioremediation of 1,4-dioxane contaminated groundwater, Bioresour. Technol. 171 (2014) 59–65.
[12] A. Nykänen, H. Kontio, O. Klutas, O.P. Penttinen, S. Kostia, J. Mikola, M. Romantschuk, Increasing lake water and sediment oxygen levels using slow release peroxide, Sci. Total Environ. 429 (2012) 317–324.
[13] M. Viisimaa, O. Karpenko, V. Novikov, M. Trapido, A. Goi, Influence of biosurfactant on combined chemical–biological treatment of PCB-contaminated soil, Chem. Eng. J. 220 (2013) 352–359.
[14] D.L. Pardieck, E.J. Bouwer, A.T. Stone, Hydrogen peroxide use to increase oxidant capacity for in situ bioremediation of contaminated soils and aquifers: a review, J. Contam. Hydrol. 9 (1992) 221–242.
[15] M.M. Joshi, S. Lee, Effect of oxygen amendments and soil pH on bioremediation of industrially contaminated soils, Energy Sources 18 (1996) 233–242.
[16] A. Zhang, Y. Li, Removal of phenolic endocrine disrupting compounds from waste activated sludge using UV, H_2O_2, and UV/H_2O_2 oxidation processes: effects of reaction conditions and sludge matrix, Sci. Total Environ. 493 (2014) 307–323.
[17] M.I. Stefan, A.R. Hoy, J.R. Bolton, Kinetics and mechanism of the degradation and mineralization of acetone in dilute aqueous solution sensitized by the UV photolysis of hydrogen peroxide, Environ. Sci. Technol. 30 (1996) 2382–2390.
[18] J. Khodaveisi, H. Banejad, A. Afkhami, E. Olyaie, S. Lashgari, R. Dashti, Synthesis of calcium peroxide nanoparticles as an innovative reagent for in situ chemical oxidation, J. Hazard. Mater. 192 (2011) 1437–1440.
[19] Y. Ma, B.T. Zhang, L. Zhao, G. Guo, J.M. Lin, Study on the generation mechanism of reactive oxygen species on calcium by chemiluminescence and UV–visible spectra, Luminescence 22 (2007) 575–580.
[20] R.C. Borden, R.T. Goin, C.M. Kao, Control of BTEX migration using a biologically enhanced permeable barrier, Ground Water Monit. Rem. 17 (1997) 70–80.
[21] V.M. Novotortsev, I.O. Mel'nikov, T.A. Tripol'skaya, N.S. Busygina, S.A. Rodionova, A.V. Artemov, Examination of the disinfecting properties of calcium peroxide and its suitability for improving hydrodynamic characteristics of surface water bodies, Russ. J. Appl. Chem. 85 (2012) 726–730.
[22] D.P. Cassidy, R.L. Irvine, Use of calcium peroxide to provide oxygen for contaminant biodegradation in a saturated soil, J. Hazard. Mater. B69 (1999) 25–39.
[23] A.W. Petrocelli, Peroxide, Superoxide, and Ozonides of Alkali and Alkaline Earth Metals, first ed. Springer, New York, 1966.
[24] J. Blamey, E.J. Anthony, J. Wang, The calcium looping cycle for large-scale CO_2 capture, Prog. Energy Combust. Sci. 36 (2010) 260–279.
[25] M.B. Brodsky, R.C. Dynes, K. Kitazawa, H.L.Tuller, High Temperature Superconductors, MRS Symp. Proc, Materials Research Society, vol. 99, 1988.