Central European Journal of Energetic Materials
ISSN 1733-7178; e-ISSN 2353-1843

Cent. Eur. J. Energ. Mater. 2017, *14*(1): 120-133; DOI: 10.22211/cejem/68391

Synthesis, Characterization, and Application of Stabilized-Ni/Fe Bimetallic Nanoparticles for the Selective Elimination of Chlorate Impurity in Military Grade Ammonium Perchlorate

Ali Reza Zarei,* **Ali Moloudi, Seyed Ghorban Hosseini**

Malek Ashtar University of Technology, Lavizan, Tehran, Iran
**E-mail: zarei1349@gmail.com*

Abstract: Ammonium perchlorate (AP) is used as the most common oxidizer in composite solid propellants. Control of chlorate impurity in military grade ammonium perchlorate is important, since it has an undesirable effect on the thermal decomposition of ammonium perchlorate. In this work stabilized Ni/Fe bimetallic nanoparticles (S-Ni/Fe NPs) were synthesized using the borohydride reduction method (BRM) in the presence of starch as a stabilizing agent, and they were characterized by field emission scanning electron microscopy (SEM), and their X-ray diffraction pattern (XRD). The results showed that the synthesized S-Ni/Fe bimetallic nanoparticles were spherical in shape and had nearly uniform distribution, with particle sizes of 20-50 nm. The prepared nanoparticles were then used for the selective elimination of chlorate impurity in ammonium perchlorate. The main factors controlling the elimination of chlorate, such as the initial pH of the solution, dosage of S-Fe/Ni NPs, initial chlorate and perchlorate concentrations, reaction temperature, and reaction time, were optimized by using an experimental design based on the Taguchi method. An L9 orthogonal array (L9-OA) was used to design experiments with four 4-level factors (3^4). Under the optimal conditions, *i.e.*, pH 6.5, at 30 °C and a dosage of 50 mg S-Ni/Fe NPs, chlorate was eliminated with nearly 100% efficiency in 50 mL of a solution containing 2.0 $\mu g \cdot mL^{-1}$ and 100 $\mu g \cdot mL^{-1}$ of chlorate and perchlorate, respectively, without change in perchlorate concentration.

Keywords: ammonium perchlorate, chlorate, selective elimination, stabilized-Ni/Fe bimetallic nanoparticles, solid propellants

1 Introduction

Composite solid propellants are the most important class of solid propellants that basically contain an oxidizer ammonium perchlorate (AP) (60-80%), a binder such as hydroxyl terminated polybutadiene (HTPB, 10-15%) and a metallic fuel such as aluminum powder (Al, 15-20%) [1]. The high content of oxygen in AP (54.5% w/w) and its high loading in a matrix polymer make AP an exceptional and irreplaceable oxidative compound in composite rocket propellants [2]. The characteristics of the thermal decomposition of AP affect the performance of solid rocket propellants and are remarkably sensitive to the presence of impurities [3-6]. Based on the specification of defence standard requirements of AP for military uses, the chlorate concentration should not exceed 0.02% (200 $\mu g \cdot g^{-1}$) [7].

The production of AP on a semi-industrial or pilot scale is based on sodium chlorate ($NaClO_3$) as the basic raw material. Sodium chlorate is submitted to electrolysis, whereby it is converted to sodium perchlorate ($NaClO_4$), and then by crystallization, converted to ammonium perchlorate (NH_4ClO_4) in a double exchange reaction with ammonium chloride (NH_4Cl). Thus, the production of AP is performed in three stages: electrolytic oxidation of sodium chlorate to sodium perchlorate, conversion of sodium perchlorate to AP by a double exchange process, and crystallization of AP [2, 8, 9]. In this method, the ammonium ions may be combined with chlorate ions to form ammonium chlorate, which is an unstable compound and will explode at 100 °C [10]. So, it is very dangerous when mixed with combustible materials and is liable to ignite spontaneously at much lower temperatures. Therefore, chlorate is destroyed in the electrolytic solution by chemical means before commencing the conversion to AP and crystallization [11]. Residual chlorate is usually destroyed using a reducing agent, such as sodium sulfite or iron(II) sulfate, and the sulfate produced is precipitated as insoluble $BaSO_4$ using $BaCl_2$ solution leaving NaCl in solution. In another method, chlorate is destroyed via reaction with a strong acid, such as hydrochloric acid to a pH of 1 to 2, and the solution is then boiled [11, 12]. In this method, chlorine dioxide is produced which is explosive and toxic. Therefore, the development of simple and safe methods to remove of the chlorate impurity from AP is highly desirable.

Nano-sized zero valent metals (nZVM) are interesting for their various applications such as catalysts, magnets, elimination of contaminants, and so on. The use of nZVM for the destruction of persistent pollutants such as explosives and nitrosamines were considered, due to their large specific surface area and high density of reactive surface sites of the nanometals, to rapidly transform contaminants in controlled laboratory experiments. Metal nanoparticles have become increasingly important in environmental remediation, especially of contaminants such as halogenated organics [13], heavy metals [14, 15], explosives [16-18] and N-nitroso-dimethylamine (NDMA) [19-21].

The nanometals used for these purposes include nano iron and zinc (Fe^0 or Zn^0), however nanoscale zero valent iron (nZVI) is most commonly used. In addition, other metals such as nickel or palladium have been added to increase the reduction rate. This combination of nZVI with a noble metal is referred to as a bimetallic nanoparticle. The iron-noble metal couple essentially creates numerous galvanic cells wherein the iron serves as the anode and becomes preferentially oxidized. Meanwhile, the noble metal (cathode) is protected and remains unchanged. Therefore, bimetallic nanoparticles typically consist of a metal such as iron as the electron donor and a zero valent second metal (such as nickel, palladium, *etc*.) as an activator [22-25].

Because ZVI-based reactions are surface mediated processes, increasing the surface area of ZVI was found to increase reaction rates [26]. It has also been shown that decreasing the size of ZVI particles to the nanoscale can greatly enhance the reaction rates [27]. However, nanoscale ZVI particles tend to agglomerate rapidly. Therefore, nZVIs without a stabilizer are agglomerated to the micro scale. To prevent agglomeration, and also to stabilize the metal nanoparticles, various stabilizers have been reported [28-33]. Compared with conventional non-stabilized nZVIs, the stabilized nanoparticles display much greater surface area, superior physical stability, and faster reaction rates. Water soluble starch and sodium carboxymethyl cellulose (CMC) are widely used as stabilizers, because they are environmentally friendly food grade materials [34, 35].

In the present work, we mainly focused on the feasibility of using starched bimetallic nanoparticles for the selective elimination of chlorate impurity in AP. Based on a literature survey, there are no reports on chlorate elimination in AP using bimetallic nanoparticles.

2 Experimental

2.1 Experimental equipment

A Hitachi model 3310 UV-Vis spectrophotometer with 1-cm quartz cells was used for recording absorbance spectra. The pH measurement was by a pHmeter (PH.Z.S. PTR79). FE-SEM images were acquired using an electron microscope Sigma model (Zeiss Ltd. Co., Germany). The XRD analyses were carried out using a Model STOE diffractometer.

2.2 Materials

All of the chemicals and reagents which were used in this work were of analytical grade. Sodium borohydride ($NaBH_4$, 98%) was purchased from Fluka. Starch ($(C_{12}H_{22}O_{11})_n > 99\%$), ferrous chloride ($FeCl_2 \cdot 4H_2O > 99\%$), ammonium perchlorate ($NH_4ClO_4 > 99\%$), potassium chlorate ($KClO_3 > 99\%$), hydrochloric acid (HCl), methylene blue, methyl orange, sulfuric acid (H_2SO_4) and chloroform ($CHCl_3$) were purchased from Merck (Merck, Darmstadt, Germany). Nickel(II) acetate tetrahydrate ($Ni(OCOCH_3)_2 \cdot 4H_2O$) were obtained from Sigma-Aldrich. In all of the experiments, deionized water was used to prepare the solutions.

2.3 Preparation of stabilized Ni/Fe bimetallic nanoparticles

Ni/Fe nanoparticles were synthesized by modifying the method described by He and Zhao [34]. In synthesizing stabilized Fe/Ni NPs, a starch solution (1% w/v) was initially prepared. $FeCl_2 \cdot 4H_2O$ (7.5 mmol) and $Ni(OCOCH_3)_2 \cdot 4H_2O$ (0.225 mmol) (Ni:Fe molar ratio, 3:100) were dissolved in deionized water (10 mL) and mixed with the starch solution (100 mL). $NaBH_4$ solution (1.6 M, 50 mL) was then added dropwise to the solution during 2 h to reduce the metal ions according to Equations 3 and 4. N_2 gas was used to remove O_2 at all stages of the synthesis.

$$2Fe^{2+}_{(aq)} + BH^{-}_{4(aq)} + 2H_2O_{(l)} \rightarrow 2Fe^{0}_{(s)} \downarrow + BO^{-}_{2(aq)} + 2H_{2(g)} + 4H^{+}_{(aq)} \quad (1)$$

$$Fe^{0}_{(s)} + Ni^{2+}_{(aq)} \rightarrow Ni^{0}_{(s)} + Fe^{2+}_{(aq)} \quad (2)$$

Finally, the Ni/Fe nanoparticles were separated from the solution using a strong magnet (1.2 Tesla) and dried in a vacuum oven at 50 °C for 3-4 h.

2.4 Elimination of chlorate in the presence of perchlorate

A batch procedure was carried out for the elimination process. A portion of a solution (50 mL) containing chlorate ($2\ mg \cdot L^{-1}$) and perchlorate ($50\ mg \cdot L^{-1}$) was transferred to a three-neck flask, the pH of the solution was adjusted to 4.8 using HCl ($0.1\ mol \cdot L^{-1}$) and/or NaOH ($0.1\ mol \cdot L^{-1}$) and the solution was deoxygenated with N_2 gas ($1\ L \cdot min^{-1}$) for 30 min. Stabilized Ni/Fe bimetallic nanoparticles (50 mg; metal/chlorate molar ratio, 745:1) were then added and the solution was stirred for 14 min. Finally, the nanoparticles were separated using a strong magnet (1.2 Tesla). The concentrations of chlorate and perchlorate in the final solution were measured spectrophotometrically according to Section 2.5. See later (Section 2.6) for specific variations of the conditions.

2.5 Spectrophotometric determination of chlorate and perchlorate

For monitoring of the chlorate in the elimination process, a simple spectrophotometric method based on the reduction of chlorate by chloride ion in acidic media to form chlorine (methyl orange was colorless in the presence of chlorine), was used [36]. In this work, an aliquot of the chlorate solution, chosen so that its final concentration would be in the range of 1.0-20 $\mu g \cdot mL^{-1}$, was mixed with methyl orange solution (2.0 mL of 0.07 $g \cdot L^{-1}$), sulfuric acid solution (2.0 mL of 10 $mol \cdot L^{-1}$) and NaCl solution (1 mL of 0.5 $mol \cdot L^{-1}$), the mixture was transferred into a 25-mL volumetric flask and was placed in a hot water bath at 80 °C for 30 min. After reaching ambient temperature, it was diluted with deionized water to 25 mL and the absorbance measured at 504 nm.

For monitoring of the perchlorate, a simple spectrophotometric method based on ion pair formation of perchlorate ion with methylene blue in acidic media was used [37]. In this work, an aliquot of the perchlorate solution, chosen so that its final concentration would be in the range of 1.0-10 $\mu g \cdot mL^{-1}$, was mixed with methylene blue solution (1.0 mL of 1.5×10^{-3} $mol \cdot L^{-1}$) and sulfuric acid solution (1.0 mL of 2 $mol \cdot L^{-1}$) and transferred into a 10-mL centrifuge tube and stirred for 5.0 min. Chloroform (3 mL) was then added to the centrifuge tube and stirred for 5 min and, after separation of the two phases, the absorbance of the organic phase was measured at 576 nm. Elimination percent for chlorate and perchlorate were calculated as follows:

$$\%R = \frac{(C_0 - c)}{C_0} \times 100 \tag{3}$$

where R is the elimination efficiency (%), C_0 and c represent the initial and final (after elimination) concentrations in $mg \cdot L^{-1}$ for chlorate or perchlorate, respectively.

2.6 Design of experiments

Design of experiments is a powerful analysis tool for the modelling and statistical analysis of the controlling factors of a process. In the design of the experiments, selection of the factors affecting the desired response is the most important step. Therefore, many factors are considered, which may then be removed because of their negligible impact and lesser importance. Chlorate and perchlorate are reduced with nZVI to produce chloride ion according to following reactions:

$$3Fe^0 \rightarrow 3Fe^{2+} + 6e^- \qquad E^0 = -0.44\ V \tag{4}$$

$$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O \qquad E^0 = +1.45\ V \tag{5}$$

$$ClO_3^- + 3Fe^0 + 6H^+ \rightarrow 3Fe^{2+} + Cl^- + 3H_2O \qquad E^0 = +1.89\ V \qquad (6)$$
$$ClO_4^- + 8H^+ + 8e^- \rightarrow Cl^- + 4H_2O \qquad E^0 = +1.287\ V \qquad (7)$$
$$ClO_4^- + 4Fe^0 + 8\ H^+ \rightarrow 4Fe^{2+} + Cl^- + 4H_2O \qquad E^0 = +1.727\ V \qquad (8)$$

In the experimental design, factors such as pH, temperature, dosage of nanoparticles and reaction time were studied. Perchlorate is a stable ion in solution due to the high activation energy of the reduction reaction, and is reduced only under harsh conditions such as high temperature, low pH and long time. Therefore, perchlorate showed a longer induction period than chlorate and the reduction of chlorate began immediately after mixing with the S-Ni/Fe nanoparticles. Because of these differences and by choosing suitable conditions, chlorate can be eliminated nearly completely without changing and eliminating perchlorate. The Taguchi experimental design establishes a systemic, simple and cost-effective methodology for the optimization of the significant parameters with a set of well-defined experiments [38]. For the present study, an L9 orthogonal array (L9-OA) was used to design the experiments with four 4-level factors (3^4). The factors are designated in the column in random order. The results of the evaluations were singly analyzed. Data analysis was performed by the use of the statistical analysis of variance (ANOVA) method. Furthermore, the optimal conditions were determined by combining the optimal levels of the significant factors and verified using a confirmation test. All calculations were analyzed using Design-Expert 7.1.3 software. The four considered factors (for 50 mL of chlorate/perchlorate solution – see Experimental) were (i) pH (4.5, 6.5, 8.5), (ii) reaction time (10 min, 30 min, 50 min), (iii) dosage of nanoparticles (30 mg, 40 mg, 50 mg), and (iv) temperature (30 °C, 50 °C, 70 °C).

3 Results and Discussion

3.1 Characterization of bimetallic nanoparticles

Figure 1 shows a FE-SEM image of the synthesized Ni/Fe NPs. It was observed that all of the NPs were spherical with an average diameter of 20-50 nm. The energy dispersive X-ray spectroscopic (EDS) analysis of fresh S-Ni/Fe is shown in Figure 2. The elemental compositions of Fe and Ni in the S-Ni/Fe nanoparticles were 96.9 wt.% and 3.1 wt.%, respectively. The crystalline phase of the Ni/Fe bimetallic nanoparticles was determined using the X-ray diffraction pattern (Figure 3). The apparent peaks at 2θ of 44.64°, 65.16° and 85.5° indicated the presence of Ni/Fe nanoparticles. The broad iron peak at 44.64° shows that the synthesized Ni/Fe nanoparticles possessed a chemically disordered crystal structure.

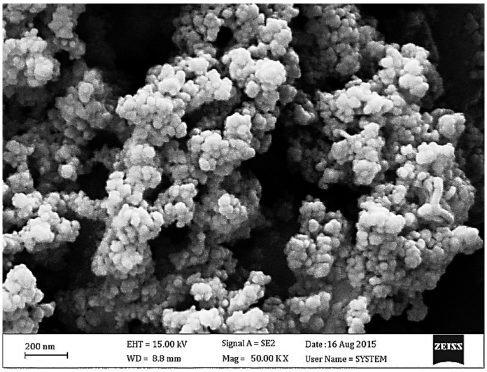

Figure 1. FE-SEM image of the synthesized S-Ni/Fe nanoparticles

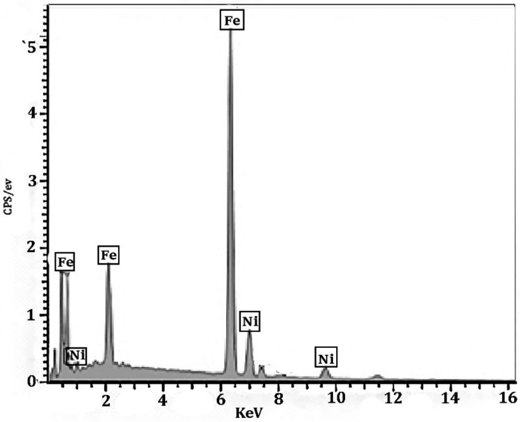

Figure 2. EDS spectra of Ni/Fe nanoparticles (Ni:Fe molar ratio, 3:100)

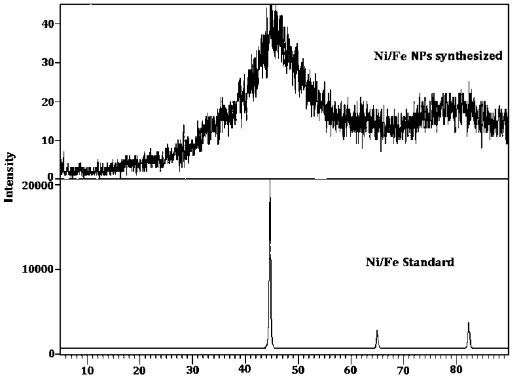

Figure 3. XRD pattern of the synthesized S-Ni/Fe nanoparticles

3.2 Experimental design

The effect of the four important parameters in the elimination of chlorate such as pH, dosage of the nanoparticles, temperature and stirrer time were assessed. Initially, to determine the range of the variables, some preliminary experiments were performed using relevant existing literature values [39]. The range of variables and their levels are presented in Table 1. Nine tests with different operational conditions, based on the Taguchi methodology were designed (Table 2).

Table 1. The range and levels of the independent variables

Variables	Range and level		
	−1	0	+1
A: pH	4.5	6.5	8.5
B: Temperature [°C]	30	50	70
C: Time [min]	10	30	50
D: Dosage of nanoparticles [mg]	30	40	50

Table 2. The experiments designed by the Taguchi methodology for the elimination of chlorate and perchlorate

Run	A	B	C	D	$\%R_1$	$\%R_2$
1	4.5	30	10	30	99.8	0.3
2	4.5	50	30	40	75.6	15.02
3	4.5	70	50	50	84.8	32.7
4	6.5	30	30	50	87.9	28.02
5	6.5	50	50	30	74.5	46.02
6	6.5	70	10	40	56.6	32.02
7	8.5	30	50	40	55.8	59.02
8	8.5	50	10	50	34.6	47.02
9	8.5	70	30	30	28.8	65.02

The tests were performed and regression analysis showed that the data can be modelled by the following second order polynomial equations:

$$R_1 = +66.49 - 23.50\mathrm{A} - 12.22\mathrm{B} + 4.02\mathrm{C} + 0.70\mathrm{D} \tag{9}$$

$$R_2 = +36.13 + 20.51\mathrm{A} + 7.07\mathrm{B} + 9.73\mathrm{C} - 0.60\mathrm{D} \tag{10}$$

where R_1 and R_2 are the elimination efficiencies of chlorate and perchlorate, respectively. The analysis of variance (ANOVA) for the Taguchi model was investigated so that values of "Prob>F" (p-value) less than 0.05 indicate the model terms are significant and values greater than 0.10 indicate they are not significant. In the present work, pH, dosage of nanoparticles, temperature and time were the significant model terms which were retained, and interactions between these factors were not significant. The analysis of variance for the reduced quadratic model is shown in Tables 3 and 4. The model *F*-value of 618.68 and the *p*-value of less than 0.0001 imply that the model is significant. Pred*R*-Squared, represents how good the model predicts a response value. In this work, the Pred*R*-Squared values of 0.7219 and 0.9861 are in reasonable agreement with the "Adj. *R*-Squared" of 0.8335 and 0.9968 for chlorate and perchlorate, respectively. "Attack Precision" measures the signal to noise ratio and a ratio greater than 4 is desirable. For the reduced model, this ratio was 9.146 and 74.336 for chlorate and perchlorate, respectively, which indicates an adequate signal. The overall performance of the model is expressed by *R*, as the degree of correlation between the observed and predicted values is expressed by "Adj. R^2" [40]. R^2 and Adj. R^2 for R_1 were 0.9168 and 0.8335 and for R_2 were 0.9984 and 0.9968, respectively, which suggests that the model can be used for predicting the process behaviour at the designed space. The influence of individual factors on the elimination yields (R_1 and R_2) is represented in Figures 4 and 5.

Table 3. Analysis of variance for R_1 by the Taguchi model

Source	Sum of squares	df	Mean square	F-value	p-value Prob> F
Model	4308.72	4	1077.18	11.01	0.0196
A: pH	3313.50	1	3313.50	33.88	0.0043
B: Temperature	895.48	1	895.48	9.16	0.0389
C: Time	96.80	1	96.80	0.99	0.3761
D: Dosage of nanoparticles	2.94	1	2.94	0.030	0.8708
Residual	391.23	4	97.81		
Cor Total	4699.95	8			

Table 4. Analysis of variance for R_2 by the Taguchi model

Source	Sum of squares	df	Mean square	F-Value	p-value Prob> F
Model	3393.35	4	848.34	618.68	< 0.0001
A: pH	2523.14	1	2523.14	1840.10	< 0.0001
B: Temperature	299.63	1	299.63	218.51	0.0001
C: Time	568.43	1	568.43	414.55	< 0.0001
D: Dosage of nanoparticles	2.16	1	2.16	1.58	0.2778
Residual	5.48	4	1.37		
Cor Total	3398.84	8			

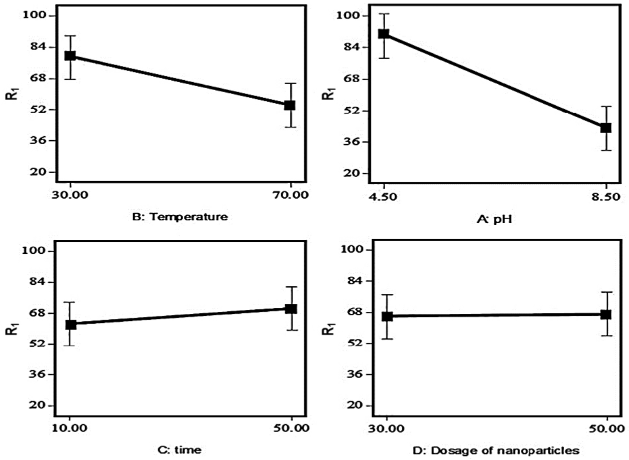

Figure 4. Individual factor performances at different levels for R_1

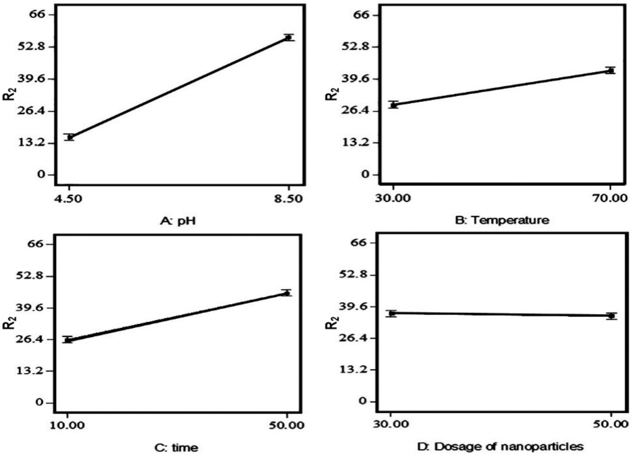

Figure 5. Individual factor performances at different levels for R_2

3.3 Optimization of the process

Here, optimization of the process means the finding of the values of the operating factors to reach a desired value of R_1 and R_2, based on the proposed Taguchi model. The optimization was performed using the related numerical facilities of the applied software. Practically, the goals of the variables were set to "maximize for R_1 and minimize for R_2". Under the settings, for 50 mL of 50 $\mu g \cdot mL^{-1}$ of perchlorate and 2 $\mu g \cdot mL^{-1}$ of chlorate solution, the software predicted 99.74% and 0.29% for R_1 and R_2, respectively. So, the optimum value of pH, dosage of nanoparticle, temperature and time were 4.50, 49.70 mg, 30 °C and 14.24 min, respectively. To evaluate the accuracy of the model prediction, further confirmatory experiments were performed under the optimum conditions; elimination of 99.7% and 0.3% was obtained practically for chlorate and perchlorate, respectively.

3.4 Selectivity

To evaluate the selectivity of bimetal nanoparticles in the elimination of chlorate in the presence of perchlorate, solutions with different ratios of chlorate and perchlorate in the range of 1:10 to 1:100 were tested. The results showed that at 1:50, the elimination efficiency was close to 100% for chlorate and less than 0.3% for perchlorate. Furthermore, even at 1:100, only 4% of elimination was observed for perchlorate. Therefore, it seems that the proposed method provides good selectivity for elimination of chlorate in the presence of high concentrations of perchlorate.

3.5 Performance evaluation

The applicability and reliability of the proposed method for the elimination of chlorate was investigated with industrial military grade AP, produced via the electrolysis process. This solution contained 700 $g{\cdot}L^{-1}$ of perchlorate and 17 $g{\cdot}L^{-1}$ of chlorate. When it was treated under the proposed procedure, the results showed that >99% of chlorate was eliminated, while the loss of perchlorate was negligible (<0.5%).

4 Conclusions

The thermal behaviour of AP is strongly influenced by impurities. Thus, elimination of impurities in the production steps of AP is necessary. In this work, we have examined the use of stabilized bimetallic Fe/Ni nanoparticles for the elimination of chlorate in AP. The most outstanding findings of the work can be briefly stated as follows: (i) stabilized-Ni/Fe bimetallic NPs with a size range of 20-50 nm were successfully prepared, (ii) a new method for the elimination of chlorate in AP using the bimetallic nanoparticles was developed, and (iii) based on the model prediction, the process can achieve 99.7% of chlorate elimination with the loss of less than 0.3% of the perchlorate under the optimum conditions, *viz.* initial pH 4.50, dosage of nanoparticles = 50 mg, T = 30 °C, and time = 14.5 min.

References

[1] Jain, S.; Nandagopal, S.; Singh, P. P.; Radhakrishnan, K. K.; Bhattacharya, B. Size and Shape of Ammonium Perchlorate and Their Influence on Properties of Composite Propellant. *Defense Sci. J.* **2009**, *59*(3): 294-299.

[2] Andric, A. M. Z. Crystallization of Ammonium-Perchlorate from Solution of Electrolytically Produced Sodium-Perchlorate in a Pilot-Scale Plant. *European Congress of Chemical Engineering*, Copenhagen, September, **2007**.

[3] Eger, C. Determination of Small Amounts of Chlorate in Ammonium Perchlorate. *Anal. Chem.* **1955**, *27*(7): 1199-1200.

[4] Kubota, N.; Kuwahara, T.; Miyazaki, S.; Uchiyama, K.; Hirata, N. Combustion Wave Structures of Ammonium Perchlorate Composite Propellants. *J. Propul. Power* **1986**, *2*(4): 296-300.

[5] Boldyrev, V. V. Thermal Decomposition of Ammonium Perchlorate. *Thermochim. Acta* **2006**, *443*(1): 1-36.

[6] Singh, G.; Kapoor, I. P. S.; Dubey, S. Bimetallic Nanoalloys: Preparation, Characterization and Their Catalytic Activity. *J. Alloys. Comp.*, **2009**, *480*(2): 270-274.

[7] Military Specification, MIL-A-23442A. Bureau of Naval Weapons, Department of the Navy, Washington, D.C., **1965**.

[8] Long, R. A. *Manufacture of Ammonium Perchlorate*. Patent US 1453984, **1923**.

[9] Gale, W. T. *Preparation of Ammonium Perchlorate*. Patent US 3288560, **1966**.

[10] Conkling, J. A. *Chemistry of Pyrotechnics*. CRC Press, **2010**, p.p. 68-75; ISBN: 9781574447408.

[11] Stern, D. R. *Process for Producing Ammonium Perchlorate*. Patent US 3254947, **1966**.

[12] Moore, H. S.; Maurice, R. S. *Removal of Chlorate and Hypochlorite from Electrolyte Cell Brine*. Patent US 4397720, **1983**.

[13] Qiu, X.; Feng, Z. Degradation of Halogenated Organic Compounds by Modified Nano Zero Valent Iron. *Prog. Chem.* **2010**, *22*(2-3): 291-297.

[14] Suguna, M.; Kumar, N. S.; Sreenivasulu, V.; Krishnaiah, A. Removal of Pb(II) from Aqueous Solutions by Using Chitosan Coated Zero Valent Iron Nanoparticles. *Sep. Sci. Technol.* **2014**, *49*(10): 1613-1622.

[15] Teng, H.; Xu, S.; Zhao, C.; Lv, F.; Liu, H. Removal of Hexavalent Chromium from Aqueous Solutions by Sodium Dodecyl Sulfate Stabilized Nano Zero-Valent Iron: A Kinetics, Equilibrium, Thermodynamics Study. *Sep. Sci. Technol*. **2013**, *48*(11): 1729-1723.

[16] Agrawal, A.; Tratnyek, P. G. Reduction of Nitroaromatic Compounds by Zero Valent Iron Metal. *Environ. Sci. Technol.* **1995**, *30*(1): 153-160.

[17] Lin, K. S.; Dehvari, K.; Hsien, M. J.; Hsu, P. J.; Kuo, H. Degradation of TNT, RDX, and HMX Explosive Wastewaters Using Zero Valent Iron Nanoparticles. *Propellants Explos. Pyrotech.* **2013**, *38*(6): 786-790.

[18] Naja, G.; Halasz, A.; Thiboutot, S.; Ampleman, G.; Hawari, J. Degradation

of Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) Using Zero Valent Iron Nanoparticles. *Environ. Sci. Technol.* **2008**, *42*(12): 4364-4370.

[19] Schaefer, C. E.; Topoleski, C.; Fuller, M. E. Effectiveness of Zero Valent Iron and Nickel Catalysts for Degrading Chlorinated Solvents and N-Nitroso Dimethylamine in Natural Ground Water. *Water Environ. Res.* **2007**, *79*(1): 57-62.

[20] Han, Y.; Chen, Z. L.; Tong, L. N.; Yang, L.; Shen, J. M.; Wang, B. Y.; Chen, Q. Reduction of N-Nitroso Dimethylamine with Zero Valent Zinc. *Water Res.* **2013**, *47*(1): 216-224.

[21] Lin, L.; Xu, B.; Lin, Y. L.; Yan, L.; Shen, K. Y.; Xia, S. J.; Hu, C. Y.; Rong, R. Reduction of N-Nitrosodimethylamine (NDMA) in Aqueous Solution by Nanoscale $Fe/Al_2(SO_4)_3$. *Water, Air & Soil Pollut*. **2013**, *224*(7): 1-9.

[22] Toshima, N.; Yonezawa, T. Bimetallic Nanoparticles–Novel Materials for Chemical and Physical Applications. *New J. Chem.* **1998**, *22*(11): 1179-1201.

[23] Schrick, B.; Blough, J. L.; Jones, A. D.; Mallouk, T. E. Hydrodechlorination of Trichloroethylene to Hydrocarbons Using Bimetallic Nickel-Iron Nanoparticles. *Chem. Mater.* **2002**, *14*(12): 5140-5147.

[24] He, F.; Zhao, D. Y. Preparation and Characterization of a New Class of Starch-Stabilized Bimetallic Nanoparticles for Degradation of Chlorinated Hydrocarbons in Water. *Environ. Sci. Technol.* **2005**, *39*(3): 3314-3320.

[25] Lien, H. L.; Zhang, W. X. Nanoscale Pd/Fe Bimetallic Particles:Catalytic Effects of Palladium on Hydrodechlorination. *Appl. Catal. B-Environ.* **2007**, *77*(1): 110-116.

[26] Wang, C. B.; Zhang, W. X. Synthesizing Nanoscale Iron Particles for Rapid and Complete Dechlorination of TCE and PCBs. *Environ. Sci. Technol.* **1997**, *31*(7): 2154-2156.

[27] Cao, J.; Elliott, D.; Zhang, W. X. Perchlorate Reduction by Nanoscale Iron Particles. *J. Nanopart. Res.* **2005**, *7*(4-5): 499-506.

[28] Kim, D. K.; Mikhaylova, M.; Zhang, Y.; Muhammed, M. Protective Coating of Super Paramagnetic Iron Oxide Nanoparticles. *Chem. Mater.* **2003**, *15*(8): 1617-1627.

[29] Chatterjee, J.; Haik, Y.; Chen, C. J. Polyethylene Magnetic Nanoparticle: a New Magnetic Material for Biomedical Applications. *J. Magn. Magn. Mater.* **2002**, *246*(3): 382-391.

[30] Pardoe, H.; Chua-Anusorn, W.; Pierre, T. G. S.; Dobson, J. Structural and Magnetic Properties of Nanoscale Iron Oxide Particles Synthesized in thePresence of Dextran or Poly Vinyl Alcohol. *J. Magn. Magn. Mater.* **2001**, *225*(1): 41-46.

[31] Kataby, G.; Ulman, A.; Prozorov, R.; Gedanken, A. Coating of Amorphous Iron Nanoparticles by Long-Chain Alcohols. *Langmuir* **1998**, *14*(7): 1512-1515.

[32] Liu, J.; He, F.; Zhao, D.; Roberts, C. Sugar-Stabilized Pd Nanoparticles Exhibiting High Catalytic Activities for Hydrodechlorination of Environmentally Deleterious Trichloroethylene. *Langmuir* **2007**, *24*(1): 328-336.

[33] He, F.; Zhao, D. Manipulating, the Size and Dispersibility of Zero Valent Iron Nanoparticles by Use of Carboxy Methyl Cellulose Stabilizers. *Environ. Sci. Technol.* **2007**, *41*(17): 6216-6221.

[34] He, F.; Zhao, D. Preparation and Characterization of a New Class of Starch-Stabilized Bimetallic Nanoparticles for Degradation of Chlorinated Hydrocarbons in Water. *Environ. Sci. Technol.* **2005**, *39*(9): 3314-3320.

[35] He, F.; Zhao, D.; Liu, J.; Roberts, C. Stabilization of Fe-Pd Bimetallic Nanoparticles with Sodium Carboxy Methyl Cellulose for Enhanced Degradation of TCE in Water. *Ind. Eng. Chem. Res.* **2007**, *46*: 29-34.

[36] Yamasaki, S.; Ohura, H.; Yano, K.; Nakamori, I. Spectrophotometric Determination of Chlorate Ion with Methyl-Orange. *Bunseki Kagaku* **1979**, *28*(9): 566-568.

[37] Goncharuk, V. V.; Zui, O. V.; Kushchevskava, N. F. Methods of Determining Perchlorate. *J. Water. Chem. Technol.* **2009**, *31*(3): 186-194.

[38] Taguchi, G.; Chowdhury, S.; Wu, Y. *Taguchi Quality Engineering Handbook*. Wiley, **2005**, pp. 20-28; ISBN: 9780471413349.

[39] Cao, J.; Elliott, D.; Zhang, W. Perchlorate Reduction by Nanoscale Iron Particles. *J. Nanopart. Res.* **2005**, *7*(4-5), 499-506.

[40] Montgomery, D. C. *Design and Analysis of Experiments*. 5th ed., Wiley, **2000**, pp. 21-54; ISBN 9780471316497.