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The Reduction of Nitro Compounds Using $Nd_2Sn_2O_7$ Nanoceramic

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Abstract
$Nd_2Sn_2O_7$ nanoceramic was synthesized using an eco-friendly method with $SnCl_4$•$5H_2O$ and $Nd(NO_3)_3$•$6H_2O$. Structural analysis confirmed the formation of $Nd_2Sn_2O_7$ nanoceramic with a size of 20±8 nm. $Nd_2Sn_2O_7$ was thoroughly characterized using SEM, XRD, TGA, EDX, and TEM techniques. Due to its high mechanical and long-term colloidal stability, large ionic character, and thermal stability, this system is considered an ideal nanocatalyst employing the host-guest approach. This green and environmentally friendly method was tested for the reduction of nitro-aromatic compounds using the synthesized $Nd_2Sn_2O_7$ nanoceramic. The catalyst demonstrated easy and effective reusability after the reaction was completed under visible light irradiation.

Keywords
Nanoceramic; Green Chemistry; $Nd_2Sn_2O_7$; Nitro-aromatic Compounds ; Wastewater.

1.INTRODUCTION

Water pollution has emerged as a significant global issue, posing a threat to the entire biosphere and impacting countless lives worldwide. This pollution leads to various illnesses, causing numerous deaths annually. Among the rising industrial pollutants are aromatic amines, which are crucial in the production of organic chemicals, photographic materials, drugs, dyes, rubber materials, and polymers [1]. However, the residual aromatic byproducts containing amine groups from these processes present environmental and health hazards. Consequently, numerous strategies have been developed to reduce nitro substrates, including catalytic hydrogenation, homogeneous catalytic hydrogenation, metal/acid reduction, and heterogeneous catalytic transfer hydrogenation [2-4]. Despite these methods, each has notable drawbacks; for instance, the metal/acid system shows poor selectivity and poses ecological dangers, while catalytic hydrogenation requires high-temperature H_2 gas and retrieving the catalysts after the reaction is challenging [5-13].

$Nd_2Sn_2O_7$ becomes an advantageous choice for deploying in various fields [14–18] due to its favorable characteristics. $Nd_2Sn_2O_7$ can be produced through different methods [19–21]. However, these methods are not extensively applicable as they are not fast, cheap, and eco-friendly. Concerning the above-mentioned information, finding a practical and providential approach to produce $Nd_2Sn_2O_7$ seems pivotal. Generating a vast number of compounds through green chemistry procedures has attracted the attention of many researchers. These procedures are affordable and environment-friendly [22, 23].
$Nd_2Sn_2O_7$ nanoparticles were synthesized in an eco-friendly manner with $Nd(NO_3)_3$•$6H_2O$ and tin (IV) chloride pentahydrate as sources of Nd and Sn. Structural analysis confirmed the formation of $Nd_2Sn_2O_7$ nanostructures with sizes ranging from 20±5 nm. Due to its ionic properties and colloidal stability and high thermal, this system is ideal for the host-guest method. Nitro compounds were effectively removed using the synthesized $Nd_2Sn_2O_7$ nanoparticles. The catalyst

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demonstrated reusability under visible-light irradiation.

2.EXPERIMENTAL

2.1.The general method for the preparation of $Nd_2Sn_2O_7$ NPs

To prepare nanostructured $Nd_2Sn_2O_7$, an innovative and eco-friendly method was used. The $Nd(NO_3)_3{\bullet}6H_2O$ (2.9 mol) and $SnCl_4{\bullet}5H_2O$ (2.9 mol) stirred for 10 minutes at 70°C, leading to the formation of a gel-like substance due to the evaporation of water. This gel was subsequently calcined at various temperatures for 70 minutes. [24]

2.2.Comprehensive Method for Reducing Nitro Compounds

An experiment is carried out by mixing the nitro compound (1.6 mmol), sodium borohydride (3.0 mmol), and $Nd_2Sn_2O_7$ (10 mg) in water (12 ml). The mixture is then stirred continuously at 85°C. During the reaction, the catalyst is removed and subsequently eluted with methanol. The reaction mixture is then extracted with CH_3CN and dried with sodium sulfate Na_2SO_4.

3. RESULTS AND DISCUSSION

This study reports providing the nanostructured $Nd_2Sn_2O_7$. FESEM and TEM data correlated with nanoparticles were prepared (Figure 1). TEM micrographs have been prepared to investigate the shape and size of $Nd_2Sn_2O_7$ produced in ideal situations. $Nd_2Sn_2O_7$ has a spherical shape and its nanoparticles diameter is 20–30 nm.

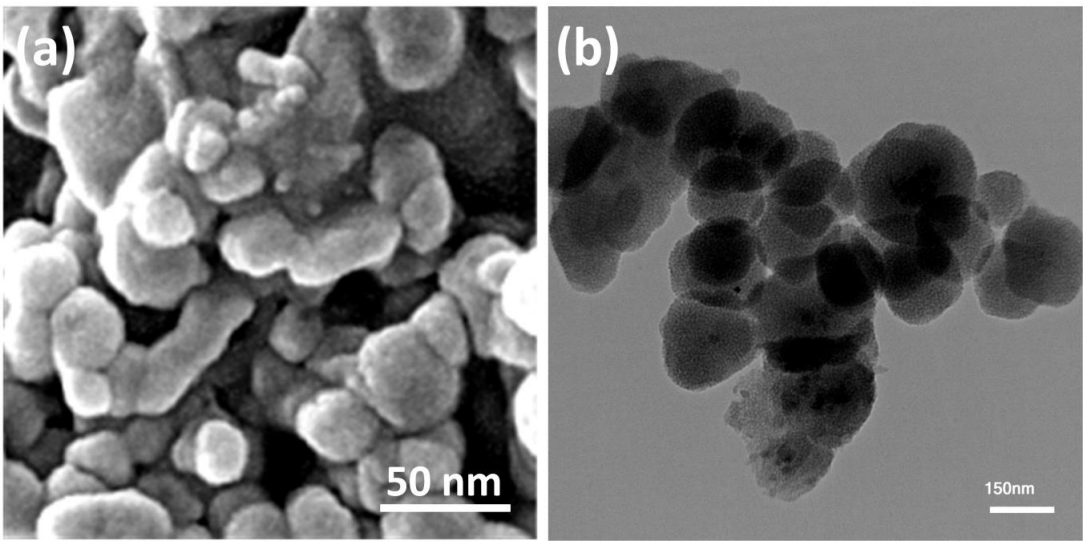

Fig. 1. FESEM (a) and TEM (b) of $Nd_2Sn_2O_7$ produced in the most appropriate conditions.

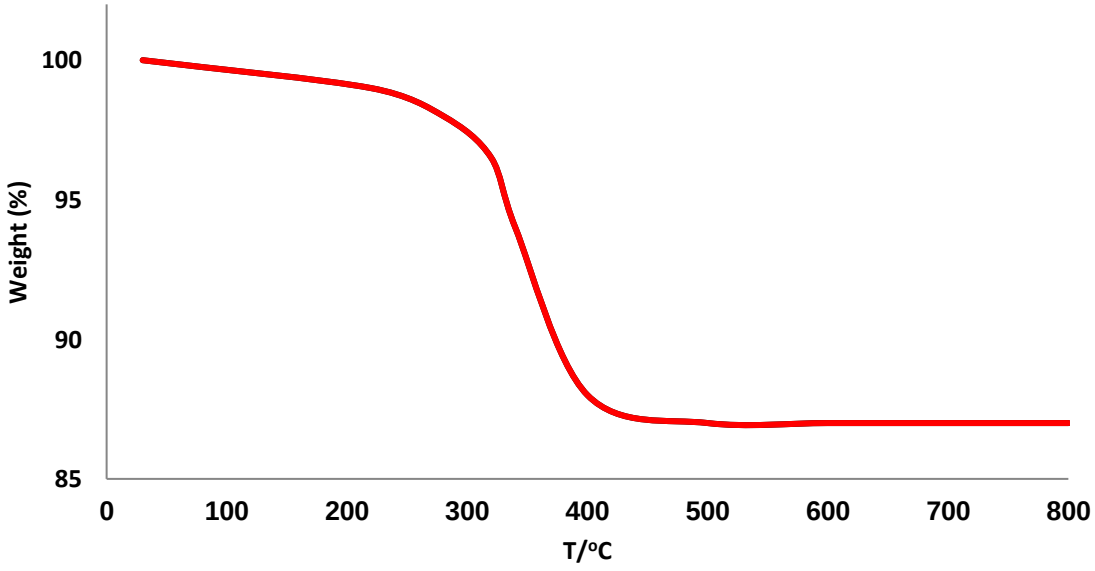

Fig. 2. TGA graph of $Nd_2Sn_2O_7$.

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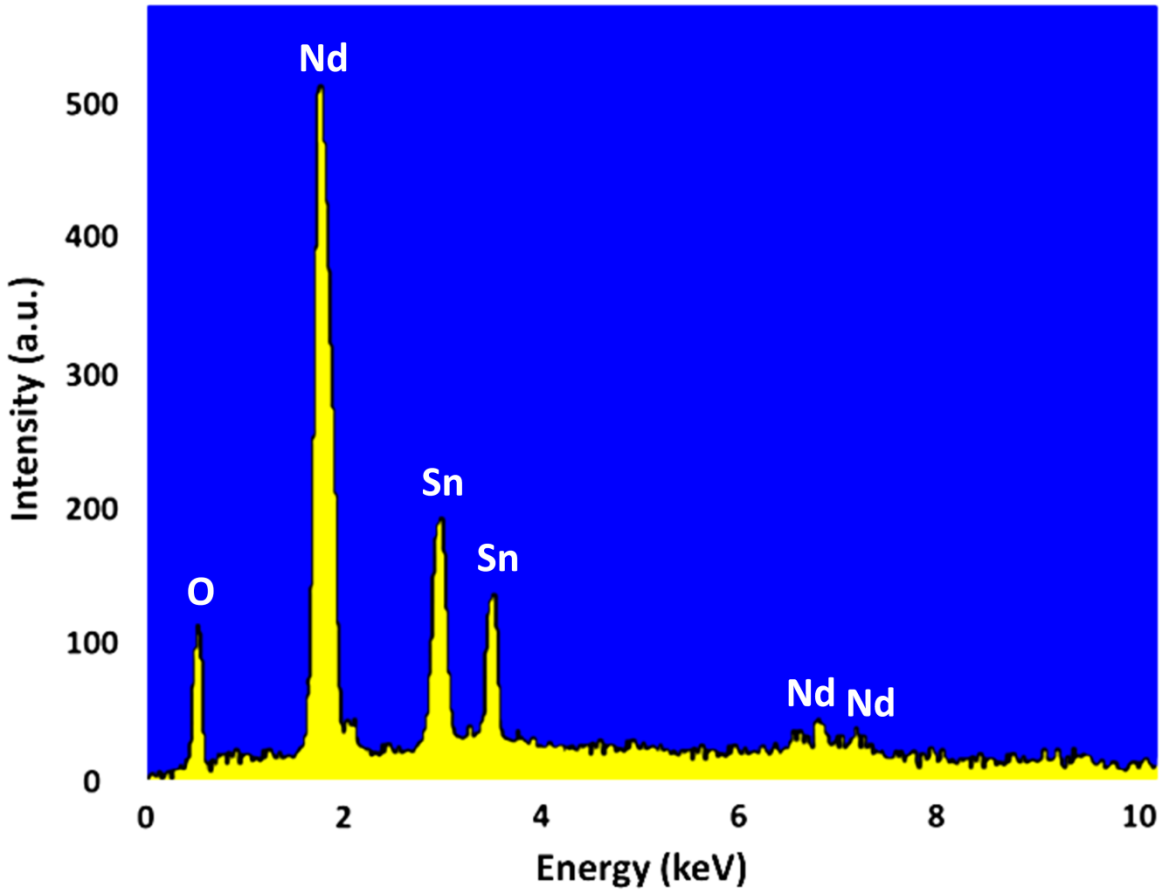

Fig. 3. EDS pattern of $Nd_2Sn_2O_7$ generated in the most appropriate condition.

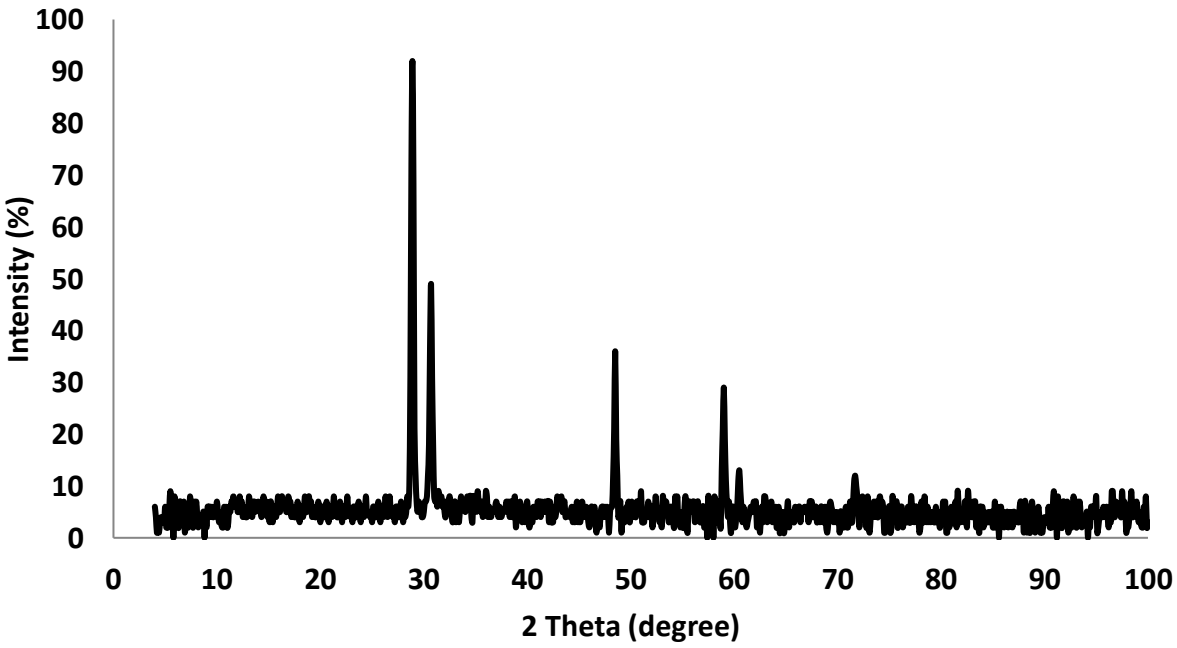

Fig. 4. XRD pattern of $Nd_2Sn_2O_7$.

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TGA data of the not-calcined gel compound showed two stages for mass reduction (Figure 2). 2% mass reduction within 30–250 °C may be connected with the release of H_2O. 12% mass reduction within 250–400 °C may be due to the destruction of organic matters and destruction of nitrate; and thereby, generation of $Nd_2Sn_2O_7$. EDS data were prepared to examine the purity of $Nd_2Sn_2O_7$ produced in the most proper condition. Nanoparticle merely signals the attributes of tin, oxygen, and neodymium (Figure 3). XRD analysis was used to identify the crystal anatomy and size of $Nd_2Sn_2O_7$ nanostructures (JCPDS No. 13-0185) (Figure 4).

The catalytic performance of $Nd_2Sn_2O_7$ is evaluated in the reduction of nitro aromatic compounds using $NaBH_4$ as the hydrogen source. Initially, the impact of the molar ratio of the hydrogen source and the solvent type on the model reaction is assessed (Figure 5). It is found that the highest reaction yield, 97%, occurs in water containing 3.0 mmol $NaBH_4$. The reduction rate of paranitrophenol in water increases as the $NaBH_4$ concentration rises from 0.5 mmol to 3.0 mmol. The reduction reaction proceeds very slowly in aprotic solvents, such as n-hexane, DMF, THF, acetonitrile, and dichloromethane. Water is chosen as the green solvent due to its environmental and biological benefits, and a fixed amount of 3.0 mmol $NaBH_4$ is used. Furthermore, the effect of nanocatalyst content on the model reaction is examined. Without the catalyst and $Nd_2Sn_2O_7$ nanoparticles, no reduction activity is observed. Increasing the $Nd_2Sn_2O_7$ amount from 8 to 10 mg of substrate enhances the reaction efficiency, likely due to the increase in the number of active sites.

As illustrated in Figure 6a, the presence of $NaBH_4$ facilitates the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP), indicated by a red shift from 400 nm to 300 nm. This shift is used to monitor the reaction kinetics of $Nd_2Sn_2O_7$ nanoparticles (NPs). During the reaction, the intensity of the 4-NP peak at 400 nm decreases while the intensity of the 4-AP peak at 300 nm increases simultaneously when using 12 mg of $Nd_2Sn_2O_7$ NPs and 3.5 mmol $NaBH_4$. Figure 6b demonstrates that a 98% conversion is achieved within just 2 minutes. This rapid conversion highlights the efficiency of $Nd_2Sn_2O_7$ NPs as a catalyst in the reduction process.

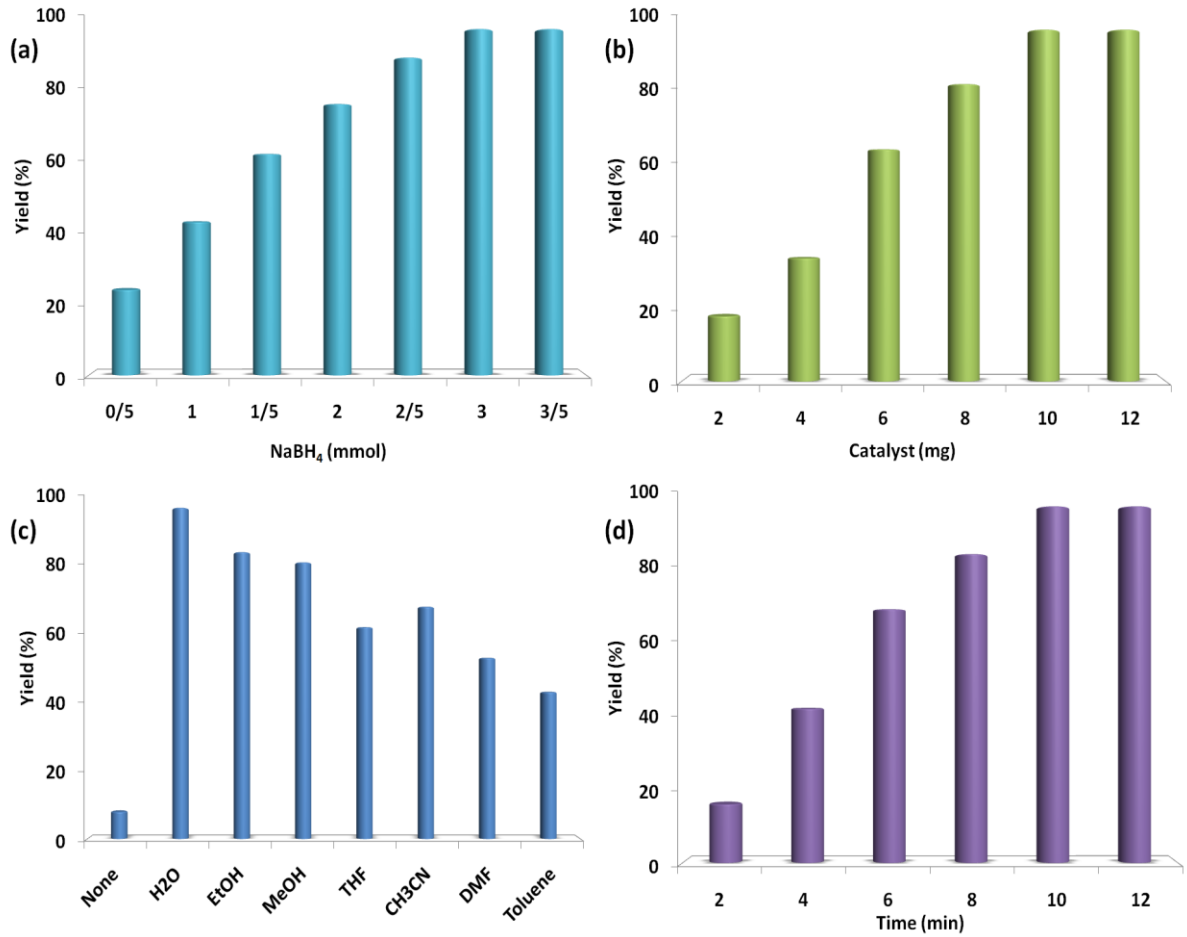

Fig. 5. Reaction the attendance of $NaBH_4$ amount (a), catalyst amount (b), various solvents (c), and time (d) by $Nd_2Sn_2O_7$.

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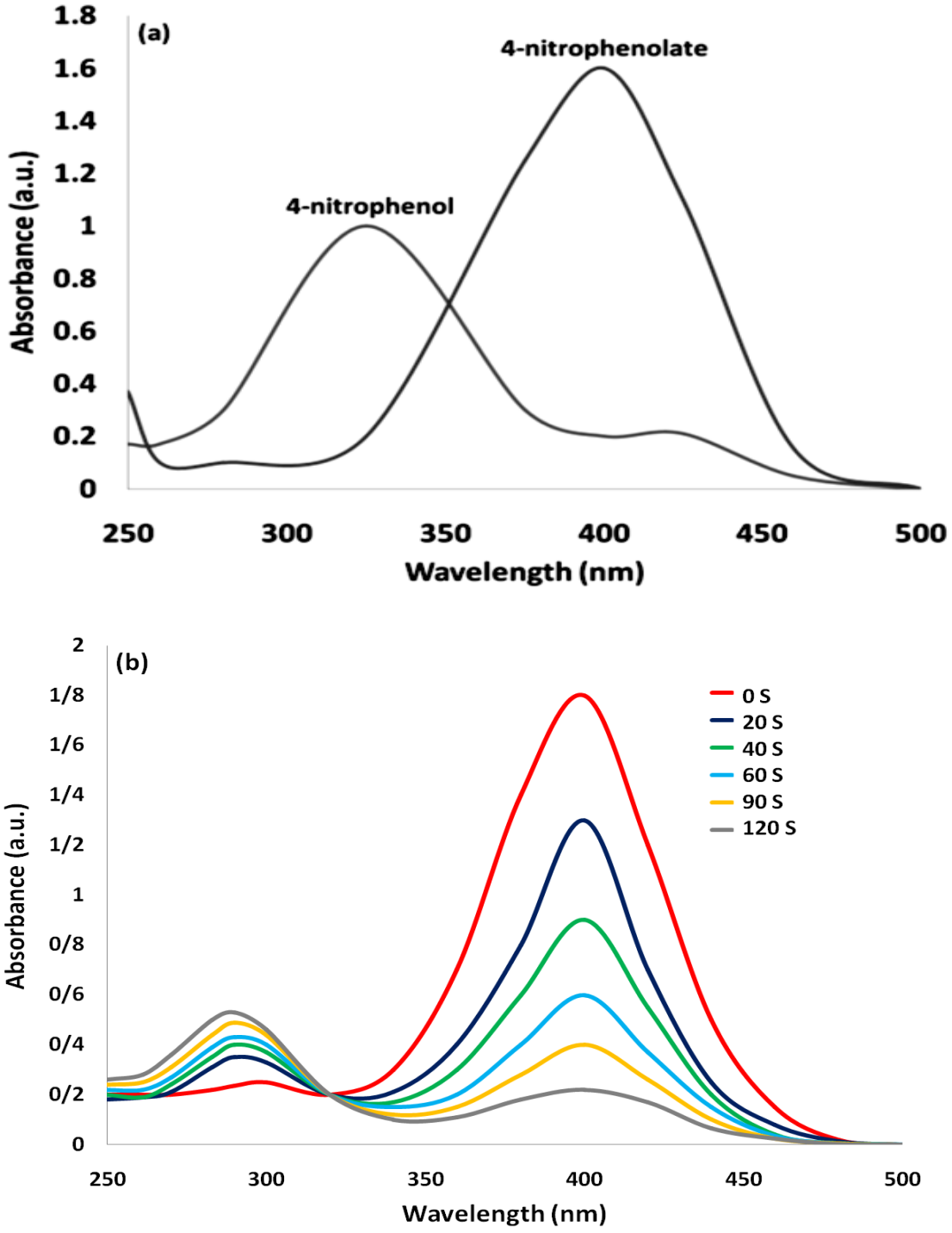

Fig. 6. UV–Vis spectra of 4-nitrophenol after and before adding $NaBH_4$ (a); and the consecutive reduction of 4-nitrophenol (b).

The conversion of the reduction was quantified using the ratio C_t/C_0, calculated from the relative strength of UV–Vis absorbance at 400 nm (A_t/A_0). Here, C_0 represents the initial concentration of 4-nitrophenol (4-NP), and Ct represents its concentration at time t. The average conversion values over the reaction period are illustrated in Figure 7. A linear relationship between $\ln(C_t/C_0)$ and time is shown in Figure 8, indicating that the reduction of 4-nitrophenol follows first-order kinetics, expressed by the equation $\ln(C_t/C_0) = -k_t$. The reaction rate constant (k) for the reduction of 4-NP using $Nd_2Sn_2O_7$ nanoparticles (NPs) is determined to be 0.968 s^{-1}. The activity factor (k'), defined as (k/M) where (M) is the mass of the nanocatalyst used, is calculated to be 9.62 $s^{-1}g^{-1}$.

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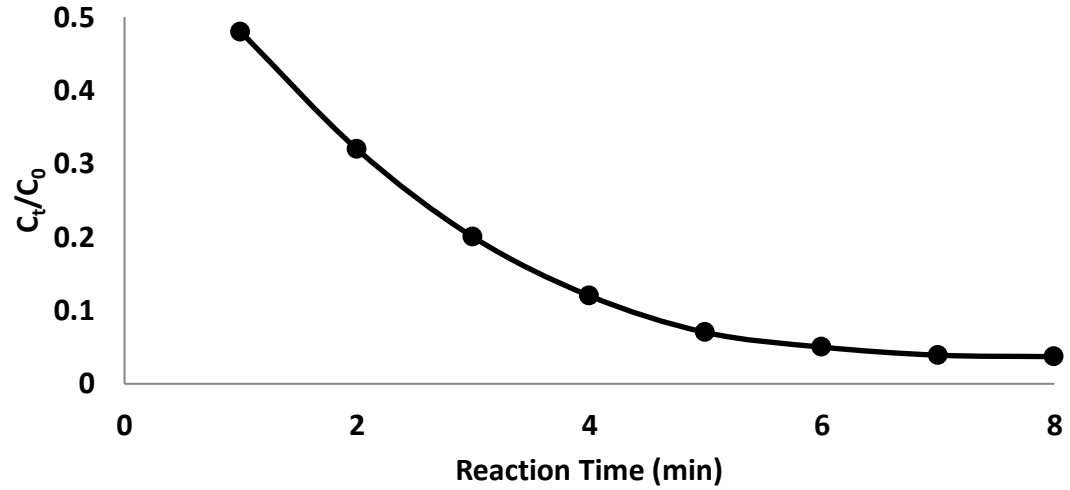

Fig. 7. The scheme of C_t/C_0 against time for the reaction over $Nd_2Sn_2O_7$.

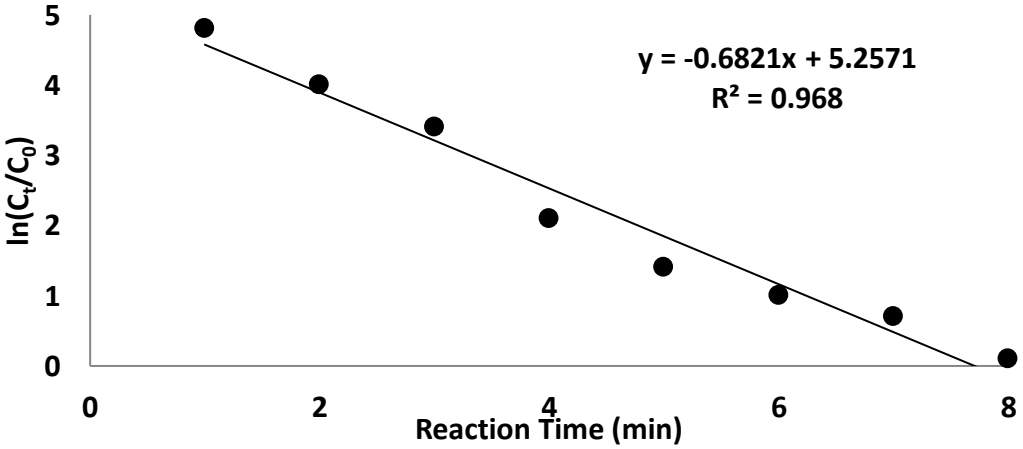

Fig. 8. The scheme of $\ln(C_t/C_0)$ against time for the reaction over $Nd_2Sn_2O_7$.

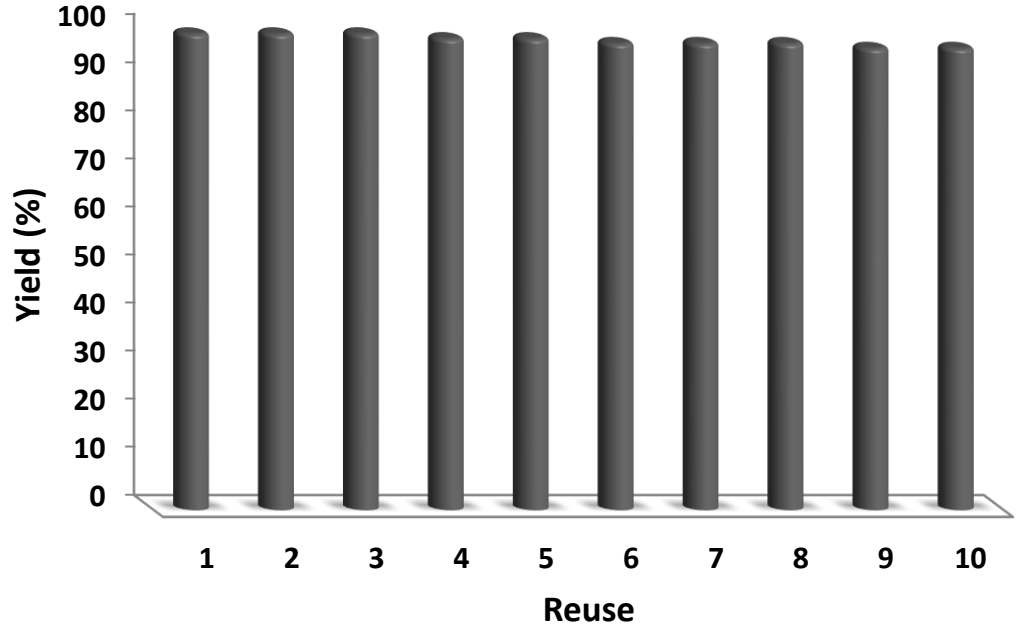

Fig.9.The reusability of $Nd_2Sn_2O_7$ for the reaction.

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In the context of green chemistry, the reusability of a catalyst is a crucial characteristic for the reaction of p-nitrophenol. The reusability of $Nd_2Sn_2O_7$ nanoparticles (NPs) was examined under optimized conditions. The $Nd_2Sn_2O_7$ NPs were easily separated from the reaction medium shortly after the reaction commenced and could be quickly reused after solvent cleaning. Figure 9 demonstrates that the catalyst was reused for ten consecutive runs. In the tenth run, a product yield of 94% was achieved, indicating only a 4% decrease in performance compared to the fresh catalyst, which yielded 98%. This slight reduction in efficiency over multiple uses highlights the robustness and durability of $Nd_2Sn_2O_7$ NPs, making them a viable option for sustainable catalytic processes.

4.CONCLUSIONS

$Nd_2Sn_2O_7$ nanoparticles were successfully synthesized using a green approach with gum of Ferula assa-foetida serving as the nanocatalyst. The synthesized nanocatalyst was characterized using SEM, TEM, TGA, XRD, and EDX techniques. The $Nd_2Sn_2O_7$ nanoparticles exhibited excellent performance in the reduction of nitro compounds. The dosage increase of $Nd_2Sn_2O_7$ nanoparticles had minimal effect on the reduction efficiency of p-nitrophenol. This separable solid nanocatalyst can be produced via cost-effective methods and reused for ten cycles without any loss in its characteristics. Therefore, this procedure stands out as a significant option for the reduction of p-nitrophenol, highlighting its potential for sustainable and efficient catalytic applications.

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کاهش ترکیبات نیترو با استفاده از نانوسرامیک $Nd_2Sn_2O_7$

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چکیده

نانوسرامیک $Nd_2Sn_2O_7$ با استفاده از یک روش سازگار با محیط زیست با $SnCl_4•5H_2O$ و $Nd(NO_3)_3•6H_2O$ سنتز شدند. تجزیه و تحلیل ساختاری تشکیل نانوسرامیک $Nd_2Sn_2O_7$ با اندازه ۸±۲۰ نانومتر را تایید کرد. $Nd_2Sn_2O_7$ به طور کامل با استفاده از تکنیک های SEM، XRD، TGA، EDX و TEM مشخص شد. این سیستم به دلیل پایداری کلوئیدی بالای مکانیکی و بلندمدت، ویژگی یونی بزرگ و پایداری حرارتی، یک نانوکاتالیست ایده‌آل با استفاده از رویکرد میزبان–میهمان در نظر گرفته می‌شود. این روش سبز و سازگار با محیط زیست برای کاهش ترکیبات نیترو–آروماتیک با استفاده از نانوسرامیک سنتز $Nd_2Sn_2O_7$ مورد آزمایش قرار گرفت. کاتالیزور قابلیت استفاده مجدد آسان و موثر را پس از تکمیل واکنش تحت تابش نور مرئی نشان داد.

کلید واژه ها

نانوسرامیک، شیمی سبز، ترکیبات نیترو آروماتیک، فاضلاب.

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