Preparation and application of sustained release microcapsules of potassium ferrate(VI) for dinitro butyl phenol (DNBP) wastewater treatment

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ARTICLE INFO

ABSTRACT

The encapsulated potassium ferrate(VI) (K_2FeO_4) samples were successfully prepared by phase separation method in organic solvents. The ethyl cellulose and paraffin were selected for the microcapsule wall materials (WM). The as prepared microcapsules were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). The stability can be enhanced greatly when ferrate(VI) was encapsulated in the microcapsules with a mass ratio of Fe(VI):WM in the range of 1:1–1:3 for the same conserved time in air compared for pure K_2FeO_4. The sustained release behavior of the microcapsules with different Fe(VI):WM mass ratios in 8.0 M KOH solution was also investigated. The results indicated that the Fe(VI) release was reduced with increase of Fe(VI):WM mass ratios from 1:1 to 1:3. The release kinetics of the microcapsules is found to obey Ritger–Peppas equation. The prepared Fe(VI) microcapsules has been used for the removal of a typical alkyl dinitro phenol compound, 2-sec-butyl-4,6-dinitrophenol (DNBP), from aqueous solution. The effect of pH, microcapsule concentration and reaction time was studied thoroughly. The optimal pH for DNBP degradation was 6.5, and at this pH and a microcapsule concentration of 1.2 g/L, approximately 93% of the DNBP was degraded after 80 min. The encapsulated ferrate(VI) samples were found to be very effective in the decolorization and COD reduction of real wastewater from DNBP manufacturing. Thus, this study showed the feasible and potential use of encapsulated Fe(VI) samples in degradation of various toxic organic contaminants and industrial effluents.

1. Introduction

Alkyl dinitro phenols are widely acknowledged to be a group of toxic refractory chemicals, which can be detrimental to human health and the environment. 2-sec-butyl-4,6-dinitrophenol (DNBP) is a typical example of this class of toxic compounds. It is manufactured in high quantities, most being used as polymerization inhibitor for vinyl aromatics in petrochemical industry and as a herbicide in agriculture [1,2]. DNBP is introduced into surface water from its manufacturing and application processes. DNBP has some undesirable side effects, such as toxicity and carcinogenity, and its uses and the maximum concentration level in water were restricted by the US Environmental Protection Agency (EPA) [3–5]. Thus the degradation of DNBP and its removal from the environment are of great public concern. The more complex environmental problems are that DNBP is resistant to microbial degradations and can be hardly destroyed in conventional wastewater treatment, so there is a continuing interest in the application of more efficient water treatment chemical reagents to degrade DNBP and achieve higher water quality.

It has been well documented that potassium ferrate, K_2FeO_4, is receiving considerable attention at present as an efficient wastewater treatment chemical reagent owing to the high redox potential of the ferrate(VI) ion from 2.2 to 0.7 V in acidic and basic solutions, respectively, and associated coagulation effect arising from the reduced Fe(III) species for metals and non-metals from solution [6–8]. As well as the high oxidation capacity and coagulation effect, the ferrate(VI) also possesses the disinfection function [9]. More importantly, ferrate(VI) is also an environmental friendly treatment chemical, which will not produce any harmful by-products in the treatment process. Such unique properties make the ferrate(VI) to be an environmental friendly and dual function chemical reagent and could combine the pre-disinfection/oxidation with coagulation into one unit [10,11]. Due to such unique properties, many researches have been carried out in the use of potassium ferrate(VI) for degrading various synthetic and natural organic pollutants [12]. However, the problems with the stability of the concentrated ferrate chemicals have hindered the implementation of ferrate(VI) technology in the full-scale treatment of wastewater. Currently, there is a need for further studies concerned with increasing the stability and reactivity of ferrate(VI) with contaminants of concern.

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Presently, microencapsulation is very useful for modifying chemical properties of a core material. Microcapsules are minute heterogeneous containers and generally consist of a core material enclosed within a wall material. Microcapsules are widely used to control a core material's release characteristics and to improve its stability by protecting it from environmental stimuli [13–16]. Although the performance of encapsulated potassium ferrate(VI) for oxidative remediation of trichloroethylene contaminated groundwater has been investigated recently [17], no comparative study results have been reported to address the preparation of encapsulated potassium ferrate(VI) using various methods and the performance of the encapsulated ferrate(VI) in the degradation of different organic pollutants, which is one of the objectives of this paper. In the present study, microcapsules of potassium ferrate(VI) were successfully synthesized by phase separation method in cyclohexane which was chosen as an organic solvent. The characteristics of the prepared microcapsules of potassium ferrate(VI) were analyzed by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). Specifically, this paper aims to investigate the performance of encapsulated potassium ferrate(VI) for aqueous degradation of 2-*sec*-butyl-4,6-dinitrophenol, which was chosen as a typical alkyl dinitro phenol organic pollutant.

2. Materials and methods

2.1. Chemicals

The core material K_2FeO_4 (purity >98.5%) was prepared with a high yield (>80%) by the modified wet oxidation method via reacting ferric nitrate with hypochlorite in strongly basic media and then isolation from the saturated KOH solution [18]. The wall materials (abbr. as WM) used were ethyl cellulose and paraffin (from Sinopharm Chemicals). DNBP was used as an alkyl dinitro phenol pollutant and obtained from Retell Fine Chemical Co., Ltd. (Tianjin, China). A stock solution of DNBP (1.7×10^{-4} M) was prepared by dissolving DNBP in deionized water. All other chemicals and reagents used were of analytical reagent (AR) grade and purchased from Kermel Chemical reagent Co. Ltd. (Tianjin, China) unless otherwise indicated.

2.2. Experimental procedures

2.2.1. Preparation of Fe(VI) microcapsules

Microcapsules of potassium ferrate(VI) were prepared by a phase separation method in an organic solvent. The synthesis method was as follows: To a cyclohexane solution (50 mL) was added the wall materials ethyl cellulose (0.5 g) and paraffin (2.5 g) slowly. After complete addition, the mixture was stirred at 800 rpm for 15 min and heated to 60 °C until the wall materials were dissolved completely. Then, the various amounts of core material K_2FeO_4 were slowly introduced to keep the mass ratios of Fe(VI):WM from 1:1 to 1:3, and the solution was sonicated and refluxed for 30 min. After cooling to room temperature, the supernatant liquid was poured off and the final product was collected, washed twice with cyclohexane, dried in vacuo and stored in a vacuum desiccator prior to further use.

2.2.2. Characterization of the microcapsules

The X-ray diffraction patterns of the prepared microcapsule samples were obtained on a Shimadzu XRD-6000 diffractometer using Cu Kα radiation (40 kV, 30 mA) with a scan rate of $0.06° \, s^{-1}$. FT-IR studies were carried out in the 500–4000 cm^{-1} frequency range in the transmission mode (Avatar 360, Thermo Nicolet Co., America).

2.2.3. Stability of the microcapsules

An accurate of the prepared microcapsules, equivalent to 0.5 g of K_2FeO_4 and 0.5 g of pure K_2FeO_4 were kept in air at 25 °C for 30 days to evaluate for their stability. At different time intervals, the microcapsule samples were taken, accurately weighed and washed with 50 mL of cyclohexane at 60 °C for 20 min to remove the wall materials completely. The decomposition of Fe(VI) was monitored by determining the content of Fe(VI) at different time intervals. The degree of decomposition (*D%*) can be calculated by the following

$$D\% = \frac{W_0 - W_t}{W_0} \times 100\% \tag{1}$$

where W_0 and W_t are the Fe(VI) content at time $t = 0$ and t, respectively.

2.2.4. Encapsulated Fe(VI) release test

The release of encapsulated potassium ferrate(VI) was carried out using 200 mL of 8 M KOH solution as dissolution medium at 25 °C. An accurate weight of the microcapsules, equivalent to 50 mg of potassium ferrate(VI) was added in dissolution medium while the solution was agitated for 40 min. The sample solution was withdrawn at predetermined interval to analyze the Fe(VI) concentration by spectroscopy method. An equal volume of the same dissolution medium was added to maintain a constant volume. The Fe(VI) release amounts were plotted as the cumulative amount and percentage content in the dissolution medium against the release time.

2.2.5. Degradation of DNBP

Oxidative reaction between encapsulated Fe(VI) samples and DNBP was carried out using 100 mL conical borosilicate glass reactors in which DNBP solution was agitated with magnetic stirrers when an accurate weight of the microcapsules was added. The reactors were mechanically stirred for selected time periods. For analysis, sodium sulfite was added to the sample immediately at selected intervals to stop any further reaction. The samples were then filtered and the filtrate was centrifuged at 6000 rpm for 10 min before analysis. All the experiments were carried out at room temperature (25 ± 1 °C).

Oxidative reaction time, solution pH and encapsulated Fe(VI) concentration were investigated for their effect on the oxidation performance in terms of DNBP removal, defined as removal $(\%) = (C_0 - C)/C_0 \times 100$, where C_0 and C are the concentration of DNBP at $t = 0$ and t, respectively.

2.2.6. Analytical methods

In this study, the determinations of the ferrate(VI) concentration were carried out according to spectroscopy method. K_2FeO_4 dissolved as FeO_4^{2-} has a distinctive UV–vis spectrum with a maximum absorbance at 510 nm. The molar absorptivity at 510 nm has been determined as 1150 $M^{-1} \, cm^{-1}$ by Bielski and Thomas in 1987 and colloidal ferric oxide interference is minimized by a 385 nm baseline correction in this analysis [19]. UV–vis absorption was measured with a UV-1201 spectrophotometer (Beijing Rayleigh Analytical Instrument Corp., China). DNBP concentration was quantified by high performance liquid chromatography (HPLC) (Hewlett–Packard, HP series 1100) (CA, USA), comprising quaternary pumps, a UV detector and an auto sampler. In the HPLC analysis, a ZOBAX 5 μm C18 (4.6 mm × 250 mm) column was employed and a mobile phase of methanol/water (7:3, v/v) was used at a flow rate of 1.0 mL min⁻¹. An injection volume of 20 μL was used and the concentration of DNBP was determined by the UV detector at 271 nm.
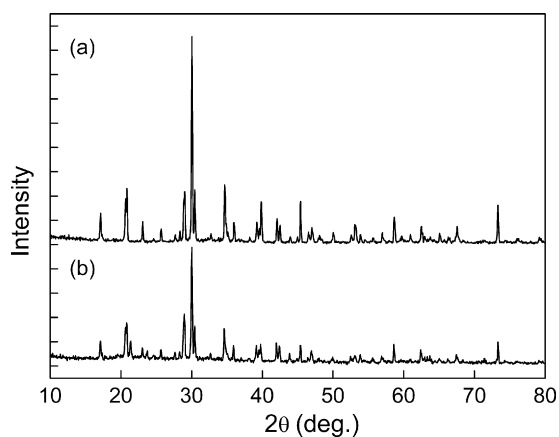
Fig. 1. XRD patterns of (a) K_2FeO_4 and (b) encapsulated K_2FeO_4.

Fig. 3. Stability comparison of K_2FeO_4 and encapsulated K_2FeO_4.

3. Results and discussion

3.1. Characteristics of the encapsulated Fe(VI) samples

The XRD patterns of the prepared solid potassium ferrate and encapsulated Fe(VI) samples are shown in Fig. 1. The XRD pattern of the encapsulated potassium ferrate contains the same characteristic peaks as that of K_2FeO_4 with an orthorhombic unit cell possessing the spaces group D_{2h} (*Pnma*) [20], but with a lower intensity. Fig. 2 presents the transmittance FT-IR spectra of K_2FeO_4 and the encapsulated Fe(VI) sample, as measured in a conventional KBr pellet. It can be seen that the IR absorption spectra of the two samples possess a primary peak of $808\,cm^{-1}$ and a shoulder peak of $780\,cm^{-1}$, which is the characteristic peak of FeO_4^{2-} [21,22]. While the band centered around $2916\,cm^{-1}$ as well as absorption bands at about 1471 and $720\,cm^{-1}$ in the encapsulated Fe(VI) sample can be attributed to stretching and bending vibrations of paraffin. The characteristic peak at $1100\,cm^{-1}$ should assigned to the stretching vibration of the intramolecular ether bond of ethyl cellulose. The FT-IR analysis indicates that no chemical reaction occurs between potassium ferrate(VI) and the corresponding wall materials in the process of preparing the microcapsules.

3.2. Stability of the microcapsules

A set of experiments was carried out at 25 °C using encapsulated Fe(VI) samples with the mass ratios of Fe(VI):WM from 1:1 to 1:3 and pure K_2FeO_4 to investigate the stability of the prepared microcapsules in air. The experimental results are shown in Fig. 3. It
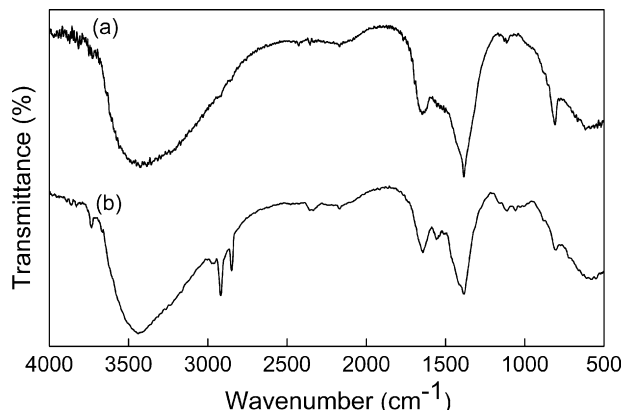
can be seen that the degree of decomposition of solid K_2FeO_4 in air increases more significantly than that of the encapsulated Fe(VI) samples with the prolongation of conserved time. The degree of decomposition of the microcapsules with Fe(VI):WM mass ratios of 1:1, 1:2, and 1:3 for 30 days in air are 12.0%, 11.2%, and 9.2%, respectively, and the corresponding data for K_2FeO_4 is 84%. The relatively better stability of encapsulated Fe(VI) samples can be attributed to the existence of wall materials which can trap the solid K_2FeO_4 and protect it from water and reducing substances in environment.

3.3. Sustained release behavior of the encapsulated Fe(VI) samples

Fig. 4 shows the sustained release behavior of the microcapsules in 8.0 M KOH solution at 25 °C, which indicated that the release of K_2FeO_4 from the microcapsules with Fe(VI):WM mass ratios of 1:1, 1:2, and 1:3 reached 87.6%, 64.7%, and 56.3%, respectively, at the first 20 min, and 96.8%, 84.2%, and 72.6%, respectively, at 40 min in 8.0 M KOH solution. The results show that the microcapsules with a higher mass ratio of WM/Fe(VI) contained more wall materials and possessed a thicker film around their core material so that Fe(VI) was more slowly released.

Analysis of the K_2FeO_4 release kinetics from the prepared microcapsules with different mass ratios of Fe(VI):WM was performed by calculating the kinetic constant *k*. Data obtained from the controlled release tests were tested graphically for fitting various kinetic equations including the zero-order kinetic equation, the first-order kinetic equation, the Higuchi equation [23]and the
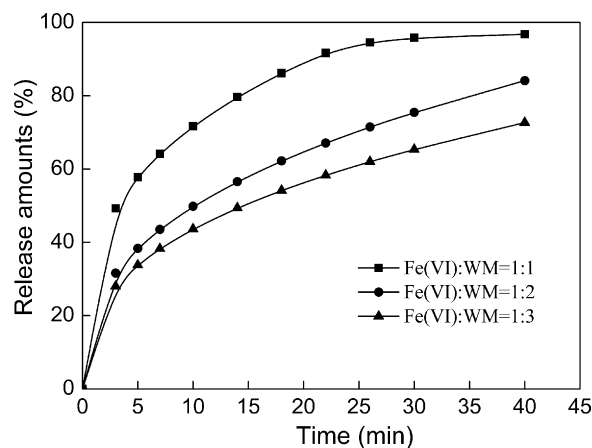

Fig. 2. FT-IR spectra of (a) K_2FeO_4 and (b) encapsulated K_2FeO_4.

Fig. 4. Time (*t*) dependencies of Fe(VI) release from microcapsules with various Fe(VI):WM mass ratios in 8.0 M KOH.

Table 1
The calculated values of diffusional exponent (n) and kinetic constant (k) for the microcapsules with different Fe(VI)/WM mass ratios.

Fe(VI)/WM	n	k	R^2
1:1	0.298	35.84	0.9956
1:2	0.376	20.86	0.9896
1:3	0.368	18.70	0.9798

Fig. 6. The rate constant, k ($M^{-1}\,s^{-1}$) versus pH at 25 °C.

Ritger–Peppas equation [24]. By far the best fit was obtained with the Ritger–Peppas equation for the encapsulated Fe(VI) samples. According to this equation the fractional Fe(VI) release Q changing with time t can be given by

$$Q = kt^n \tag{2}$$

where, Q is the fractional Fe(VI) release, k is a kinetic constant, t is the release time and n is the diffusional exponent.

This equation predicts a linear plot between values of $\ln Q$ and $\ln t$. n and k can be calculated using the slope and the ordinate axis intercept of the straight line. The calculated values of diffusional exponent (n) and kinetic constant (k) for the microcapsules with different Fe(VI)/WM mass ratios are presented in Table 1, which reveals that the Fe(VI) releasing process of the testing microcapsules in 8.0 M KOH was accorded to Ritger–Peppas equation, and the releasing mechanism was non-Fick's diffusion. It also can be seen that the kinetic constant k decreases with an increase in WM/Fe(VI) mass ratios.
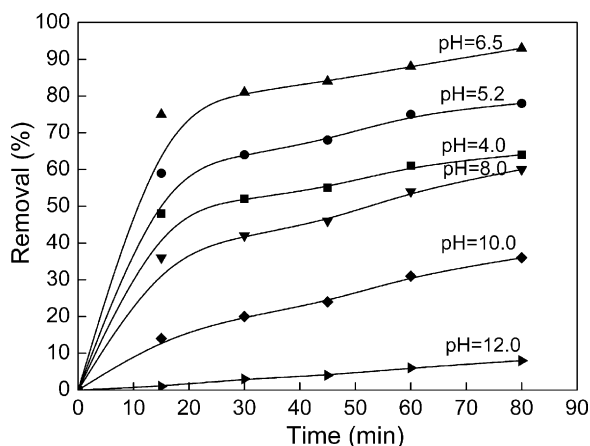
3.4. Degradation of DNBP by the encapsulated Fe(VI) samples

The effect of reaction variables such as reaction time, pH of the solution and concentration of the encapsulated Fe(VI) was studied and the results are delineated below.
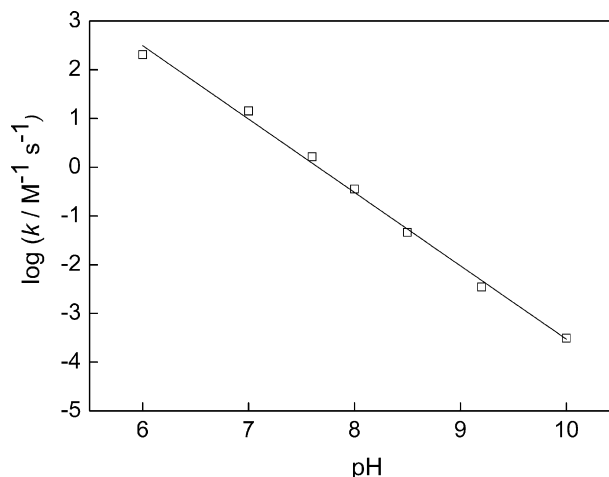
3.4.1. Effect of pH

To study the reaction of DNBP with encapsulated Fe(VI) and the influence of pH, a set of experiments was carried out with DNBP (40 mg/L) and encapsulated Fe(VI) with Fe(VI):WM mass ratio of 1:1 (1.2 g/L) at different pH values from pH 4.0 to pH 12.0 following 80 min reaction time. The experimental results are shown in Fig. 5. It is evident from Fig. 5 that removal of DNBP was accelerated with increasing pH value up to pH 6.5, beyond which the removal started to decrease, indicating an optimum pH of approximately 6.5 for best performance.

Previous work by some of the authors has demonstrated that the initial pH value has a remarkable influence in the oxidative ability and aqueous stability of the ferrate ion [25]. The stability of the fer-

rate increases and the oxidative ability decreases with increasing pH. DNBP dissociates in aqueous conditions and has a pK_a of 4.62 at 25 °C. The degree of dissociation of DNBP increases with pH and the reactivity of DNBP is also known to be pH dependent. In order to clarify the pH dependency of the reactivity of ferrate(VI), the reaction rate constants (k) for the reaction of pure potassium ferrate(VI) with DNBP were determined as a function of pH according to the method described by Noorhasan and Sharma [7]. Fig. 6 shows the k of the reactions between ferrate(VI) with DNBP, which decreased with increasing pH throughout the entire pH range examined. The pH dependence of k for the reaction of Fe(VI) with DNBP can be quantitatively modeled by Eq. (3):

$$k[Fe(VI)]_{tot}[DNBP]_{tot} = \sum_{\substack{i=1,2,3 \\ j=1,2}} k_{ij}\alpha_i\beta_j[Fe(VI)]_{tot}[DNBP]_{tot} \tag{3}$$

where $[Fe(VI)]_{tot} = [H_2FeO_4] + [HFeO_4^-] + [FeO_4^{2-}]$, $[DNBP]_{tot} = [DNBP] + [DNBP^-]$, α_i and β_j represent the respective species distribution coefficients for Fe(VI) and DNBP, respectively, and k_{ij} is the species-specific second-order rate constant for the reaction between the Fe(VI) species i with the DNBP species j. As shown in Fig. 7, there is a linear relationship between the rate constants k and fraction of $HFeO_4^-$ species at higher pH, while deviation occurs in the linearity at lower pH. At a lower pH, the equilibrium of DNBP and reaction between H_2FeO_4 with $DNBP^-$ caused non-linearity in the relationship. The fraction of $HFeO_4^-$ species increases with

Fig. 5. Effect of pH on DNBP removal (%). (DNBP concentration = 40 mg/L; microcapsule concentration = 1.2 g/L; reaction time = 80 min).
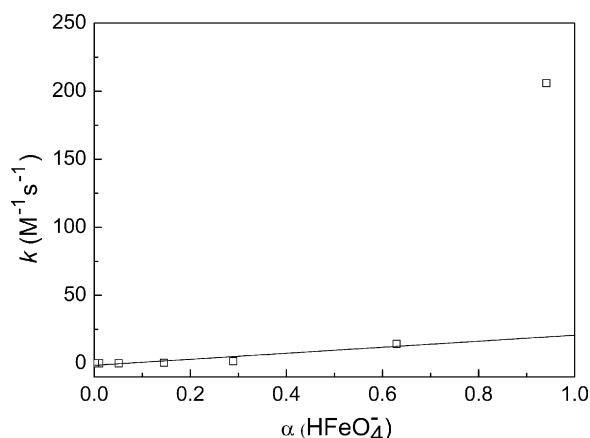

Fig. 7. Rate constant, k ($M^{-1}\,s^{-1}$) dependence the speciation of Fe(VI).
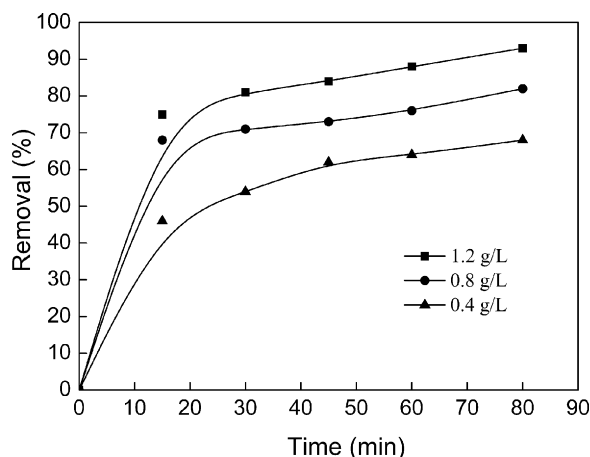
Fig. 8. Effect of microcapsule concentration on DNBP removal (%). (DNBP concentration = 40 mg/L; pH 6.5; reaction time = 80 min).

decrease in pH and thus contributes to an increase in the rate with a decrease in pH. This is consistent with the faster rates for the spontaneous decomposition of Fe(VI) with a decrease in pH. $HFeO_4^-$ is also known to have a higher reactivity and oxidation ability than FeO_4^{2-}. The de-protonated compounds have been found to be more readily oxidized [26]. The experimental results suggest that the optimal degradation requires the DNBP to be in its de-protonated form and the ferrate to be stable.

3.4.2. Effect of encapsulated Fe(VI) concentration

Experiments were performed to study the influence of encapsulated Fe(VI) concentration on the degradation of DNBP in aqueous solution. A set of tests was carried out by varying the addition amount of encapsulated Fe(VI) with Fe(VI):WM mass ratio of 1:1 from 0.4 to 1.2 g/L following 80 min reaction time with a fixed pH 6.5. A summary of the experimental results for the removal of DNBP with various encapsulated Fe(VI) concentration is shown in Fig. 8. It can be observed that the removal of DNBP increased sharply with encapsulated Fe(VI) concentration. DNBP was reduced after 80 min by 68%, 82%, and 93% with the encapsulated Fe(VI) dosage of 0.4, 0.8, and 1.2 g/L, respectively.

Fig. 9 shows the typical encapsulated Fe(VI) concentration dependent UV–vis spectra. As can clearly be seen, DNBP exhibits one characteristic absorbance band at 375 nm in the visible region [27], which progressively disappeared upon increasing encapsulated Fe(VI) concentration. The absorption peak was observed at
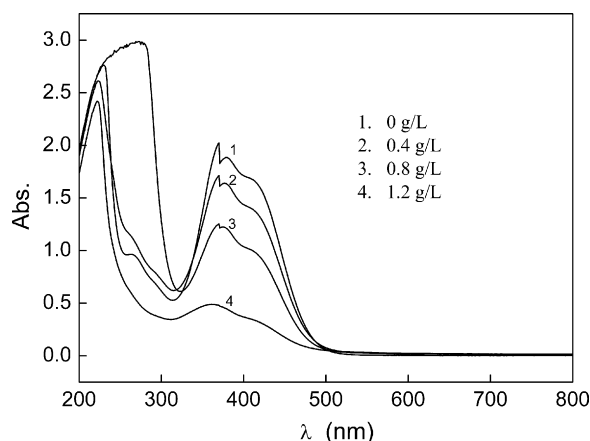

Fig. 9. Encapsulated Fe(VI) concentration dependent UV–vis spectra of DNBP.

375 nm which decreased gradually indicating that the decomposition of the organic compound was taking place.

3.4.3. Effect of reaction time

The effect of reaction time on the oxidative degradation of DNBP from its aqueous solution was investigated with DNBP (40 mg/L) and encapsulated Fe(VI) (1.2 g/L) at pH 6.5. It can be found that the reaction between DNBP and the encapsulated Fe(VI) samples was very rapid. A major removal of DNBP occurred during the first 20 min, followed by a more gradual further removal over the next 20–40 min. The removal of DNBP increased with time, up to 80 min, and, thereafter, it leveled off (Fig. 8). This was the case for all the microcapsules with mass ratios of Fe(VI):WM from 1:1 to 1:3. This indicates that the degradation of DNBP with encapsulated Fe(VI) samples for 80 min is the optimum reaction time. Overall, these results indicate that DNBP is very readily degraded by encapsulated Fe(VI) samples under these conditions.

3.4.4. Use of encapsulated ferrate(VI) samples in real wastewater treatment

The use of encapsulated Fe(VI) samples as a multi-function chemical reagent offers significant advantages in terms of increasing the stability of ferrate(VI) salts, and of a more simplified and cheaper process. This will be of direct practical value for wastewater treatment in general. We conducted a study to determine the potential use of encapsulated Fe(VI) samples for decolorization and chemical oxygen demand (COD) reduction of wastewater from DNBP manufacturing. The original wastewater with orange color for the experiments was provided by Tairui Fine Chemical Co., Ltd. (Tianjin, China). The COD and the color of the samples are estimated by dichromate method and the Platinum–Cobalt Standard method, respectively [28]. Experiments were carried out using the real wastewater with 1.2 g/L encapsulated Fe(VI) samples at pH 6 and 80 min reaction time to investigate the removal of color and reduction in COD. The removal of COD and decrease in color for the wastewater after 80 min treatment were 84% and 80%, respectively, which confirms the destruction of the organic molecules in the wastewater. The microcapsule wall materials ethyl cellulose and paraffin are not readily degraded by ferrate(VI) under the reaction conditions and can be separated from the test solution easily by simple filtration operation. Since industrial wastewaters such as the one examined in this study contain a complex combination of chemicals compounds, the encapsulated Fe(VI) samples are hopeful to be used in the full-scale treatment of wastewater containing various toxic organic contaminants and industrial effluents. Further investigation is in progress.

4. Conclusions

In this study, the microcapsules containing potassium ferrate(VI) for use as wastewater treatment reagent were synthesized by phase separation method in cyclohexane. Experiments have demonstrated that the encapsulated Fe(VI) samples are more stable than pure potassium ferrate in air for the same conserved time. The microcapsules exhibited relatively good sustained release in 8.0 M KOH, with 96.8%, 84.2%, and 72.6% release after 40 min for the encapsulated Fe(VI) samples with the Fe(VI):WM mass ratios of 1:1, 1:2, and 1:3, respectively. In this work, DNBP was studied as a model alkyl dinitro phenol chemical and was successfully degraded by encapsulated Fe(VI) samples. The optimal conditions for the oxidative degradation of DNBP were determined to be: pH value, 6.5; microcapsule concentration, 1.2 g/L; reaction time, 80 min. The prepared microcapsules of potassium ferrate(VI) was found to be very effective in the decolorization and COD reduction of real wastewater from DNBP manufacturing and this made the application of

encapsulated Fe(VI) for degrading various organic pollutants and industrial effluents more practical.

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