



Synthesis of calcium peroxide nanoparticles as an innovative reagent for in situ chemical oxidation

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ARTICLE INFO

Article history:

Received 24 January 2011

Received in revised form 26 April 2011

Accepted 23 June 2011

Available online 14 July 2011

Keywords:

Calcium Peroxide

Fenton chemistry

Nanoparticles

Polyethylene glycol

ABSTRACT

Chemical oxidation is one of the many different methods of site remediation that has emerged lately as an alternative method to traditional techniques. According to this research calcium peroxide is suitable choice for contaminant biodegradation in soil and ground water but speed of oxidation reaction between calcium peroxide and contaminant is slow. Synthesis of calcium peroxide in nano size by increased ratio of surface to volume can increase the speed of reaction and solve the problem. We have developed a simple surface modification technique to avoid irreversible agglomeration of calcium peroxide nanoparticles. The technique is based on hydrolysis–precipitation procedure, using CaCl_2 as a precursor. Polyethylene glycol 200 (PEG200) is used as a surface modifier. CaO_2 was identified and studied by characterization techniques, including XRD and TEM. The results indicate the ability of this method for synthesis of new reagent in nano size and improve quality of in situ chemical oxidation. Size determination by TEM image indicates the size of calcium peroxide nanoparticles approximately 15–25 nm.

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1. Introduction

In situ chemical oxidation (ISCO) is based on the delivery of chemical oxidants to contaminated media in order to either destroy the contaminants by converting them to innocuous compounds commonly found in nature. ISCO is being used for ground water, sediment, and soil remediation. It can be applied to a variety of soil types and sizes (silt and clay). Chemical oxidation has been shown to be effective at the destruction of the dissolved phase of non-aqueous phase liquids, which are known to be difficult to remediate through other tactics. Therefore, if administered correctly, ISCO has the potential to be a low-cost, fast, effective, and relatively low maintenance remediation technology [1].

The four main species used today in ISCO industry are permanganate, persulfate, hydrogen peroxide, and calcium peroxide. The characteristics of four main species used in ISCO are given in Table 1. Permanganate is frequently sold in the form of the salt potassium permanganate. It is a well-known and widely used oxidant in ISCO [2,3], with a few benefits and limitations. The most well-known limitations of permanganate are that it has a long half-life. This long half-life is that permanganate is a less powerful oxidative species [4].

Persulfate is frequently sold in the form of the salt sodium persulfate, $\text{Na}_2\text{S}_2\text{O}_8$, and is in many ways similar to permanganate. Persulfate does suffer from the fact that it generates sulfate during cleanup, which has a secondary maximum contaminant levels (MCLs). This MCL is much higher than the MCL for manganese: 250 mg/L for sulfate, as opposed to 0.05 mg/L for manganese. Persulfate, like permanganate, also has been shown to have little impact on naturally occurring bacteria colonies, and therefore should not inhibit bioremediation to any significant degree [4].

Hydrogen peroxide is the oxygen source most commonly used to ISCO for bioremediation applications. Hydrogen peroxide decomposes to form molecular oxygen and water in the presence of catalase (an enzyme found in aerobic microorganisms, and certain abiotic catalysts) [5]. Virtually all aerobic microorganisms produce catalase [6]. Hydrogen peroxide can be effective in promoting contaminant biodegradation in soil [7,8], but is readily scavenged by metals and humic substances. This results in rapid exhaustion of the oxygen source [9]. Oxygen released at a rate greater than by which it can be consumed by microorganisms escapes unused via volatilization or dissolved in groundwater. Furthermore, hydrogen peroxide can be toxic at concentrations required to achieve biological treatment [7,9].

Recent studies suggest that calcium peroxide (CaO_2) is a more effective source of H_2O_2 for ISCO than liquid H_2O_2 [10,11]. CaO_2 dissolves to form H_2O_2 and $\text{Ca}(\text{OH})_2$, liberating a maximum of 0.47 g H_2O_2 /g CaO_2 [12]. The advantage is that the released H_2O_2 is

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Table 1
Comparison between four species used in ISCO industry.

Oxidant	Strength	Longevity	MCL for residual product	Effect on natural bacteria
Permanganate	Moderate (selective)	Long	0.5 mg/L	Minimal
Activated persulfate	Very strong	Very long until activated	250 mg/L	Minimal
Hydrogen peroxide	Very strong	Very short	None	Decrease significantly
Calcium peroxide	Strong/very strong	Moderate	None	Increase significantly

auto-regulated by the rate of CaO_2 dissolution, reducing disproportionation since not all the H_2O_2 is available at once as with liquid H_2O_2 . Ndjou'ou and Cassidy compared the treatment of a soil contaminated with petroleum hydrocarbons using a commercially available CaO_2 -based oxidant and liquid H_2O_2 at pH of 8. CaO_2 removed 96% of total petroleum hydrocarbons (TPH), compared with 74% using liquid H_2O_2 [11]. Several studies have reported that addition of calcium peroxide in saturated soil and ground water is suitable choice for contaminant degradation [13–21]. But the rate of the oxidation reaction between calcium peroxide and contaminant is slow. Synthesis of calcium peroxide in nano size can increase the ratio of surface to volume, so increase the speed of reaction and solve the problem [22].

The aim of our work is development of a simple surface modification technique to avoid irreversible agglomeration of calcium peroxide nanoparticles. The technique is based on hydrolysis–precipitation procedure, using CaCl_2 as a precursor. Polyethylene glycol 200 (PEG200) is used as a surface modifier. CaO_2 was identified and studied by a variety of characterization techniques, including XRD and TEM. The result indicates the ability of this method for synthesis of new Fenton reagent in nano size and improve quality of in situ chemical oxidation. Size determination by TEM image indicate the size of calcium peroxide nanoparticles is approximately 15–25 nm.

2. Experimental

2.1. Materials

Calcium chloride (Merck, 99.5%); hydrogen peroxide aqueous solution H_2O_2 (Merck, 35%); PEG 200, $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ (Fluka), ammonia (Merck, 25%), silver nanoparticles (NANOPAC PERSIA Co.) and sodium hydroxide, NaOH (Merck) were used in their commercial forms.

2.2. Preparation of CaO_2 nanoparticle solution

Three grams of calcium chloride was dissolved in 30 mL distilled water, 15 mL ammonia solution (1 M) and one 120 mL of PEG 200 was added to the stirring mixture. Then 15 mL of 30% H_2O_2 was added to the mixture by rate of 3 drops per minute. The preparation procedure was carried out in a continuously stirred opened glass beakers, $V=0.25\text{ L}$, at room temperature. The stirrer velocity was kept constant for all the experiments. After 2 h of stirring, a clear and colorless to yellowish solution has been received.

2.3. Preparation of CaO_2 nanoparticle powder

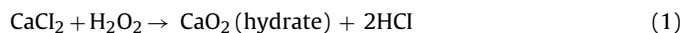
In order to precipitate the product, NaOH solution (pH 13) was added to form a basic medium. This was done until a pH value of 11.5 was achieved. Upon the addition of the NaOH , the mixture was changed to a white color suspension. The white precipitate was separated by centrifuge and after the centrifugation process the powder was washed three times by NaOH solution. Finally, two additional washes by distilled water were done until final pH of 8.4 for the residue water was reached. The resultant precipitate was dried at 80°C for 2 h in an evacuated oven.

3. Results and discussion

3.1. Characterization of the CaO_2 nanoparticles

There are two general methods for synthesizing peroxides [23]. The first involves heating the oxide in a stream of pure, CO_2 -free dry oxygen. This method is favored for making peroxides that are considerably more stable than the corresponding oxide, for example, for the preparation of BaO_2 . In fact, BaO_2 is commercially made by heating BaO at 500°C in flowing, pure oxygen. The synthesis of the less stable SrO_2 requires more drastic conditions, namely heating the oxide at a temperature of 350°C in a bomb containing high pressure oxygen (250 atm). Finally, CaO_2 , the least stable of the three, cannot be conveniently synthesized by direct combination of oxide with oxygen.

The second technique, which is more suitable for the preparation of less stable peroxides, involves precipitating the insoluble peroxide from aqueous solution by adding H_2O_2 to a basic solution of the metal salt. For example using for synthesis CaO_2 , Eq. (1).



Addition of aqueous ammonia to neutralize the HCl, forces the reaction to favor the precipitation of the peroxide hydrate, Eq. (2).



In a previous work [24] nano-sized zinc peroxide has been synthesized by this method and stabilized successfully by polyethylene glycol 200 (PEG200). This report presents the preparation of calcium peroxide nanoparticles using the second synthesis technique and PEG200 as a surface modifier. The thermal decomposition properties of CaO_2 were also investigated.

XRD analysis was done on CaO_2 powders in order to identify the material. A representative result is shown in Fig. 1, the three dominant peaks: $2\theta=30.1, 35.6, 47.3$ match to the XRD of CaO_2 (card number 03-0865). The XRD result strongly proved that the CaO_2 nanoparticles compound was formed by this procedure.

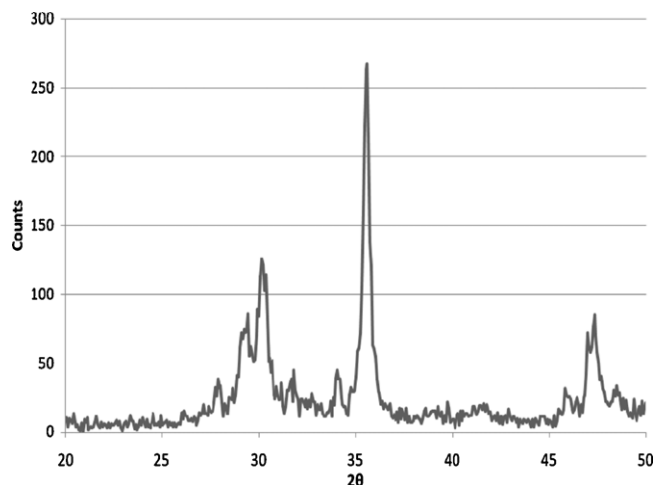


Fig. 1. XRD of CaO_2 with polyethylene glycol.

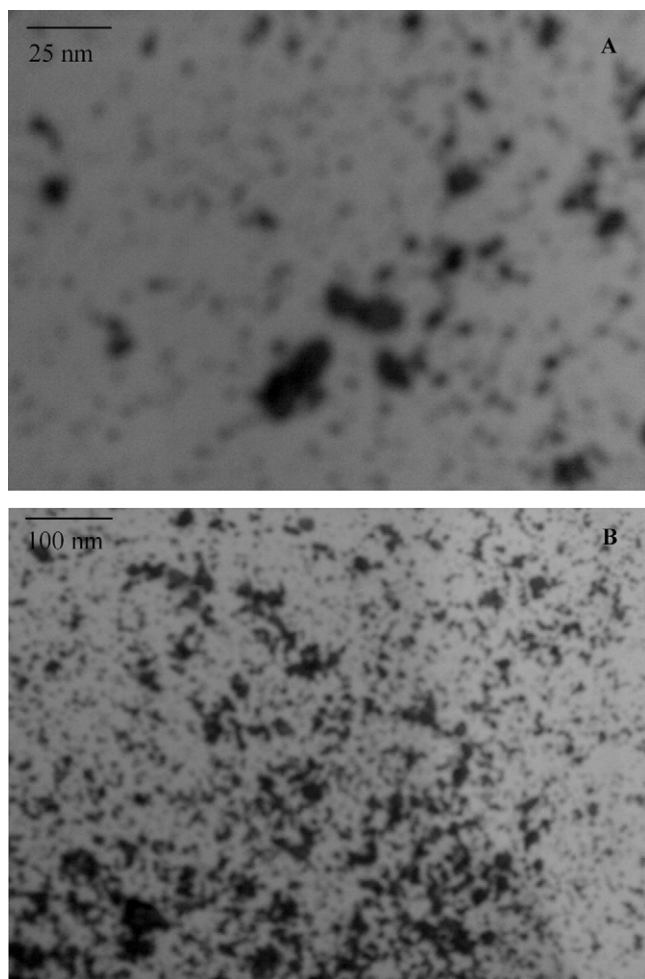


Fig. 2. TEM images of precipitated CaO_2 with polyethylene glycol. The bars are 25 and 100 nm.

TEM images of CaO_2 nanoparticles prepared with hydrolysis–precipitation method shows in Fig. 2A and B, from the images, it can be seen that the CaO_2 particles are faceted nanocrystals with low aggregation and low average size with a moderate size distribution.

3.2. Improve quality of in situ chemical oxidation (ISCO)

LSPR is well known to be excited on nanostructured noble metals such as gold and silver. Noble metals have intrigued people for centuries because of their optical properties, which include the display of a bright glow in various attractive colors. As described by the Mie theory, these properties are strongly dependent on the size, shape, interparticle distance, and the local environment of the noble metal nanostructures [25]. Briefly, as the size of the metal structures decreases from the bulk-scale to the nano-scale, the movement of electrons through the internal metal framework is restricted. As a result, metal nanoparticles display specific absorption bands in the UV–vis spectra when the incident light resonates with the conduction band electrons on their surfaces. These charge density oscillations are simply defined as LSPR [26]. Fig. 3 shows the absorption spectra of the AgNPs plasmon was purchased from NANOPAC PERSIA Co., against reagent blank.

For comparison between oxidation ability of CaO_2 in nano and micro size we design this experiment (Scheme 1). CaO_2 decompose in the presence of water to produce hydrogen peroxide. The silver nanoparticles (AgNPs) have the catalytic ability for the decompo-

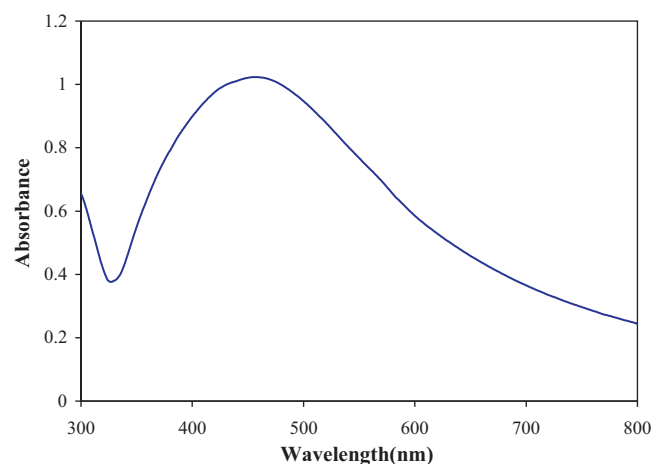
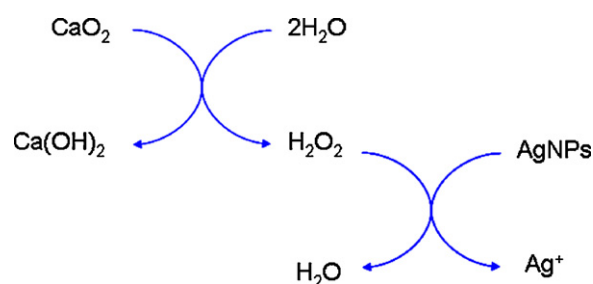


Fig. 3. Absorption spectra of the AgNPs.



Scheme 1. Reaction mechanism between CaO_2 and AgNPs.

sition of hydrogen peroxide; then the decomposition of hydrogen peroxide induces the degradation of silver nanoparticles. Hence, a remarkable change in the localized surface plasmon resonance absorbance strength could be observed. The amount of decrease in surface plasmon resonance band of AgNPs corresponded to the concentration of hydrogen peroxide could be directly monitored using the spectrophotometric methods.

Fig. 4 shows change in absorbance vs. time for the reaction of CaO_2 in nano and micro size with AgNPs. As it is obvious the reaction of CaO_2 in nanoparticles with AgNPs is faster than it is with CaO_2 in micro size and is almost completed within 8 h. It seems

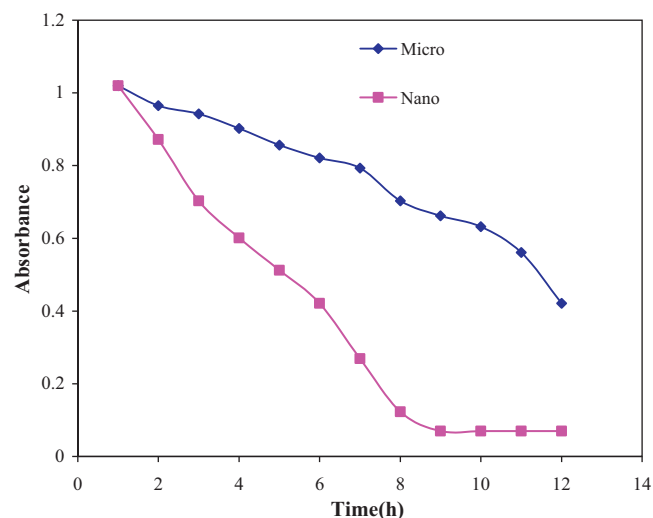


Fig. 4. Change in absorbance vs. time for the reaction of CaO_2 in nano and micro size with AgNPs (pH = 7).

that at this rate oxygen releases with a rate equal to the rate of its consumption by microorganisms and suitable rate for degradation of contaminants.

4. Conclusion

Stabilized nanoparticles of calcium peroxide were formed by an improved and simple technique. The process is spontaneous and no additional equipment or energy source is required. The calcium peroxide preparation method is based on oxidation–hydrolysis–precipitation procedure, with polyethylene glycol 200 as a surface modifier. Pure, stabilized nanoparticles of calcium peroxide remained in the nano-scale during all stages.

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