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Research Article

Recovery of Cerium Dioxide from Spent Glass-Polishing Slurry and Its Utilization as a Reactive Sorbent for Fast Degradation of Toxic Organophosphates

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The recovery of cerium (and possibly other rare earth elements) from the spent glass-polishing slurries is rather difficult because of a high resistance of polishing-grade cerium oxide toward common digestion agents. It was shown that cerium may be extracted from the spent polishing slurries by leaching with strong mineral acids in the presence of reducing agents; the solution may be used directly for the preparation of a ceria-based reactive sorbent. A mixture of concentrated nitric acid and hydrogen peroxide was effective in the digestion of partially dewatered glass-polishing slurry. After the removal of undissolved particles, cerous carbonate was precipitated by gaseous NH_3 and CO_2. Cerium oxide was prepared by a thermal decomposition of the carbonate precursor in an open crucible and tested as reactive sorbent for the degradation of highly toxic organophosphate compounds. The samples annealed at the optimal temperature of approximately 400°C exhibited a good degradation efficiency toward the organophosphate pesticide fenchlorphos and the nerve agents soman and VX. The extraction/precipitation procedure recovers approximately 70% of cerium oxide from the spent polishing slurry. The presence of minor amounts of lanthanum does not disturb the degradation efficiency.

1. Introduction

Because of its superior glass-polishing ability, cerium oxide is consumed in great quantities in manufacturing precise optics and other branches of the glass industry [1]. Typically, the polishing agents are used in the form of an aqueous suspension (i.e., slurry). As a result of mechanical crushing and chemical reactions, which both participate in the glass-polishing process [1, 2], the polishing agents gradually lose their efficiency and must be replaced, whereas the spent polishing sludge is discarded without further exploitation. To some extent, the lifetime of a polishing slurry may be prolonged by removing small glass particles and other undesirable admixtures by flotation [3]. However, complete refining and recovery of pure cerium compounds require more sophisticated chemical procedures consisting of dissolving cerium dioxide (and possibly also other rare earth elements present in the polishing agents) and the subsequent separation of cerium. Unfortunately, cerium oxide is known to be poorly soluble in most of the common chemical agents, including strong mineral acids. This is especially true when cerium oxide is prepared by annealing at a high temperature, which is required for its use as a polishing powder. Kim et al. [3] suggested a relatively complex procedure to obtain pure cerium from polishing slurries; specifically, the procedure consists of roasting the dried sludge at 600°C, leaching it with concentrated sulfuric acid, and separating the material by selective precipitation.

We previously developed several procedures for the recovery of rare earth elements (REEs) from spent polishing

sludges [4–6]. The digestion of cerium oxide could be performed effectively in a mixture of a strong mineral acid and a reducing agent, such as hydrochloric acid with potassium iodide [4]. Real waste sludge from optical glass polishing was treated successfully with nitric acid and hydrogen peroxide (acting here as the reducing agent) [5]. Cerium was then precipitated from the solution as cerous carbonate and then converted into cerium oxide by annealing in an open crucible or rotary kiln [6]. In our previous work [7], we demonstrated that cerium oxide prepared by thermal decomposition of cerous carbonate may serve as an effective reactive sorbent capable of destroying highly toxic organophosphate compounds in minutes.

In the present work, we demonstrated that an effective ceria-based reactive sorbent may be prepared not only from pure cerium salts but also from the glass-polishing waste sludge. A facile and easily scalable preparation route consisted of an acid digestion of the partially dewatered polishing sludge in the presence of hydrogen peroxide, removal of the undissolved portion of the sludge by sedimentation/filtration, precipitation of cerium carbonate with a gaseous mixture [8] of CO_2 and NH_3, and calcination of the dried cerium carbonate in a muffle furnace to obtain the respective oxide. A series of the reactive sorbents was prepared from the carbonate precursor by calcination at various temperatures ranging from 200 to 900°C, and their degradation efficiencies were tested for the organophosphate pesticide fenchlorphos. Furthermore, the sorbent was demonstrated to be effective in the destruction of the nerve agents soman and VX.

2. Materials and Methods

2.1. Materials and Chemicals. Waste polishing slurry was collected in the glass-polishing factory Dioptra, Turnov, Czech Republic, where high-grade ceria-based polishing powders of the Cerox type (Rhodia, La Rochelle, France) are used in the form of an aqueous slurry for the precise polishing of various optical pieces. The waste slurry was collected in several portions over a six-month time period, stored in PE containers, and partially dewatered by sedimentation before further treatment (the water content was then approximately 50%). An elemental composition of the dewatered sludge is given in Table 1. Cerous nitrate, $Ce(NO_3)_3{\cdot}6H_2O$, was obtained from Sigma-Aldrich (Steinheim, Germany) as a reagent grade product with a purity of 99.9% (trace metal basis). Technical gases NH_3 and CO_2 were obtained from Linde Gas (Ústí nad Labem, Czech Republic). Fenchlorphos and 2,4,5-trichlorophenol (2,4,5-TCP) were obtained from Sigma-Aldrich as analytical standards.

2.2. Cerium Recovery and Preparation of the Reactive Sorbent. Partially dewatered waste sludge was treated with concentrated nitric acid and hydrogen peroxide. Both chemicals were used in 20% excess over stoichiometry (with respect to the total REE content), and hydrogen peroxide was added in several subportions. The mixture was heated and extensively stirred at a temperature of 65–70°C for 3 h and then left to cool until the next day. An undissolved portion of the sludge was removed by filtration, and the total concentration of REEs in solution was adjusted to 0.2 mol/L by diluting with deionized water. Under continuous stirring, gaseous NH_3 was introduced through a glass frit to neutralize an excess of nitric acid until pH > 4; then, gaseous CO_2 was introduced along with NH_3. The absorption of CO_2 was not complete under the given conditions (in contrast to the NH_3 absorption), and thus CO_2 was used in excess; specifically, the molar ratio of $CO_2 : NH_3$ was 5 : 1. During precipitation, the pH of the mixture was maintained at approximately 7.2. The pH value rose suddenly to 9.5 when the precipitation of REE carbonates was complete. The introduction of NH_3 was then stopped, and the mixture was saturated with CO_2 for 1 h. The mixture was then left until the following day. Finely crystalline precipitate was separated by filtration, washed with water, and dried at 110°C. A series of cerium oxides was prepared by annealing at different temperatures ranging from 200 to 900°C for 2 h in a muffle furnace; the samples were denoted by D-200 to D-900. For comparison, sample B-400 was prepared from a 0.2 mol/L cerous nitrate solution using a similar procedure. In this case, the calcination temperature was 400°C.

Table 1: Elemental composition of waste polishing sludge and recovered CeO_2 (expressed as respective oxides).

Element	Polishing sludge (% wt.)[(a)]	Recovered CeO_2 (% wt.)[(a)]
CeO_2	8.85	92.8
La_2O_3	1.49	3.75
SiO_2	57.6	0.69
Al_2O_3	1.00	—
Na_2O	13.3	0.07
K_2O	6.89	0.06
CaO	2.94	0.28
MgO	0.30	0.08
ZnO	1.98	—
Fe_2O_3	0.06	—

[(a)]Dry mass basis.

2.3. Methods of Characterization. The scanning electron microscope (SEM) Tescan Vega LSU was used to examine the morphology of the sorbents. X-ray diffraction (XRD) measurements were performed on a MPD 1880 diffractometer (Philips). The specific surface area of the sorbents was measured by the BET method (N_2 adsorption) with a Sorptomatic 1900 Carlo Erba instrument. Thermogravimetric analysis of the cerium carbonate precursor was performed using a Netzsch Instrument STA 409.

2.4. Chemical Analyses and Data Evaluation. Liquid chromatographic determinations of fenchlorphos and its degradation products were performed using a LaChrom HPLC system (Merck/Hitachi) consisting of an L-7100 pump, an L-7450A diode array detector, a Rheodyne 7725i injection valve with a 20 μL sampling loop, and a C18 analytical column (Tessek, Prague, Czech Republic), 150 × 4.6 mm, with 5 μm packing material. The composition of the mobile phase

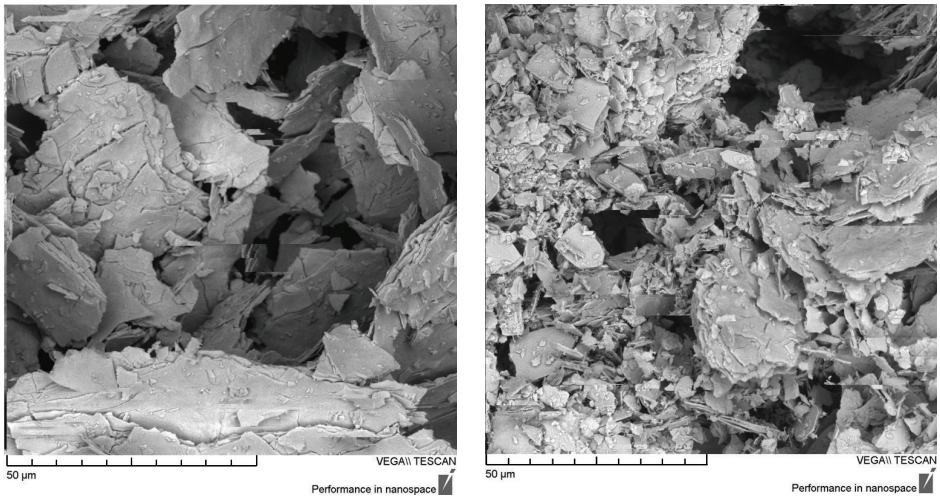
was methanol (HPLC-grade, Labscan, Dublin, Ireland)/0.1% H_3PO_4 (w/w) 80/20 (v/v) at a flow rate 0.3 mL/min. The gas chromatograph Varian GC 3800 coupled with an ion trap mass spectrometer (Varian 4000) and a fused silica capillary column (VF-5; 20 m × 0.25 mm ID × 0.25 μm), all from Varian (Varian Inc., Palo Alto, USA), were used to confirm the identity of the target analytes. The gas chromatograph Agilent 6890 with an HP-5 column (5% phenyl methyl siloxane, 30 m × 0.32 mm ID × 0.25 film thickness) was used to follow the degradation of the nerve agents VX and soman.

An elemental composition of the solid part of the sludge was determined by X-ray fluorescence analysis (Philips PW 1660); the total REE content in solution was determined by complexometric titration. The DataGraph 3.2 (Visual Data Tools, USA) and OriginPro 9.1 (OriginLab, USA) software packages were used for calculations and data evaluations.

2.5. Pesticide Degradation on the Reactive Sorbents. The testing procedure was derived from those used for an examination of chemical warfare degradation [9]. Briefly, constant amounts (50 mg) of the sorbent were weighted into a series of glass vials (Supelco, 4 mL) and wetted with 400 μL of acetonitrile. After rigorous shaking, the wetted sorbent was left to stand for 5 min. Then, an exact volume (100 μL) of the pesticide solution (10 000 mg/L) in acetonitrile was added to each vial (corresponding to a dosage of 1 mg of pesticide per 50 mg of the sorbent). The vials were sealed with caps and covered with aluminium foil to protect the reaction mixture from sunlight. At predetermined time intervals (0.5, 8, 16, 32, 64, 96, and 128 min), the reaction was terminated by the addition of methanol (4 mL), and the sorbent was separated immediately by centrifugation (4,000 rpm for 7 min). The supernatant was decanted and transferred into a 50 mL volumetric flask, and the sorbent was redispersed in 4 mL of methanol and centrifuged again. The extraction of the sorbent with methanol was repeated three times. All of the supernatants were combined in one volumetric flask, made up to the mark with methanol, and analysed immediately by high-performance liquid chromatography (HPLC) and gas chromatography with mass-spectrometric detection (GC-MS). All degradation experiments were performed at a laboratory temperature of 22 ± 1°C in an air-conditioned box. In each series of measurements, several types of quality-control experiments were performed: procedural blank experiments with the sorbent and solvents, without the presence of pesticide, and 2-3 experiments with various concentrations of pesticide in working solutions without the presence of sorbent. The recovery of 2,4,5-trichlorophenol as the main degradation product of fenchlorphos was examined using a spiked sample. Under the given HPLC conditions, the limits of detection were 0.06 and 0.04 mg/L for fenchlorphos and 2,4,5-trichlorophenol, respectively. The standard deviations of repeatability were 0.019 and 0.013 mg/L for fenchlorphos and 2,4,5-trichlorophenol, respectively, at a concentration of 1 mg/L. The relative standard deviations (RSD) of the entire degradation test were estimated from a series of duplicate measurements (n = 9, degradation time: 128 min) and expressed in terms of the fenchlorphos disappearance (RSD = 12.6%) and 2,4,5-trichlorophenol production (RSD = 14.7%). The degradation of the nerve agents soman and VX was examined using a similar procedure; gas chromatography was used to follow the decrease of the nerve agent concentration.

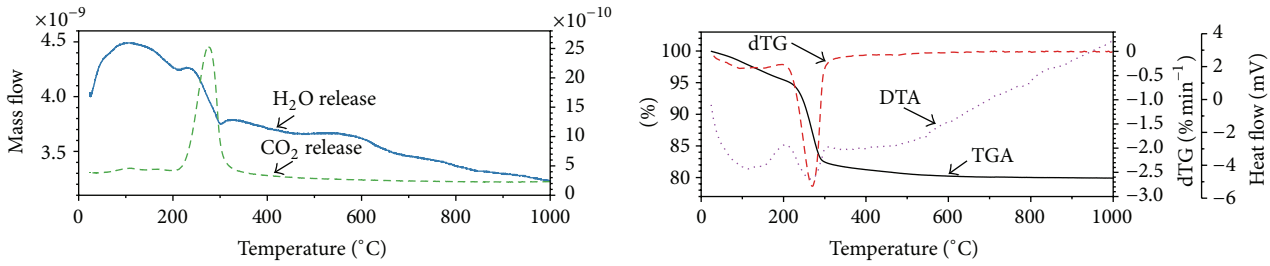
3. Results and Discussion

Waste polishing sludges mainly contain fine glass particles and spent polishing agents consisting of CeO_2 and minor amounts of other rare earth elements. The presence of other admixtures, such as Zn (Table 1), may not be excluded. During the thermal treatment with nitric acid and hydrogen peroxide, the glass particles remained undissolved, whereas the rare earth elements are dissolved (cerium is simultaneously reduced to its trivalent state). The properties of the polishing sludge varied with time and were dependent on the type of polishing agent used, the composition (concentration) of the polishing slurry, the type of glass parts polished, the residence time of the polishing agent in the polishing machine, and other operational parameters. During the six-month period, the total content of rare earth elements in the waste polishing slurry varied between approximately 8% and 15% (dry mass basis). These values differ markedly from those determined several years ago. Our work in the 1980s [5] utilized waste sludge from the same source containing as much as 60% of CeO_2 in dry mass (compare with the data in Table 1). This sludge was digested with nitric acid and hydrogen peroxide in the same manner as described in this paper, but no (external) heating was used because the reaction enthalpy was sufficient to reach the desired reaction temperature. In the present work, external heating was necessary to maintain the temperature in the range of 65–70°C. The yield of the cerium during the acid digestion was approximately 70%. In the following steps (precipitation, drying, and calcination) the losses were negligible. The cerous carbonate was precipitated from the diluted leachate with a gaseous mixture of NH_3 and CO_2, as described in the experimental section. This procedure exhibits a sufficient selectivity for the group of REEs, as is evident from a comparison of the elemental composition of the waste sludge and recovered cerium oxide (Table 1). Cerous carbonate was recovered from the solution as a fine microcrystalline precipitate that was easily separable by sedimentation or filtration. The product obtained by drying at 110°C was a white powder without an exact chemical structure; XRD patterns showed that amorphous phases predominate, but minor amounts of poorly crystalline hydrated basic and oxocarbonates were also identified [8], for example, $Ce_2O(CO_3)_2{\cdot}H_2O$. As seen from the SEM image in Figure 1(a), cerous carbonate consists of thin microplates (with a thickness on the order of nanometers) assembled together to form relatively large aggregates (a slate-like structure). During calcination, the microplates are broken down into smaller plates, but the product retains an overall morphology of the carbonate precursor (Figure 1(b)). Several samples of cerium oxide were prepared from the carbonate precursor by annealing at different temperatures ranging from 200 to 900°C. The thermal decomposition of cerous carbonate in air is a rather



(a) (b)

Figure 1: SEM images of cerium carbonate (a) and CeO_2 annealed at 400°C (b).



(a) (b)

Figure 2: Thermogravimetric analysis of cerium carbonate (b) with mass-spectroscopic detection of released gases (a).

complex process involving not only decarbonization and dehydration but also oxidation of Ce(III) to Ce(IV). These reactions may occur simultaneously in a wide temperature range, but most of them are completed in the range of 200–300°C. A thermogravimetric analysis showed that carbon dioxide was released as a single peak in the temperature range of 230–300°C, whereas water was released gradually up to approximately 800°C (Figure 2). We observed a continuously growing weight loss with increasing calcination temperature (from 21.5% at 200°C to 24.9% at 800°C) during calcination of the carbonate precursor under static conditions in an open crucible. It is assumed that the conversion of carbonate to cerium oxide occurred at temperatures below 300°C, but a complete dehydration requires temperatures above 800°C [10]. Strongly bound water molecules and residual –OH groups at the surface of the annealed cerium oxide play a significant role in the degradation of organophosphate compounds, as will be discussed later.

The XRD analysis identified a single crystalline phase in the calcination products obtained in the temperature range of 200–900°C: cerium dioxide with its characteristic face-centred cubic fluorite-type structure. With increasing calcination temperature, the diffraction peaks narrowed, suggesting that the crystallites grew and acquired a more ordered structure (see Figure 3). Crystallite sizes increased from approximately 15 to > 200 nm with increasing calcination temperature. Simultaneously, specific surface area decreased from approximately 150 to 5 m^2/g; characteristic sigmoidal dependencies were published in our previous paper [7]. Despite the presence of some other elements (i.e., La, minor amounts of Ca, and Si; see Table 1), the XRD patterns of the recovered samples confirmed the presence of a single crystalline phase corresponding to the structure of pure cerium dioxide. The absence of additional peaks indicated the formation of a single phase of the $Ce_{1-x}Ln_xO_{2-y}$ type (Ln = lanthanide) [11].

3.1. Degradation of Fenchlorphos on Recovered Cerium Oxide. Several solvents were tested as media for the degradation of fenchlorphos, ranging from nonpolar solvents, such as heptane or nonane, to polar aprotic solvents, such as acetone. Based on our previous investigations [7], we chose acetonitrile as the reaction medium because of its miscibility with water, which may be useful in some environmental applications. Using the procedure described in the experimental section, the fenchlorphos degradation was examined for various samples of the recovered cerium oxides prepared

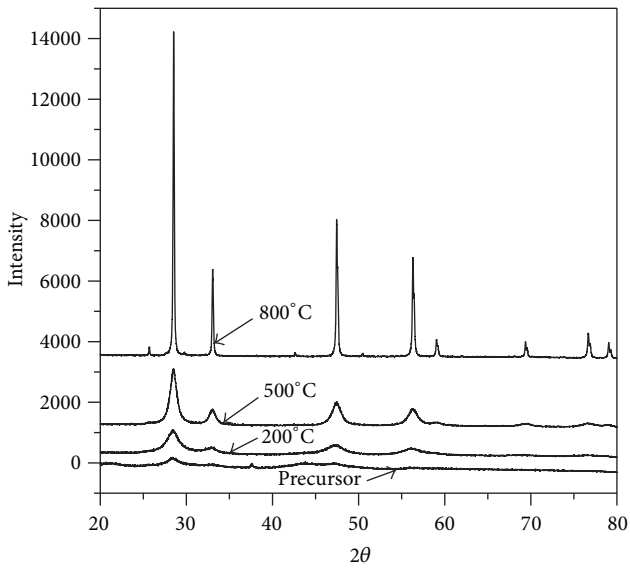


Figure 3: XRD plots of cerium carbonate precursor and cerium oxides annealed at different temperatures.

by annealing at temperatures ranging from 200 to 900°C. Pure cerium oxide annealed at 400°C (B-400) was used in the study for comparison. The kinetic curves showing the time dependencies for the disappearance of the pesticide accompanied by the formation of 2,4,5-trichlorophenol (2,4,5-TCP) as the main degradation product are presented in Figure 4. The kinetic dependencies for the fenchlorphos removal were fitted to a single-exponential-decay equation (a simplified form of the equation used previously [12] to describe the degradation kinetics of chemical warfare agents):

$$y_t = y_\infty + y_0 \exp(-kt), \quad (1)$$

where y_t is the fenchlorphos concentration at time t, y_0 is the initial concentration of fenchlorphos, and y_∞ is the residual concentration of fenchlorphos at the end of the reaction (i.e., at equilibrium). k is the pseudo-first-order rate constant, which may be related to all processes contributing to the pesticide disappearance, for example, (physical) adsorption and chemical destruction. Similarly, the formation of 2,4,5-TCP was described by the equation

$$y'_t = y'_\infty \left(1 - \exp\left(-k't\right)\right), \quad (2)$$

where y'_t and y'_∞ are the concentrations of 2,4,5-TCP at time t and at equilibrium, respectively, and k' is the pseudo-first-order rate constant for the formation of 2,4,5-TCP. Model parameters obtained by a nonlinear regression are listed in Tables 2 and 3.

Although both processes (i.e., pesticide degradation and 2,4,5-TCP formation) were treated independently, they are closely related. The mass balance in Figure 4 illustrates that the amount of the disappeared pesticide is nearly equal to the amount of 2,4,5-TCP created. The main mechanism responsible for the pesticide degradation is a chemical reaction, namely, hydrolysis, giving rise to the formation of 2,4,5-TCP, whereas other (side) reactions and physical adsorption (without a subsequent chemical reaction) contribute to the pesticide removal process to a lesser degree.

Table 2: Parameters of the pseudo-first-order kinetic model for the degradation of fenchlorphos.

Sample	y_∞		k (min^{-1})		$t_{1/2}$ (min)	R^2
	Value	SE[(a)]	Value	SE[(a)]		
D-200	0.857	0.012	0.035	0.010	19.8	0.940
D-300	0.692	0.028	0.035	0.012	19.7	0.913
D-400	0.655	0.023	0.067	0.019	10.4	0.929
D-500	0.665	0.041	0.020	0.007	35.0	0.949
D-600	0.741	0.019	0.045	0.013	15.5	0.931
D-700	0.842	0.011	0.081	0.025	8.51	0.919
D-800	0.883	0.015	0.033	0.014	21.0	0.876
D-900	0.805	0.128	0.010	0.013	67.1	0.790
B-400	0.047	0.033	0.208	0.056	3.33	0.967

[(a)]Standard error.

Table 3: Parameters of the pseudo-first-order kinetic model describing the 2,4,5-TCP formation.

Sample	y'_∞		k' (min^{-1})		$t_{1/2}$ (min)	R^2
	Value	SE[(a)]	Value	SE[(a)]		
D-200	0.036	0.003	0.032	0.009	21.5	0.928
D-300	0.252	0.015	0.027	0.004	25.7	0.978
D-400	0.288	0.019	0.050	0.012	14.0	0.936
D-500	0.256	0.021	0.033	0.008	21.1	0.941
D-600	0.205	0.004	0.039	0.003	17.7	0.995
D-700	0.134	0.012	0.022	0.005	31.8	0.964
D-800	0.118	0.017	0.011	0.003	61.0	0.981
D-900	0.088	0.005	0.027	0.004	26.1	0.981
B-400	0.622	0.042	0.214	0.100	3.23	0.881

[(a)]Standard error.

Mechanisms for the degradation of organophosphate compounds in heterogeneous systems remain somewhat unclear, especially at an atomistic level. Kuo et al. [13] recently demonstrated that an S_N2 nucleophilic substitution is the main mechanism responsible for the degradation of sarin, which was used as a model organophosphate compound; the degradation may be accelerated in the presence of hydrophilic surfaces by lowering the reaction barrier. However, in their computational study, they used an idealized glass surface as the heterogeneous part of the system, which is unlikely to be an accurate representation of metal oxide-based sorbents. We hypothesized that the (residual) –OH groups or adsorbed H_2O on the sorbent surface participate in the S_N2 nucleophilic substitution starting with the cleavage of the P–O–aryl bond in the pesticide molecule and thus accelerate the transformation of organophosphate pesticide to the respective phenolic compound. It is generally believed that coordinatively unsaturated sites at the edge surfaces, vacancies, and defects in the crystal structure serve as active sites when ceria is used as the catalyst; their number and activity may be increased by doping with other metal cations [14–16]. Therefore, the presence of lanthanum may enhance the activity of ceria-based reactive sorbents. In this context,

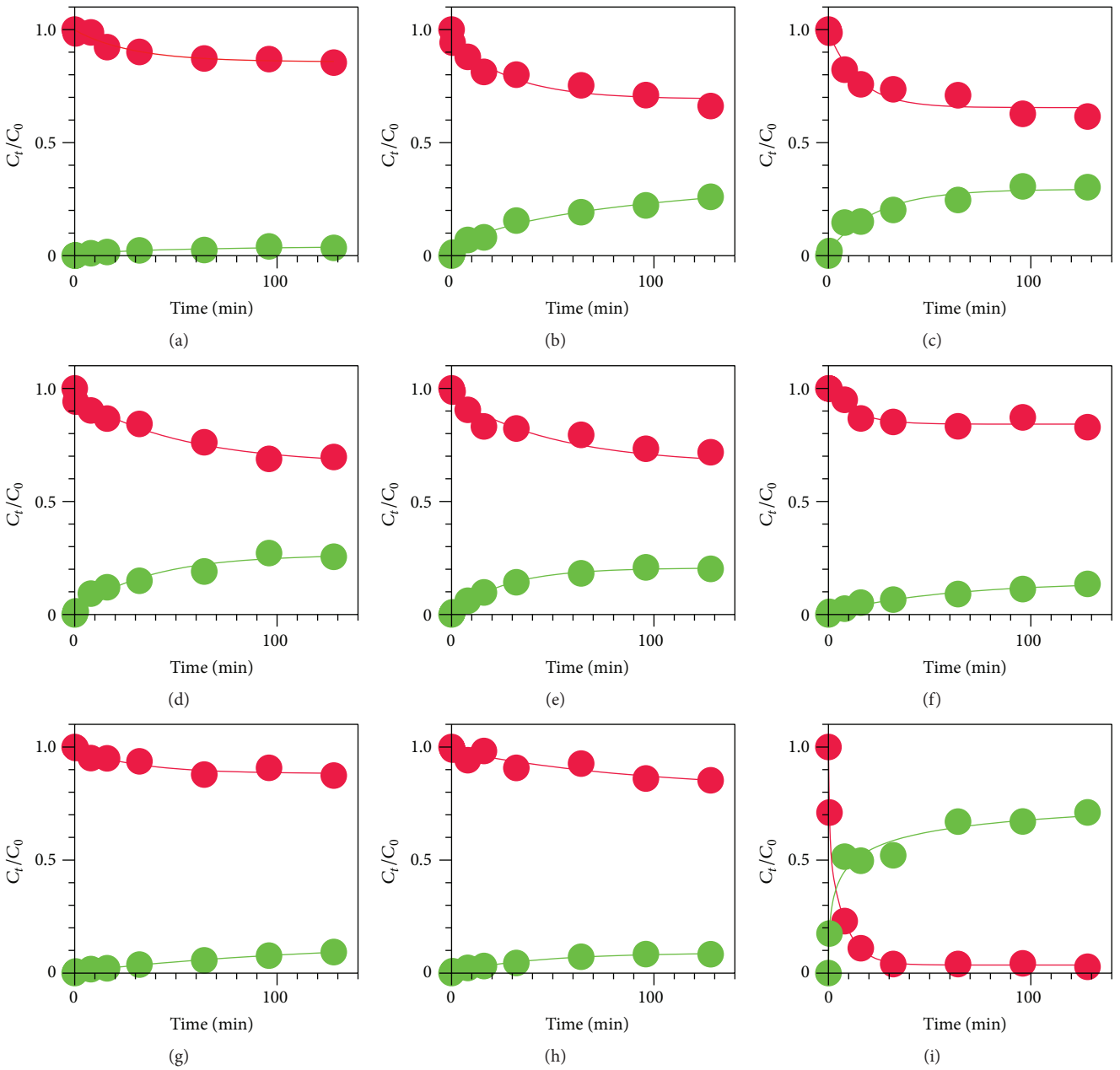


FIGURE 4: Time dependencies for the degradation of fenchlorphos on CeO_2 annealed at different temperatures. Recovered cerium oxide annealed at temperature (a) 200°C; (b) 300°C; (c) 400°C; (d) 500°C; (e) 600°C; (f) 700°C; (g) 800°C; (h) 900°C. (i) Pure cerium oxide annealed at 400°C.

trivalent cerium behaves as a "foreign" cation, similar to other lanthanide cations, and contributes to the formation of active sites. This effect likely predominates over the doping effect of foreign cations. By the method of X-ray photoelectron spectroscopy (XPS), we confirmed the presence of certain amounts of Ce^{3+} in both kinds (pure and recovered) of cerium oxide; the $Ce^{3+}:Ce^{4+}$ ratio ranged from ca. 20 : 80 to 25 : 75 in the pure cerium oxide, but it could not be quantified in the recovered cerium oxide. It should be noted that as much as 40% of Ce^{3+} was found in some types of biologically active cerium oxide nanoparticles [17]. The creation of active sites on the cerium oxide surface and their role in the degradation of fenchlorphos are shown schematically in Figure 5.

The above considerations regarding the pesticide removal mass balance hold true for the recovered cerium oxides from series D but to a lesser degree for the pure CeO_2 (B-400) (see Figure 4(i)). The fenchlorphos elimination proceeded rapidly (with a half-time of approximately 3 min) and nearly completely on this sorbent, but the amount of the produced 2,4,5-TCP was lower than the amount of fenchlorphos that disappeared. A certain portion of fenchlorphos likely remained bonded irreversibly to the sorbent surface under the given

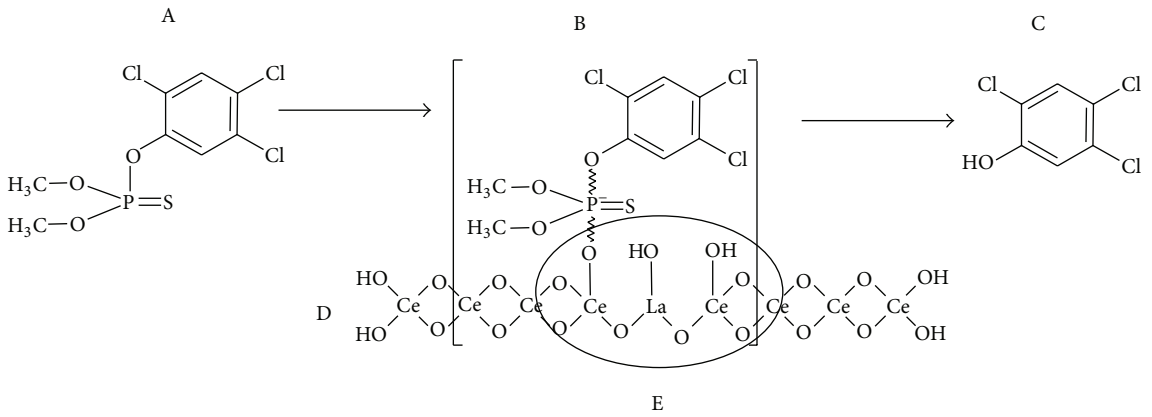


FIGURE 5: Degradation of fenchlorphos on cerium dioxide. A: reactant (fenchlorphos); B: transition state; C: product (2,4,5-trichlorophenol); D: cerium dioxide doped with La; E: reactive site on the sorbent surface.

conditions, without a subsequent chemical destruction, as no other product of any potential side reaction was identified in the reaction mixture by GC-MS. This phenomenon was not observed for the degradation of other organophosphate pesticides on similar types of CeO_2-type reactive sorbents [7].

The kinetic dependencies and data in Tables 2 and 3 demonstrate that the best degradation efficiency toward fenchlorphos was for the recovered cerium oxides annealed at relatively low temperatures below 500°C, whereas the efficiency of the samples annealed at 600–900°C was rather poor. The same trend was observed for the cerium oxides prepared from pure cerium nitrate. Samples D-400 and B-400 prepared by annealing at 400°C were tested for their ability to degrade the nerve agents VX (*O*-ethyl *S*-[2-(diisopropylamino)ethyl] methylphosphonothioate) and soman (GD, *O*-pinacolyl methylphosphonofluoridate), which belong to the most dangerous class of chemical warfare agents. As shown in Figure 6, both sorbents are highly effective at degrading the organophosphorus nerve agents, being capable of destroying the VX agent almost completely within several hours (a substantial degree of conversion was achieved within the first 30 min). Good degradation efficiency was also observed for soman.

As can be seen from Figures 4 and 6, the degradation efficiency of the recovered cerium oxide towards toxic organophosphates was somewhat lower in comparison with that of the pure cerium oxide prepared in a similar way, probably because of the presence of impurities originating from the polishing slurry. The presence of other lanthanides (3.75% La_2O_3) probably does not disturb the degradation process, as they are incorporated into the crystalline structure of cerium oxide (a negligible effect of La, Nd, and Pr on the degradation efficiency was confirmed in our previous work [7]). It is therefore hypothesized that nonlanthanide elements, although present in minor amounts (Ca, Si), have an adverse effect on the degradation efficiency.

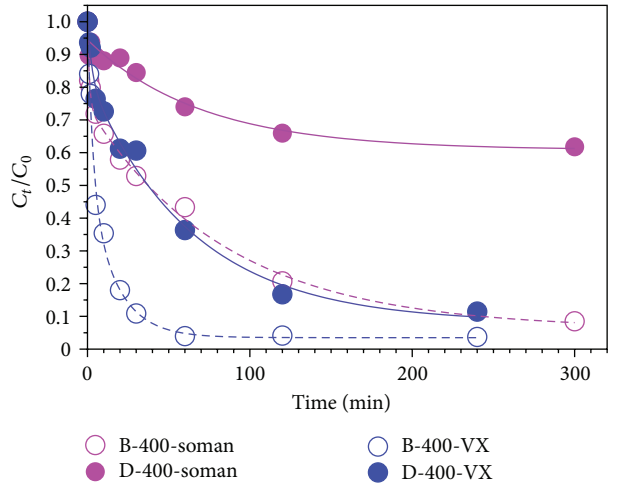


FIGURE 6: Time dependencies for the degradation of nerve agents VX and soman using recovered (solid symbols, bold lines) and pure (open symbols, dashed lines) cerium oxide.

4. Conclusions

Cerium was extracted from waste glass-polishing sludge by leaching with concentrated nitric acid in the presence of hydrogen peroxide and subsequently precipitated as cerous carbonate by gaseous NH_3 and CO_2. Cerium oxide was prepared by a thermal decomposition of the carbonate precursor in an open crucible and tested as a reactive sorbent for the degradation of highly toxic organophosphate compounds. The samples annealed at the optimal temperature of approximately 400°C exhibited a good degradation efficiency toward organophosphate pesticide fenchlorphos and the nerve agents soman and VX.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

[1] J. B. Hedrick and S. P. Sinha, "Cerium-based polishing compounds: discovery to manufacture," *Journal of Alloys and Compounds*, vol. 207-208, pp. 377–382, 1994.

[2] L. M. Cook, "Chemical processes in glass polishing," *Journal of Non-Crystalline Solids*, vol. 120, no. 1–3, pp. 152–171, 1990.

[3] J.-Y. Kim, U.-S. Kim, M.-S. Byeon, W.-K. Kang, K.-T. Hwang, and W.-S. Cho, "Recovery of cerium from glass polishing slurry," *Journal of Rare Earths*, vol. 29, no. 11, pp. 1075–1078, 2011.

[4] P. Janoš, J. Novák, and M. Broul, "Recovery of rare earth salts," CS Patent 256541, 1987.

[5] P. Janoš, J. Novák, M. Broul, and T. Loučka, "Regeneration of polishing powders based on REE oxides from glass polishing sludges," *Chemicky Prumysl*, vol. 37–62, pp. 189–194, 1987.

[6] P. Janoš and M. Petrák, "Preparation of ceria-based polishing powders from carbonates," *Journal of Materials Science*, vol. 26, no. 15, pp. 4062–4066, 1991.

[7] P. Janos, P. Kuran, M. Kormunda et al., "Cerium dioxide as a new reactive sorbent for fast degradation of parathion methyl and some other organophosphates," *Journal of Rare Earths*, vol. 32, no. 4, pp. 360–370, 2014.

[8] P. Janoš, J. Novák, and M. Broul, "Preparation of cerium-based polishing powders by thermal decomposition of carbonates," *Chemicky prumysl*, vol. 39–64, pp. 419–424, 1989.

[9] V. Štengl, T. M. Grygar, F. Opluštil, and T. Němec, "Ge^{4+} doped TiO_2 for stoichiometric degradation of warfare agents," *Journal of Hazardous Materials*, vol. 227-228, pp. 62–67, 2012.

[10] V. D. Kosynkin, A. A. Arzgatkina, E. N. Ivanov et al., "The study of process production of polishing powder based on cerium dioxide," *Journal of Alloys and Compounds*, vol. 303-304, pp. 421–425, 2000.

[11] S. Patil, S. Seal, Y. Guo, A. Schulte, and J. Norwood, "Role of trivalent la and Nd dopants in lattice distortion and oxygen vacancy generation in cerium oxide nanoparticles," *Applied Physics Letters*, vol. 88, no. 24, Article ID 243110, 2006.

[12] V. Štengl, T. M. Grygar, F. Opluštil, and T. Němec, "Sulphur mustard degradation on zirconium doped Ti-Fe oxides," *Journal of Hazardous Materials*, vol. 192, no. 3, pp. 1491–1504, 2011.

[13] I.-F. W. Kuo, C. D. Grant, R. H. Gee, S. C. Chinn, and A. H. Love, "Determination of the surface effects on sarin degradation," *Journal of Physical Chemistry C*, vol. 116, no. 17, pp. 9631–9635, 2012.

[14] P. Dutta, S. Pal, M. S. Seehra, Y. Shi, E. M. Eyring, and R. D. Ernst, "Concentration of Ce^{3+} and oxygen vacancies in cerium oxide nanoparticles," *Chemistry of Materials*, vol. 18, no. 21, pp. 5144–5146, 2006.

[15] C. Zhang, A. Michaelides, D. A. King, and S. J. Jenkins, "Oxygen vacancy clusters on ceria: decisive role of cerium f electrons," *Physical Review B*, vol. 79, Article ID 075433, 11 pages, 2009.

[16] E. Shoko, M. F. Smith, and R. H. McKenzie, "Charge distribution near bulk oxygen vacancies in cerium oxides," *Journal of Physics: Condensed Matter*, vol. 22, no. 22, Article ID 223201, 2010.

[17] M. H. Kuchma, C. B. Komanski, J. Colon et al., "Phosphate ester hydrolysis of biologically relevant molecules by cerium oxide nanoparticles," *Nanomedicine: Nanotechnology, Biology, and Medicine*, vol. 6, no. 6, pp. 738–744, 2010.