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Modeling the heterogeneous peroxymonosulfate/Co-MCM41 process for the degradation of caffeine and the study of influence of cobalt sources

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HIGHLIGHTS

- Co-MCM41/PMS exhibited effective efficiency with low metal leaching.
- Effects of cobalt sources in Co-MCM-41 for the caffeine decay were identified.
- An operational model was established to predict the caffeine decay in Co-MCM41/PMS.

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ABSTRACT

The potential of using cobalt incorporated MCM41 (i.e. Co-MCM41) prepared from different cobalt sources to activate peroxymonosulfate (PMS) for the degradation of caffeine in aqueous solution was evaluated. Experimental results showed that the Co-MCM41/PMS process could effectively degrade caffeine with a very low cobalt leaching (<5%) for the catalyst preparing from different cobalt sources. Cobalt was found being incorporated into the structure of MCM41 and resided within the crystal cell as cobalt cation, which play a critical role in dominating caffeine decay (via radical oxidation). Inhibiting effects of chloride and bicarbonate ions indicated that the sulfate radical was the key/active species for caffeine degradation. The inhibiting mechanism of phosphate on the same process, however, was mainly due to the complexation reaction between phosphate and cobalt cation in the structure of Co-MCM41. A series of kinetic experiments on CAF decay and the simultaneous PMS consumption were investigated. A mathematically operational model was therefore developed and verified to be capable of predicting the CAF decay successfully at various reaction conditions.

1. Introduction

As the increasing use of pharmaceuticals (PhACs) by human and animals, the accumulation of PhACs in wastewaters has become a worldwide concern [1,2]. The presence and potential risks of PhACs in different water matrixes such as rivers [3], lakes [4] and domestic sewage [5] have been reported. In water, the presence of PhACs will produce significant effects on the environment due to their resistance to natural degradation and potential toxicity to animal and human [6]. Therefore, it is important to remove PhACs from water to minimize their harmful effects. Caffeine (CAF) is one of the most commonly used legal drugs in the world [7]. Also, it is a typical kind component of foods and beverages [8]. It is readily metabolized by humans, the disposal of the unconsumed coffee and caffeinated soft drinks are the predominant sources of CAF being introduced into the sewerage [9]. Because of its high solubility (21.7 g L^{-1}) and negligible volatility, CAF is likely to be persistent in the water. It was detected in the influents and effluents in sewage treatment plant, raw water, and drinking water [10]. Several AOPs including ozonation [11], photo-Fenton process [12] and heterogeneous photo-catalytic processes using TiO_2 [13] have been evaluated for CAF degradation in water.

In recent years, studies showed that sulfate radicals ($SO_4^{\cdot-}$) generated by the combination of persulfate or peroxymonosulfate (PMS) with transition metals [14] or supported metal oxides [15–17] are promising in the degradation of organic contaminants. The $SO_4^{\cdot-}$ demonstrates a higher standard reduction potential (2.5–3.1 V [18]) than hydroxyl radicals ($^{\cdot}OH$, 1.8–2.7 V [19]) at neutral pH; and is more selective in oxidizing organics than $^{\cdot}OH$ at acidic pH [20]. Both homogeneous [21] and heterogeneous [22–26] activated PMS system were reported in degradation organic pollutants in wastewater. However, utilizing cobalt ions has the potential to increase the toxicity of the treated water, because of the heavy metal's characteristic. The development of an efficient heterogeneous catalytic process therefore is useful in this respect

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by simply recovering the used catalysts by a solid–liquid separation.

In our previous study, a mesoporous catalyst (named as Co-MCM41) was explored by incorporating cobalt into MCM41, a mesoporous silica with hexagonal order pore canal [27]. Its effective performance and short reaction time were observed on the removal of CAF. But the effect of surface property of Co-MCM41 on the performance was not investigated in detail. In this study, different Co sources were used to incorporate cobalt into the structure of MCM41. In this study, the physicochemical properties of catalysts were characterized in detail. The performance and catalytic reaction mechanism of catalysts prepared from different Co sources were discussed. Generally, there are many anions in the natural water, such as chloride, nitrate, carbonate/bicarbonate, sulfate, and phosphate. Their presence shows negative or positive effect on the performance of $SO_4^{\cdot-}$ based AOPs, depending on their concentration [28–30]. To evaluate the performance of Co-MCM41 in $SO_4^{\cdot-}$ based AOPs, the effect of typical anions in a wider concentration range was carried out in this study. Moreover, a degradation operational model was developed to predict the decay of CAF at various reaction condition, such as reaction time, dosages of Co-MCM41 and PMS.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals are analytic reagent grade and all solvents are HPLC grade; they were used as received without any further purification. Oxone ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$, 1 mol Oxone gives 2 mol HSO_5^-) was purchased from Sigma–Aldrich Inc. (USA), while CAF (99%) was purchased from International Laboratory (USA). The salts supplying anions used in this study including $NaHCO_3$, NaH_2PO_4, $Co(NO_3)_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$ and $C_4H_6O_4Co{\cdot}4H_2O$ were obtained from British Drug Houses (BDH, England). Distilled-deionized water with a resistivity of 18.2 MΩ cm generated from a Bamstead NANO pure water treatment system (Thermo Fisher Scientific Inc., USA) was used to prepare all the solutions. Acetonitrile (Tedia Company Inc.) was degassed before being used in high performance liquid chromatography (HPLC). Nitric acid and/or sodium hydroxide were used to adjust the initial pH of the solutions. To prepare MCM41 or Co-MCM41, tetraethylorthosilicate (TEOS, 98% GC) and hexadecyl trimethyl ammonium bromide (CTAB) were used and purchased from Sigma–Aldrich Inc. (USA).

2.2. Synthesis of Co-MCM41 catalysts

Cobalt incorporated into the structure of MCM41 was named as Co-MCM41. The synthesis of Co-MCM41 followed the procedure as described by de Souza et al. [31]. Typically, 2.4 g CTAB was dissolved in 120 mL de-ionized water by ultrasound. After CTAB being dissolved completely, cobalt source (0.0008 mol from various sources) was added into the clear solution with intensive stirring. Then 10.5 mL aqueous ammonia solution (25 m/m%) was added to this clear solution and stirred for another 15 min. During the mixing, 10.0 g (0.048 mol, 10.7 mL) of TEOS was added drop-wise within a couple of minutes. After finishing the addition of TEOS, the gel started to form. The mixture was stirred for 2 h and aged for additional 16 h. After that, the precipitates were filtered and rinsed several times until a neutral pH was reached. Then the samples were dried for 12 h at 333 K. Template removal was achieved by heating the samples in air up to 813 K at a heating rate of 2 K min^{-1}, and followed by the isothermal treatment at the same temperature for 6 h in air. In this study, the ratio of Si and Co was fixed at 60, unless stated otherwise. The synthesis of MCM41 was similar as stated above, except no Co was added. Catalysts with different cobalt sources defined as Co-MCM41-N, Co-MCM41-C, Co-MCM41-A and were prepared from $Co(NO_3)_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, and $C_4H_6O_4Co{\cdot}4H_2O$, respectively.

2.3. Characterization of Co-MCM41 catalysts

The crystalline form of the catalysts was identified by an X-ray diffractometer (XRD, Rigaku D/MAX-rA, Japan) with Cu Kα radiation at a scanning rate of 2° min^{-1}, and the samples were scanned at 2θ from 1° to 90°. The surface area and pore characterization of catalyst was determined by N_2 adsorption–desorption at 77 K with a BRT-BJH Quantachrome (model Nova 1200). The atomic composition of the MCM41 and Co-MCM41 were detected by X-ray photoelectron spectroscopy (XPS). The XPS spectrum was recorded on an Axis Ultra photoelectron spectrometer (Kratos Analytical Ltd., Japan) with Al Kα (1486.6 eV) as the X-ray source. All XPS spectra were corrected using the C 1s line at 284.6 eV. UV–Vis diffuse reflectance spectroscopic (DRS) studies were carried out using a UV-2550 (Shimadzu, Japan) equipped with an integrating sphere at the room temperature in air. $BaSO_4$ was used as the reference material. The spectra were recorded over the wavelength range of 240–800 nm.

2.4. Kinetic study of caffeine oxidation in Co-MCM41 activated PMS

The catalytic oxidation of CAF was carried out in a 500 mL reactor containing 0.05 mM of CAF solution in room temperature. A known amount of oxidant, PMS from stock solution, was added to the mixture, then a known dose of catalyst was added into the reactor to initiate the reaction. At predetermined time intervals, 10.0 mL sample was withdrawn from the reactor, and the sample went through a syringe filter before the high performance liquid chromatography (HPLC) quantification. The reaction was quenched by $Na_2S_2O_3$ (0.5 mL) at 1.0 M. The concentration of CAF was analyzed using a HPLC (from Waters Instrument, USA) with a UV detector at the wavelength of 273 nm with a Restek pinnacle octylamine (5 μm, 0.46 × 25 cm) column of which the temperature is 25°. The mobile phase was defined as 0.6 mL/min as the isocratic elution and the composition was 60% CH_3CN and 40% phosphoric acid solution (0.08%). The standard deviation of CAF analysis method is below 6.30%.

The concentration of PMS before and after the reaction was analyzed by an iodometric method [32], the detecting limit was 10.0 μM and standard deviation was less than 6.5%. The dissolution of cobalt ion during the reaction was analyzed by a spectroscopic methodology [15], the detecting limit was 20 μg/L and standard deviation was less than 5.4%.

3. Results and discussion

3.1. Effect of Co sources on the performance of Co-MCM41 in activating PMS

Different cobalt precursors were found to affect the activity of Co-MCM41 catalysts as shown in Fig. 1(A). The catalysts derived from different precursors demonstrated similar activities, about 85% to over 90% of CAF was removal in 40 min, while most of the CAF oxidation was observed in the first 10 min. The performance of homogenous reaction with cobalt ions with a concentration equivalent to the cobalt used in making the Co-MCM41 catalyst (100 mg), was also shown in this figure as a reference. The homogeneous reaction as expected showed a better performance in CAF degradation than that of heterogeneous processes, but the catalyst used in the latter can be easily recycled and reused. The pairwise