Supercritical water oxidation for the recovery of dysprosium ion from aqueous solutions

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ABSTRACT: Supercritical water oxidation (SCWO) is a new green technology to produce nanoparticles, destroy organic compounds and some inorganic compounds. In this research, supercritical water oxidation technique was used as an environmentally friendly technology for the recovery of dysprosium ions from aqueous solutions in the form of dysprosium oxide particles in a batch type reactor. The effect of three parameters includes temperature, reaction time and primary concentration of aqueous solution of dysprosium (III) nitrate in the constant pH of starting solution (5.2) on reaction efficiency was investigated using 2³ fractional factorial design. By employing a regression analysis a model was proposed which can predict the percentage of reaction efficiency with acceptable confidence.

Keywords: Environment, Fractional factorial design, Reaction, Supercritical water oxidation.

INTRODUCTION

There are various metal ions in wastewater from petrochemical, metal processing, nuclear and etc. industries. These metal ions can be removed or recovered by liquid solvent extraction, distillation, filtration, chemical absorption and etc. methods. These conventional separation methods have been showed problems such as time-consuming, labor intensive, rising solvent disposal costs, energy consumption and residual chemicals in products. In recent years, supercritical fluid technology is becoming an increasing popular alternative method for the removal or extraction of different analytes (Joung et al., 2000; Ozel et al., 1997; Rabah, 2008; Jafarinejad et al., 2010).

Supercritical water oxidation is a process that occurs in water at temperatures and pressures above its critical point (Tc = 374 °C and Pc = 22.1 MPa). Under these conditions water becomes a fluid with unique properties that can be used as a reaction medium to produce nanoparticles, destroy organic compounds and some inorganic compounds. The process usually operates in a temperature range of 400–600°C and pressure range of 24–28 MPa (Jafarinejad et al., 2010a, 2010b; Wenbing et al., 2013; Fourcault et al., 2009; Bambang and Jae-Duck, 2007; Paraskeva and Diamadopoulos, 2006; Tavakoli and Yoshida, 2008).


In this research, supercritical water oxidation technique was used as a green or clean technology for the recovery of dysprosium ions from aqueous solutions in the form of dysprosium oxide particles in a batch type reactor. This study proposes an environmentally friendly technology to recover the metal ions from aqueous solutions and simultaneously produce valuable materials. Dysprosium oxide is a slightly hygroscopic powder having specialized uses in ceramics, glass, phosphors, lasers and dysprosium metal halide lamps (Curzon and Chlebek, 1973). Also, it has focused on use as a magnetic nanoparticle with numerous uses (Gossuin et al., 2008) and as high surface area supports for catalytic compounds (Happy et al., 2006).
MATERIAL AND METHODS

MATERIALS

Aqueous solutions of dysprosium nitrate was prepared by dissolving known amount of this salt, Dy(NO$_3$)$_3.5$H$_2$O, supplied by Aldrich in analytical grade in deionized water, to prepare a wastewater feed model of desired cation. The pH of the starting aqueous solutions was adjusted to desired value (5.2) with NaOH and HNO$_3$ solutions. All other cited chemicals used were of analytical reagent grade.

Apparatus

Recovery of dysprosium ions from aqueous solutions in the form of dysprosium oxide particles have done by the supercritical water oxidation method using the batch type reactor. For the batch type reaction a pressure-resistant SUS316 vessel with 180 cm$^3$ volume was used. This reactor was heated using an electrical heater. The pressure in the reactor is measured and showed using pressure transmitter model A-10 (WIKA®) and Digital Multi Panelmeter MP3 HANYOUNG NUX.

Procedure

In a typical experiment, 55 ml of the aqueous solutions of dysprosium nitrate with determined concentration and pH (5.2) was transferred to the reactor vessel. The supercritical water oxidation reaction was performed in the reactor vessel at desired temperature and reaction time. In the supercritical water condition, first, hydrated metal ions are hydrolyzed to metal hydroxide (hydrolysis reaction Eq. (1)). Then, metal hydroxides proceed to precipitate as metal oxides through dehydration (dehydration reaction Eq. (2)) (Hayashi and Hakuta, 2010; Byrappa et al., 2008; Reverchon and Adami, 2006):

\[
\text{Dy(NO}_3\text{)}_3 + 3H_2O \leftrightarrow \text{Dy(OH)}_3 + 3\text{HNO}_3
\]

\[
\text{Dy(OH)}_3 \leftrightarrow \text{DyO}_2 + \frac{3}{2}H_2O
\]

Generally, supercritical water provides an excellent reaction medium for this process, since it allows varying the reaction rate and equilibrium by shifting the dielectric constant and solvent density with pressure and temperature. One of the expected benefits is higher reaction rates and lower solubility for metal oxides, which lead to rapid nucleation and smaller particle size of the products (Byrappa et al., 2008; Reverchon and Adami, 2006). Later, the reactor vessel was quenched with cold water to stop the reaction and particles were collected by washing the reactor with deionized water followed by the repeated deionized water washing. When the dysprosium oxide particles precipitated in the vessel, the solution on the particles in this vessel recovered. Concentration of Dy$^{3+}$ ion in the solution recovered, analyzed by Inductivity Coupled Plasma Analyzer (ICP) with the precision of ±0.01 ppm, from which percentage of reaction efficiency was evaluated. For calibration of the apparatus sample solutions with different concentrations of 0.8 ppm, 2 ppm, 4 ppm, 20 ppm, 40 ppm and 80 ppm were prepared and measured everyday using the apparatus.

\[
\% \text{ reaction efficiency} = \frac{\text{weight of Dy}^{3+} \text{ in starting solution} - \text{weight of Dy}^{3+} \text{ in recovered solution}}{\text{weight of Dy}^{3+} \text{ in starting solution}} \times 100(3)
\]

When multiple variables affect processes, statistical experimental design has been shown to be a powerful tool for determining the effects of operational factors and their interactions; this allows process optimization to be conducted effectively. This technique has been used widely in the chemical and other industries (Jafarinejad et al., 2010; Montgomery, 1997).

Three factors, two-level $2^{3-1}$ fractional factorial method was designed, which means to carry out 4 experiments. Some preliminary experiments were used to plan important variables. The real amount of each parameter is presented in Table 1 at low and high levels assigned by (-) and (+), respectively. The measured pressures in reactor at 400 and 480 °C were 301 and 493 bar, respectively.

In this research, a $2^{3-1}$ fractional factorial design was employed to fit a first order polynomial model. The general equation of the first degree polynomial is stated as follows:

\[
Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_12X_1X_2 + b_13X_1X_3 + b_23X_2X_3
\]
\[ Y = \beta_0 + \sum_{i=A}^{C} \beta_i X_i + \epsilon \]  

(4) Where, \( Y \) is the predicted response (%Reaction efficiency), \( X_i \) are the uncoded or coded values of the factors (temperature denoted by A, reaction time denoted by B and concentration denoted by C), \( \beta_0 \) is a constant and \( \beta_i \) are the main effect coefficients for each variable. The first order polynomial coefficients were obtained using MINITAB software, and the model was validated for the process conditions used in this study.

**Table 1. The real amount of each factor.**

<table>
<thead>
<tr>
<th>Factors</th>
<th>Low level (-)</th>
<th>High level (+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Temperature(ºC)</td>
<td>400</td>
<td>480</td>
</tr>
<tr>
<td>B: Reaction time (h)</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>C: Concentration of salt (M)</td>
<td>0.15</td>
<td>0.25</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

The percentages of reaction efficiency of the samples are shown in Table 2. The factorial design can cover the main and interaction effects of the parameters within the whole range of selected parameters. According to the sparsity of effects principle in factorial design, it is most likely that main effects and two-factor interactions are the most significant effects, and the higher order interactions are negligible. In other words, higher order interactions such as three-factor interactions are very rare and considered as the residual which are dispersed randomly (Montgomery, 1997).

**Table 2. Results of 2^4-1 fractional factorial design for the reaction efficiency.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature (ºC)</th>
<th>Reaction time (h)</th>
<th>Concentration of solution (M)</th>
<th>%Reaction efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>400</td>
<td>1</td>
<td>0.25</td>
<td>99.88</td>
</tr>
<tr>
<td>A₂</td>
<td>480</td>
<td>1</td>
<td>0.25</td>
<td>68.72</td>
</tr>
<tr>
<td>A₃</td>
<td>480</td>
<td>2</td>
<td>0.15</td>
<td>64.11</td>
</tr>
<tr>
<td>A₄</td>
<td>400</td>
<td>2</td>
<td>0.15</td>
<td>63.68</td>
</tr>
</tbody>
</table>

The effects of the studied parameters and interaction effect between parameters on percentage of reaction efficiency are presented in Figure 1 and Figure 2, respectively. Analysis of the effect of principal factors showed that primary concentration of aqueous solution has positive effect on percentage of reaction efficiency, but temperature and reaction time have negative effect on percentage of reaction efficiency. In the considered range of parameters, primary concentration of solution is the most significant variable in achieving maximum reaction efficiency. According to positive effect of this parameter increasing in primary concentration of solution enhanced the reaction efficiency.

![Figure 1. Estimated effects of factors on reaction efficiency using fractional factorial design.](image)

Interaction effect between parameters showed that when the temperature is in high level (480 ºC), increase in reaction time and primary concentration of solution can slightly increase the percentage of reaction efficiency (Has negligible positive effect). But, when the temperature is in low level (400 ºC), increase in reaction time can
decrease the percentage of reaction efficiency, but increase in primary concentration of solution has positive effect on percentage of reaction efficiency. When the reaction time is in high level (2 h), increase in primary concentration of solution has negligible positive effect on reaction efficiency and in low level of reaction time (1 h), this parameter has positive effect on reaction efficiency. Investigation of the main parameters showed that reaction time and primary concentration of aqueous solution are the most effective parameters in reaction efficiency. The surface plot of these two parameters at low level of temperature (400 °C) is shown in Figure 3.

![Surface plot of reaction time and primary concentration](image)

Figure 2. The interaction effect between parameters on percentage of reaction efficiency using fractional factorial design.

The corresponding first-order response model for the percentage of reaction efficiency which is valid for uncoded units is:

\[
Y(\%) = 141.487 - 0.1920X_A - 15.7950X_B + 204.05X_C
\]

An experiment (sample A_5) was performed under certain conditions (Temperature= 450 °C, reaction time= 1.5 h, primary concentration= 0.2 M and pH= 5.2) for validation of the model; result showed that this model can predict the obtained reaction efficiency from this experiment (% reaction efficiency= 73.71 %) with acceptable error (2.09 %). (Percentage of reaction efficiency predicted by model is 72.17 %). Therefore, this model can predict the reaction efficiency.

**CONCLUSIONS**

In this study we have successfully demonstrated the recovery of dysprosium ions from aqueous solutions in the form of dysprosium oxide particles by the supercritical water oxidation method using the batch type reactor. The effect of three parameters includes temperature, reaction time and primary concentration of aqueous solution on reaction efficiency was investigated. Analysis of the effect of principal factors showed that primary concentration of aqueous solution has positive effect on percentage of reaction efficiency, but temperature and reaction time have negative effect on percentage of reaction efficiency. The results showed that the optimum value for percentage of reaction efficiency is 99.88 % that takes place in 400 °C, reaction time of 1 h, primary concentration of 0.25 M and pH of starting solution of 5.2.
Figure 3. The surface plot of reaction time and primary concentration of solution at low level of temperature (400 °C) for reaction efficiency.

ACKNOWLEDGEMENTS

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