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Rapid reduction of 4-nitrophenol into 4-aminophenol and industrial wastewater treatment in the presence of UiO-66/btb/MgO catalyst

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ABSTRACT

The increase in population, the expansion of industries, and technological progress are the factors that have caused an increase in water consumption and wastewater production, environmental pollution, and forced investment for treatment. In this research work, the goal is to convert 4-NP (4-nitrophenol) into 4-AP (4-aminophenol) as a non-toxic and valuable product in industries, which is near the nanocatalyst during a reduction reaction. MgO nanoparticles (NPs) formed a complex on the surface of UiO-66-NH_2 supported by 1,3-bis((dimethyl thio carbamoyl)oxy)benzene (UiO-66/btb/MgO). The effect of various physical and chemical parameters on the catalyst was investigated, and Fourier-transform infrared spectroscopy, thermal gravimetric, X-ray diffraction, transmission electron microscopy, and scanning electron microscopy analyses were used to confirm the morphology of the nanocatalyst. The results showed, the reduction of 4-NP and conversion to 4-AP in the model reaction, and industrial wastewater was carried out by the catalyst. The reaction in the presence of water solvent, $NaBH_4$ (4 mmol), time 3 min and catalyst (20 mg) had 96% yield. The UiO-66/btb/MgO heterogeneous catalyst was readily recycled by filtration from the reaction solution, and the efficiency of the recycled catalyst was slightly reduced. This research can be an effective option for the final treatment of wastewater containing low to medium concentrations of 4-nitrophenol compounds.

Keywords: Industrial wastewater; 4-Nitrophenol; Nanoparticle; Catalyst

1. Introduction

Nitrophenol, the first important and priority polluting compound on the US environmental protection list, has severe toxic and environmental effects that can affect the nervous system, cardiovascular system, and bone marrow through skin absorption and inhalation and reducing its concentration in industrial effluents has been noticed [1–3]. Nitrophenol is one of the first compounds included in the list of important pollutants by the USEPA (US Environmental

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Protection Agency) [4]. It is not possible to remove the phenolic compounds in the wastewater before discharge into surface water. Due to the resistance of these compounds, it is not possible to remove them from surface and underground water by traditional water purification methods [5,6], in various industries, the toxic compound para-nitrophenol with LD_{50} of 202 and 201.9 mg/kg is widely used. Its release into the environment harms to mice and fish and threatens the ecosystem [7].

Some examples of research done in the past years and nitro groups were converted to amine. Bekamp described for the first time reducing the nitro agents to amines using iron. Contrary to the excellent efficiency of the method, the cost and low iron toxicity, this method has disadvantages, such as the use of large amounts of iron powder, in similar conditions, several other metals, such as Co, Zn, Ti, and Mo, have been used [8–12]. Salimi et al. [13] reviewed the applications of sorbents to remove phenolic compounds from wastewater. The effect of different parameters, temperature and amount of adsorbent on pH absorption value, such as the initial concentration of phenol, was investigated. Investigations showed that low-cost adsorbents, such as adsorbents obtained from mineral materials, agricultural waste and industrial waste materials have high potential and more flexibility than many other methods for removing phenolic compounds, and adsorbents that have more surface activity, high surface and porosity are more effective, in a study conducted by Alshammari et al. [14]. Wastewater treatment was investigated by Au-Pd/TiO_2 catalyst, and their results showed that 4-nitrophenol was reduced to 4-aminophenol in the presence of reducing agent $NaBH_4$. Mirza-Aghayan et al. [15] reduced some of the nitroaromatic compounds using triethylsilane in the presence of palladium chloride catalyst, ethanol solvent, and related anilines were prepared with good efficiency. Jaleh et al. [16] synthesized bentonite/Ag nanocomposite and investigated its catalytic activity on reducing the 4-nitrophenol (4-NP) pollutant using $NaBH_4$ as reductant. Their results showed that bentonite/Ag heterogeneous nanocatalyst is efficient and excellent for removing toxic or organic pollutants.

Arnawtee et al. [17] synthesized MWNT/KL/Pd heterogeneous nanocatalysts, and investigated the efficiency of nanocatalysts in reducing 4-nitrophenol (4-NP) using sodium borohydride or formic acid as reducing agents.

Kim et al. [18] using Fe_3O_4 nanoparticles and in the presence of hydrazine hydrate, reduced nitro groups in a transfer manner. The catalyst used in this work can be separated up to five times with a magnetic field. Other metals such as Zn/NH_3, activated iron, Zn/NaOH/EtOH, Al/NH_4Cl/MeOH, $ZnCl_2$/EtOH, $Co_2(CO)_8/H_2O$, and $Mo(CO)_6$ as well have been used and other catalysts such as $SnCl_2/H_2O$, $SnCl_2$/ionic liquid, $N_2H_4/FeCl_3$, N_2H_4/Zn, $TiCl_3$, $NaHPO_2/FeSO_4$, $B_{10}H_4$/Pd/C, $FeCl_3/Zn/DMF/H_2O$, $HCOONH_4$/Pd/C and $HCOONH_4$/Mg have been used [19–35]. Many studies have been done to treat polluted water [36–39]. Various studies have been done in metal oxides, which usually have perfect catalytic behavior. Magnesium oxide is a stable catalyst with unique properties. Wastewater treatment using the absorption method has provided a suitable topic for research in this field. Low-cost absorbents have been proposed for various types of toxic chemicals in wastewater. The existing and developed materials can be modified to increase the capacity or activity by several methods, which causes more efficiency in their applications. Due to having a large surface area and porosity, nanoparticles is an excellent example for purifying almost all available pollutants. Considering the importance of catalysts in this study, the first catalyst was investigated in the model reaction and the aromatic compound of 4-nitrophenol was converted to 4-aminophenol. An industrial wastewater sample containing 4-nitrophenol compounds was prepared, and the effect of catalysts on it was investigated.

2. Materials and methods

Fourier-transform infrared spectra were obtained with the ALPHA device belonging to Bruker Company with the help of KBr tablets. The X-ray diffraction pattern was prepared with the X'Pert PRO device made by PANalytical from the Netherlands in the range 2θ between 0 and 80 and a copper lamp. Thermal gravimetric analyzer (TGA) model Polymer Laboratories Linseis in the temperature range of zero to 600°C and ultraviolet-visible spectrometer UV-Vis model RAYLEIGH UV 1800 were used. An Electrothermal 9100 device was used to calculate melting points. A Philips CM10 Transmission Electron Microscope operating at 100 kV was used to observe nanoparticle size and structure. A Hitachi S-4160 was used to take FE-SEM (field-emission scanning electron microscopy) images. TLC was used on Polygram silica gel plates SILG/UV 254 to assess the product's purity and track the reaction.

2.1. Sampling

Sampling of effluents from industrial factories and active production centers of the industrial town was carried out in several different time frames and taking into account the primary parameters, including physical and chemical conditions, pH, and temperature of the effluent.

2.2. Synthesis of MgO nanoparticles

100 g of $MgCl_2·6H_2O$ were dissolved in 500 cc of distilled water in a 1-L beaker. Then, 50 cc of 1 N NaOH solution was added. Mixing for 4 h (with a revolution of 300–400) until $Mg(OH)_2$ precipitate is formed. It was centrifuged at 3,000 rpm for 5 min to form $Mg(OH)_2$ in gel form. Then, the sample was washed several times with distilled water and dried for 24 h at 60°C. Finally, the dried powder was calcined in an oven at 450°C for 2 h.

2.3. Preparation of organic-metallic framework UiO-66-NH_2

First, 0.06 g of zirconium(IV) chloride was dissolved in 3.66 L of N,N-dimethylformamide (DMF) and then 0.087 mol of 2-aminoterephthalic acid was added to it and stirred for 10 min. The obtained mixture was kept at 100°C for 24 h. After 24 h, the resulting mixture was cooled. Then, it was washed with DMF and ethanol solvent. Finally, the solvent was removed from the pores of the obtained composition with a vacuum pump. Finally, to activate the prepared UiO-66-NH_2 organic–metallic framework, the desired composition was placed at 100°C for 1 d and night (24 h) and the yellow precipitate of UiO-66-NH_2 was obtained [40].

2.4. Synthesis method of UiO-66/btb NPs

50 mL of DMF, 1 g of UiO-66-NH_2, 3,5-dihydroxybenzoic acid (1.5 mmol) were blended. The reaction mixture was stirred for 30 h at 110°C, it was filtered and washed by DMF. Finally dried in an oven at 80°C for 24 h to produce UiO-66/btb NPs. After that, 1 g of the obtained solid, 5.5 g of potassium carbonate (K_2CO_3), and N,N-dimethylthiocarbamoyl chloride (5 g) were stirred in acetone (100 mL), then refluxed in the presence of nitrogen for 45 h. After cooling the suspension, the solvent was removed in a vacuum. After that, the separated organic phase was washed with deionized water, KOH (7%), and saturated NaCl. Finally dried over Na_2SO_4 [40].

2.5. Preparation method to obtain UiO-66/btb/MgO NPs

To get UiO-66/btb/MgO, we first mix 1 g of UiO-66/btb with 1 mmol of MgO. Then, it was placed by 20 mL of CH_2Cl_2 at 25°C for 24 h. Finally, the filter mixture was washed with acetonitrile.

There are several steps for the synthesis of UiO-66/btb/MgO nanocatalyst. There are many N–H groups on the surface of UiO-66-NH_2. Therefore, it is predicted that UiO-66-NH_2 easily participates in the reaction with 1,3-bis(dimethylthiocarbamoyloxy) benzene (btb) to form UiO-66/btb. Also, btb groups can support the MgO complex more than UiO-66/btb (Fig. 1).

2.6. General method for reduction of nitro compounds

The model reaction was carried out using nitroaromatic compounds (2 mmol), $NaBH_4$ (0.4 mmol), and 20 mg of nanocatalyst in 5 mL of H_2O, and then continuously at 90°C. It is stirred. The progress of the reaction was monitored by TLC method. The catalyst was filtered from the reaction medium. The reaction mixture was also extracted with ethyl acetate and dried by Na_2SO_4 moisture absorbent. Column chromatography was used for purification with different concentrations of hexane-ethyl acetate.

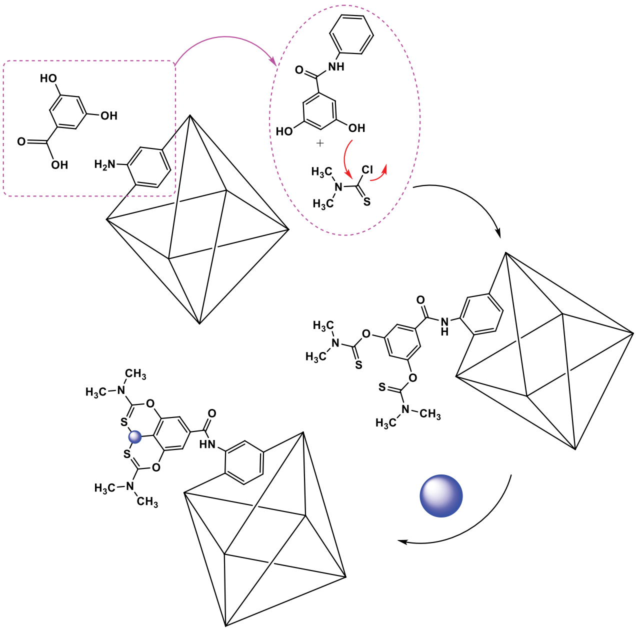


Fig. 1. Synthesis of UiO-66/btb/MgO catalyst.

Aniline: Colorless to yellow liquid.^{1}H-NMR (250 MHZ, $CDCl_3$): δ = 3.57 (br s, 2H, NH_2), 6.62–6.65 (d, 2H, J = 7.5 Hz, ArH), 6.73 (t, 1H, J = 7.5 Hz, ArH), 7.13 (t, 2H, J = 7.5 Hz, ArH) ppm; ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 115.1, 118.5, 120.2, and 146.4 ppm.

4-Aminoaniline: Light brown crystalline solid. ^{1}H-NMR (250 MHZ, DMSO-d6): δ = 4.2 (bs, 4H, $2NH_2$), 6.34 (br s, 4H, ArH) ppm; ^{13}C-NMR (63 MHz, DMSO-d6): δ = 117.3 and 138.4 ppm.

4-Methylaniline: Light brown crystalline solid. ^{1}H-NMR (250 MHZ, $CDCl_3$): δ = 2.26 (s, 3H, CH_3), 3.52 (d, 2H, NH_2), 6.61–6.65 (d, 2H, J = 7.5 Hz, ArH), 6.97–7.01 (d, 2H, J = 10.0 Hz, ArH) ppm; ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 20.5, 115.3, 127.8, 129.8, and 143.9.

4-Aminophenol: Light brown crystalline solid. ^{1}H-NMR (250 MHZ, $CDCl_3$): δ = 4.35 (br, 2H, NH_2), 6.38–6.42 (d, 2H, J = 10.0 Hz, ArH), 6.45–6.48 (d, 2H, J = 7.5 Hz, ArH), 8.34 (s, 1H, OH) ppm; ^{13}C-NMR (63 MHz, DMSO-d6): δ = 115.2, 115.5, 140.6, and 148.1 ppm.

4-Aminoacetophenone: ^{1}H-NMR (250 MHZ, $CDCl_3$): δ = 2.48 (s, 3H, CH_3), 4.03 (br s, 2H, –NH_2), 6.64 (d, 2H, J = 8.5 Hz, ArH), 7.81 (d, 2H, J = 8.5 Hz, ArH) ppm; ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 26.1, 113.7, 128.0, 130.7, 151.0, and 196.3 ppm.

4-Aminobenzoic acid: White-cream crystalline solid. ^{1}H-NMR (250 MHZ, $CDCl_3$): δ = 5.85 (br s, 2H, NH_2), 6.50–6.53 (d, 2H, J = 7.5 Hz, ArH), 7.57–7.61 (d, 2H, J = 10.0 Hz, ArH), 11.92 (s, 1H, COOH) ppm; ^{13}CNMR (63 MHz, $CDCl_3$): δ = 112.5, 116.9, 131.1, 153.0, and 167.4 ppm.

3. Results

The morphology and sizes of UiO-66/btb/MgO nanocatalyst were determined using scanning electron microscopy and transmission electron microscopy. Nanoparticles have been synthesized uniformly. UiO-66/btb/MgO nanoparticles contain spheres of uniform size and show wrinkled radial structure. Also, conical open pores are formed as folded radial structures that are stacked on top of each other. Nanoparticles have been synthesized as a uniform fabric (Fig. 2).

X-ray diffraction patterns are a standard method for investigating the structure of nanoparticles. Checking Fig. 3, X-ray diffraction patterns of UiO-66/btb/MgO, UiO-66/btb, and UiO-66-NH_2 agree with the simulated X-ray diffraction patterns. By comparing the peaks, we realize that no changes have been made in its peaks (Fig. 3c).

The reduction of para-nitrophenol is done in the presence of a hydrogen source. Which was investigated from $NaBH_4$ in different amounts from 1–5 mmol; with, the increase of $NaBH_4$, the reaction efficiency increased, but the best performance of the reaction was in the amount of four mmol. Because more than this value, the reaction efficiency has not changed significantly (Fig. 4a). The process of the reduction reaction was investigated in different solvents and

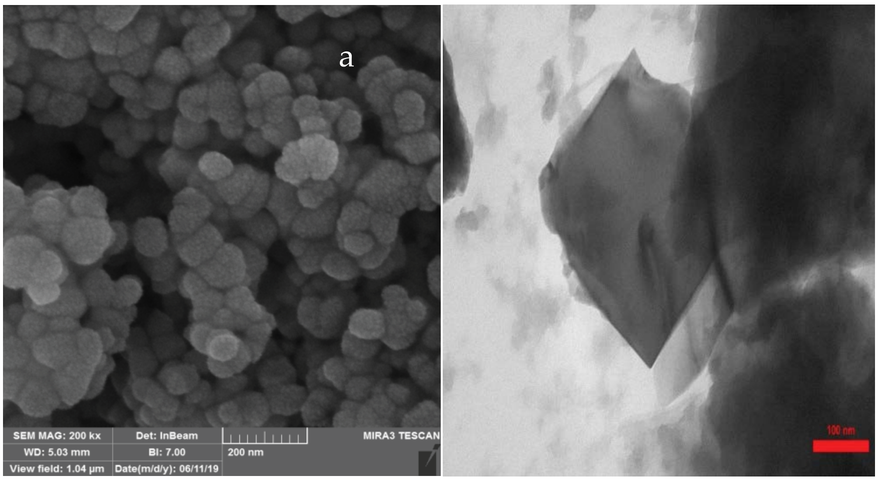


Fig. 2. (a) Scanning electron microscopy and (b) transmission electron microscopy images of UiO-66/btb/MgO.

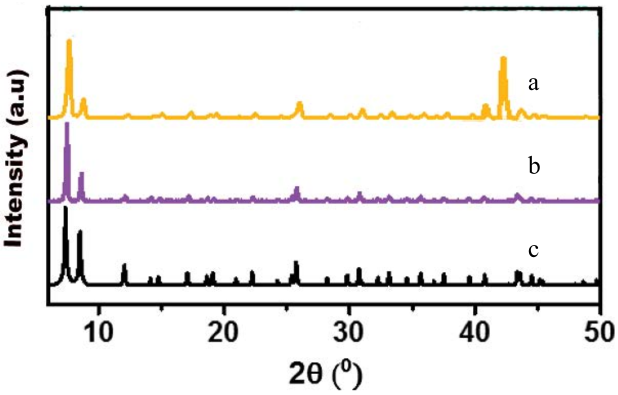


Fig. 3. X-ray diffraction results of (a) UiO-66-NH_2, (b) UiO-66/btb, and (c) UiO-66/btb/MgO.

4.0 mmol of $NaBH_4$ (Fig. 4b), in non-polar solvents such as hexane, dimethyl sulfide, acetonitrile and dichloromethane, the reaction process was very slow, and the low efficiency. The solvent is polar water used because of biological and environmental relationships. According to Fig. 4c, the effect of time on the reduction of para-nitrophenol in the solvent of water and $NaBH_4$ (4.0 mmol) was investigated. The reaction had the highest efficiency in 2 min, but the reaction efficiency did not change much after 2 min (Fig. 4c). The effect of different amounts on the model reaction is investigated in Fig. 4d. Increasing the amount of catalyst up to 20 mg increases the reaction efficiency. Also, the studied catalyst has active sites and a large contact surface.

The reaction kinetics of the model were investigated in the presence of the UiO-66/btb/MgO catalyst. The reaction rate has a direct relationship with the increase in temperature. Because in the solution, the collision speed of substances increases. Fig. 5 shows the activation energy of the model reaction by the UiO-66/btb/MgO catalyst.

The effect of temperature on the reaction kinetics of 4-NP with the catalyst was investigated in the temperature range of 10°C–50°C, as shown in Fig. 5. Using the analysis of the plot of $\ln k$ vs. $1/T$, the estimated activation energy for the degradation of 4-nitrophenol by UiO-66/btb/MgO is approximately 61.32 kJ/mol.

The effect of pH changes on para-nitrophenol compounds was investigated by keeping other parameters constant. Degradation of para-nitrophenol was done about pH = 9.2. The pH of the aqueous solution was maintained by adding the necessary amounts 0.1 N of NaOH and HCl.

In Fig. 6, it is pretty evident that the degradation of para-nitrophenol at pH less than 9 is fast enough, and it is difficult to control it in different time intervals. Sodium, tetrahydroborate aqueous solution is stable in an alkaline environment, and the chance of deprotonation of the OH-4-NP part decreases at pH > 10.

UV spectroscopy was used to evaluate the kinetics of the reaction, and the conversion reaction of 4-NP to 4-AP was performed with 20 mg of UiO-66/btb/MgO catalyst and the reducing agent $NaBH_4$. The maximum intensity of the 4-NP peak is 400 nm, and the maximum intensity of the 4-AP peak is 300 nm. According to Fig. 7, the model's reaction in 120 s increases the peak of 4-AP and decreases the peak of 4-NP. An industrial wastewater sample was prepared and the catalytic efficiency of UiO-66/btb/MgO was investigated using the reduction of 4-NP to 4-AP in the presence of $NaBH_4$. Using UV spectroscopy, the reaction time expansion method was evaluated for the reduction of 4-NP to 4-AP. As seen in Fig. 6c, the 4-NP solution shows a correct absorption peak at 300 nm, which dramatically shifts color to 400 nm.

The reduction process of various nitroaromatic compounds is expressed by considering the optimized conditions (Table 1). The results presented in Table 1 show that the electron-donating or electron-killing substitutions cannot have a significant impact on the reaction time or the yield obtained (Table 1). To further investigate the efficiency of catalysts, various tests were performed, and the obtained information is shown in the Table 1.

To further investigate the effect of UiO-66/btb/MgO catalyst, it was compared with different catalysts. As shown in Table 2, the performance of the UiO-66/btb/MgO catalyst is more efficient than the other mentioned catalysts during the reaction time of 4-NP to 4-AP conversion.

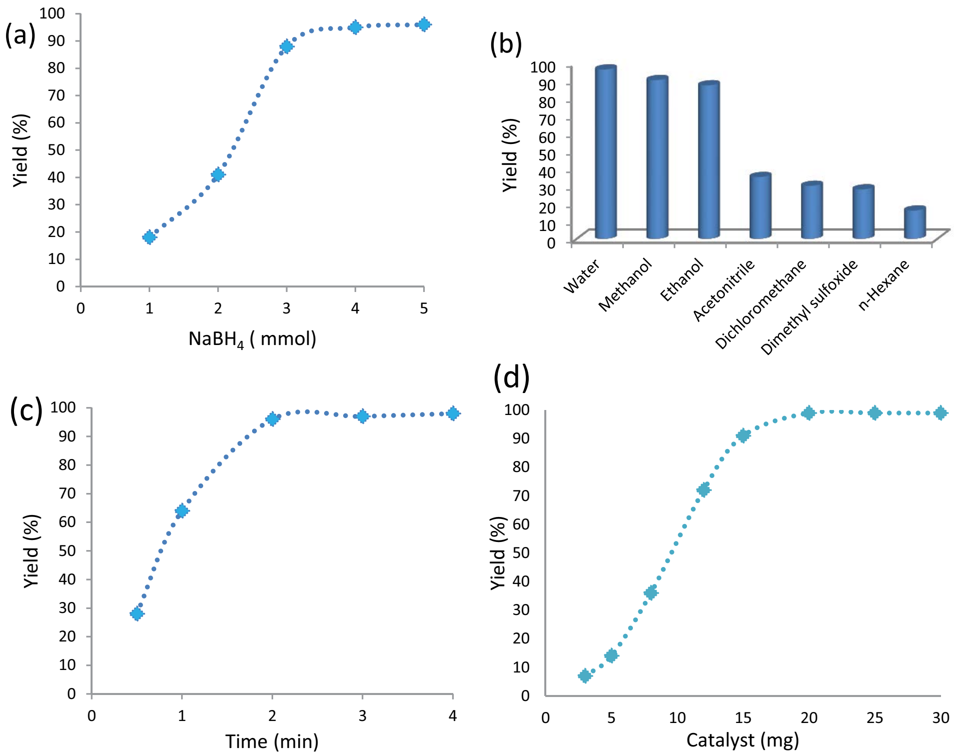


Fig. 4. Reduction of para-nitrophenol in the presence of (a) the different amounts of $NaBH_4$, (b) the different solvents, (c) the effect of time, and (d) the effect of the amount of catalyst.

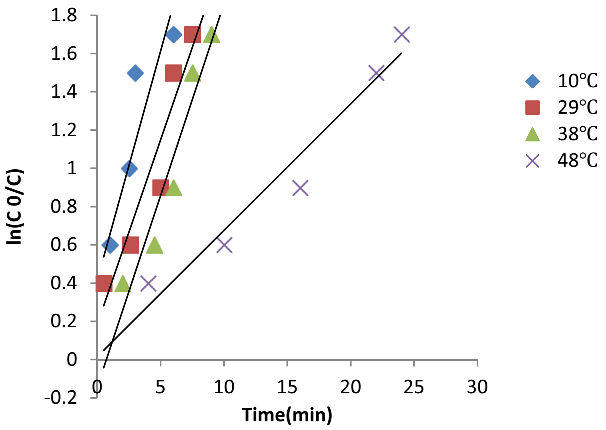


Fig. 5. Kinetic studies for the catalytic reduction of 4-NP by nano-UiO-66/btb/MgO.

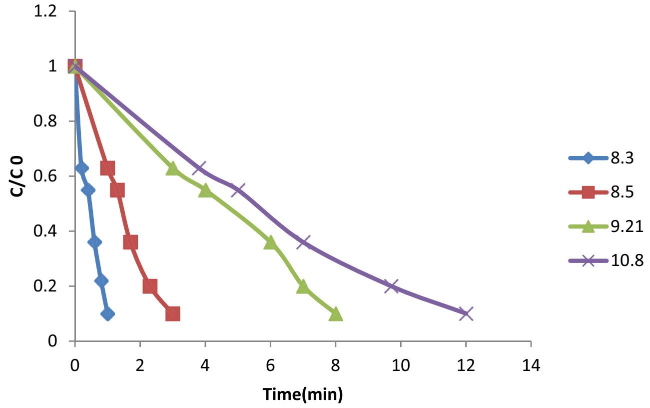


Fig. 6. Effect of pH on 4-NP using a catalyst.

After performing the catalyst recycling reaction and its reuse, a unique feature in green chemistry is expressed. The reuse of UiO-66/btb/MgO catalyst under optimal conditions was investigated. The heterogeneous UiO-66/btb/MgO catalyst was washed and dried by a separate reaction liquid filtrate, and a slight drop in the reaction efficiency was observed after each use. As shown in Fig. 8, UiO-66/btb/MgO was reused ten times. This decrease in the catalyst's performance is probably due to the destruction of its outer surface. Fig. 8 shows that the catalyst has been reused for ten consecutive times. The heterogeneous properties of UiO-66/btb/MgO NPs significantly improved industrial wastewater. The activity of the recycled catalyst was analyzed ten times and showed a significant decrease in catalytic activity. After the reaction, the catalyst was separated using a filtration process, shown in Fig. 7, and then washed with methanol and dried using a pump.

In industrial wastewater, after ten times of use, 87% of the catalyst was received, which shows a 7% loss of performance compared to the corresponding fresh catalyst equal to 94%.

The obtained results showed that the nanocatalyst has high efficiency in removing organic pollutants in the presence of $NaBH_4$ as a reducing agent. Due; to the existence of fundamental problems in physical and chemical

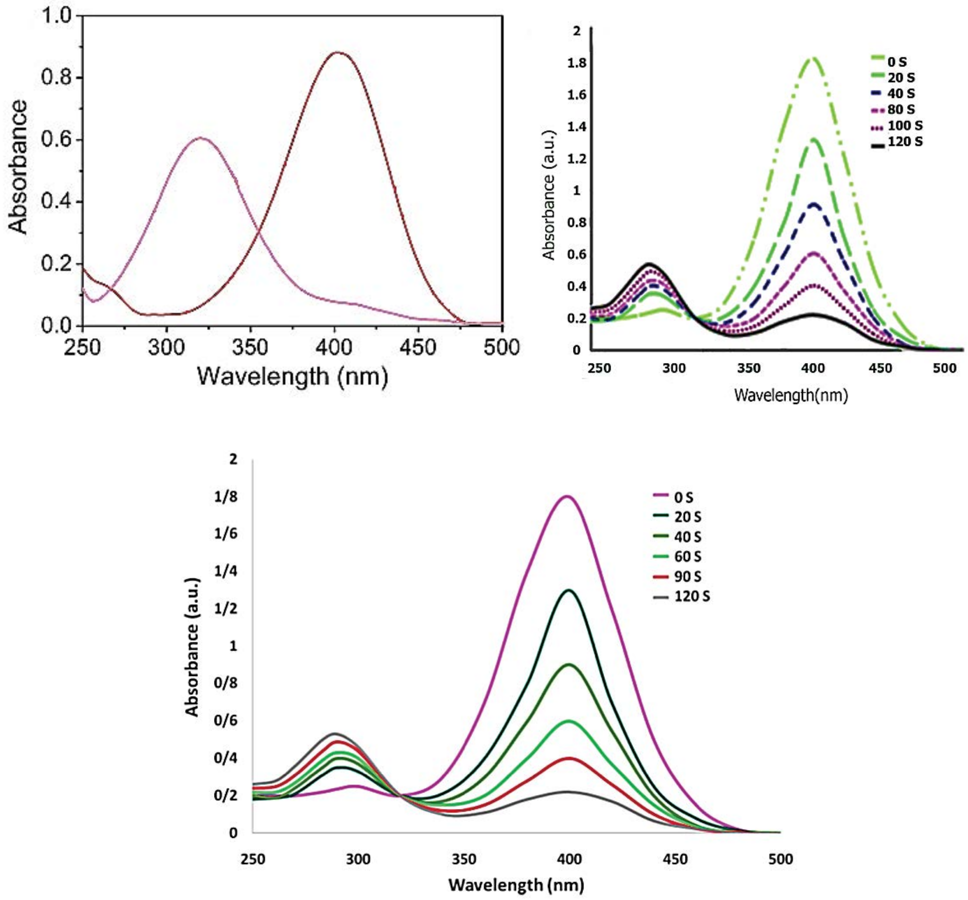
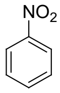
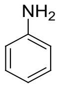
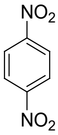
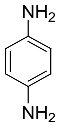
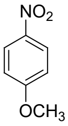
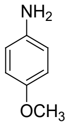
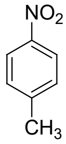
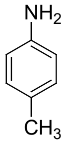
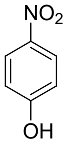
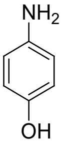
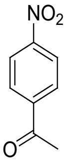
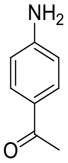
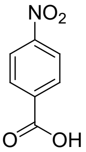
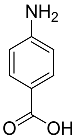


Fig. 7. UV-Vis - (a) 4-NP spectra before and after adding $NaBH_4$ solution. (b) Sequential reduction of 4-NP to 4-AP, and (c) an industrial wastewater sample.

Table 1
Reduction of various aromatic nitro compounds in the presence of UiO-66/btb/MgO NPs

Entry	Reactant	Product	Yield (%)	Mp (°C)
1			89	Liquid
2			96	140–142 [41]
3			94	60–63 [41]
4			93	36–39 [41]
5			96	180–183 [41]
6			93	103–105 [41]
7			95	180–182 [41]

methods, the use of simple, low-cost, and environmentally friendly methods is of particular importance.

This is done at different temperatures to verify the thermal stability of UiO-66/btb/MgO, as shown in Fig. 9. There

Table 2
Comparison of the catalytic activity of the synthesized nanoparticles with other reported catalysts in the reduction of 4-nitrophenol

Entry	Catalyst	Time (min)	Yield (%)
1	3DCoOs	6	100 [42]
2	CuFeCN	4	100 [43]
3	UiO-66/btb/Pd	8	99 [41]
4	UiO-66-NH_2	15	90
5	UiO-66/btb/MgO	2	96

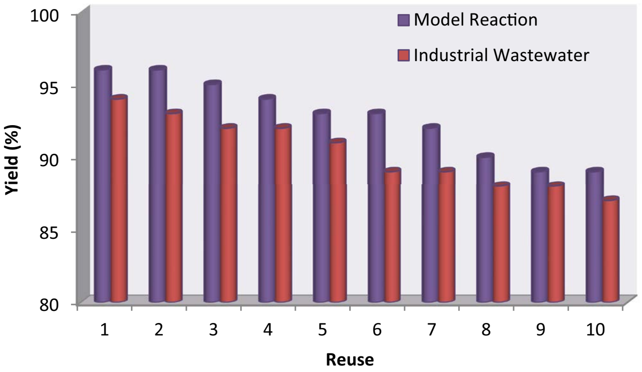


Fig. 8. Catalyst reusability for reducing p-nitrophenol.

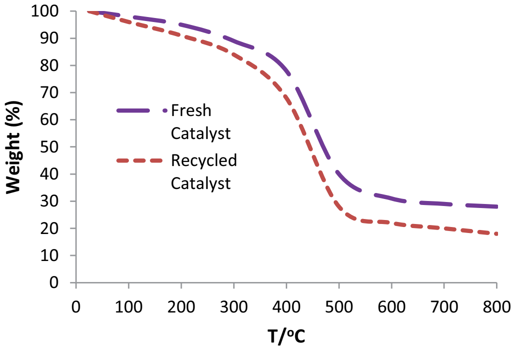


Fig. 9. Thermal gravimetric graph of UiO-66/btb/MgO.

are two stages of weight loss. Regarding the loss of small molecules such as physically adsorbed water, In the first stage, between 30°C and 230°C, about 5% weight loss is observed. The second stage's temperature ranges from 230°C to 400°C, and the weight is reduced by about 72%, which may be due to the derivatives of the organic group.

A summary of the possible reaction mechanism and the activation of hydrides on the surface of the catalyst. Scheme II depicts how they were transferred to the nitro group, in the presence of the reducing agent $NaBH_4$, the nitrogen group is broken in the first step of the B–H bond and their absorption on the surface of the metal catalyst to form a metal hydride complex. Nitrophenol is adsorbed on the metal hydride complex surface. As the development is reversible, absorption is accomplished by desorption. Thermodynamic equilibrium on the surface of the hydride complex allows the transfer of H_2 from the surface of the hydride complex to 4-NP, followed by the formation of 4-nitrophenolate (4-NP) ion [33].

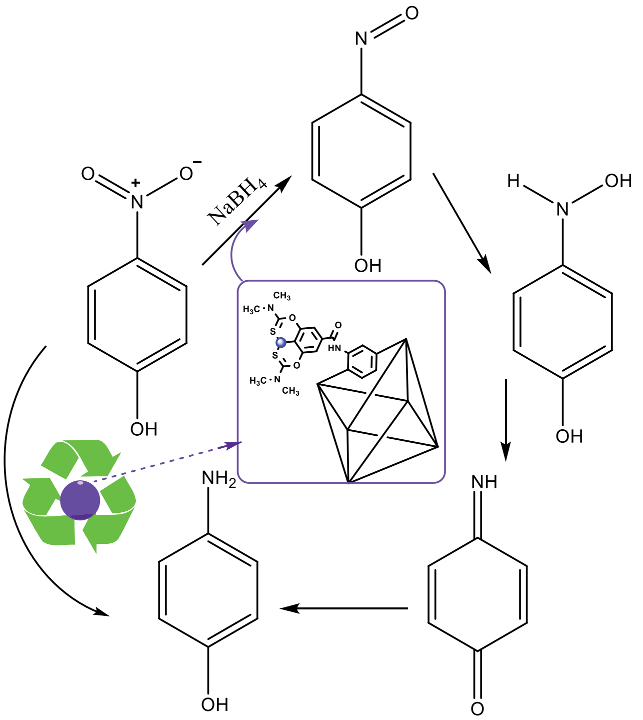


Fig. 10. Logical process for reducing p-nitrophenol.

4. Conclusion

In this study, the UiO-66/btb/MgO catalyst is considered as a metal–organic framework that has advantages such as porosity and high surface-to-volume ratio. Due to the increase of MgO based on btb to UiO-66/btb/MgO substrate, its catalytic power increases. btb/MgO has maintained its aggregation and dispersion on the UiO-66-NH_2 surface. By TGA analysis, the catalyst had good thermal stability. This reaction had the best efficiency in the presence of electron–donating derivatives, water solvent, and reducing agent $NaBH_4$. Also, it has shown an excellent catalytic activity in reducing aromatic nitro compounds in the model reaction and industrial wastewater. The UiO-66/btb/MgO heterogeneous catalyst is easy to recycle and the catalytic activity has not decreased significantly, and has maintained its structure after ten times of recycling. The results and findings show that shortly, the processes based on UiO-66/btb/MgO catalyst will be expanded to treat polluted water, remove many nitroaromatic pollutants, and degrade various organic pollutants.

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