First highly effective non-catalytic nitrobenzene reduction in UV/dithionite system with aniline production – Advanced reduction process (ARP) approach

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ABSTRACT

Advanced reduction processes (ARPs) are currently intensively investigated as an alternative to Advanced Oxidation Processes (AOPs). The study presents efficient reduction of nitrobenzene under non-catalytic conditions through reaction with free radicals having reductive potential. Effective conversion of nitrobenzene in a model wastewater solution, was obtained for sodium dithionite (SDT)/ dithionite (DTN). The developed process provide a nitrobenzene reduction efficiency of > 99.9 % within 10 min under neutral conditions, ambient temperature, with a molar ratio of reductant to pollutant (r_{red}) of 3. Additional UV radiation lowered by 10 % the dose of DTN. Interestingly, addition of titanium dioxide (TiO_2) as a photocatalyst did not show a positive effect. An extremely significant conclusion of this study is the observed excellent resistance of the reaction system to the negative influence of inorganic anions, with a reduction in efficiency in the following order: CO_3^{2-} (22%) $> NO_3^-$ (6%) $> SO_4^{2-}$ (2%) $> Cl^-$ (2%) $> NO_2^-$ (< 1%) $> S_2O_3^{2-}$ (< 1%) $> N_3^-$ ($\langle 1$%) and dissolved organic matter (DOM) (< 13%). The study showed that the process works effectively across the pH range from 3 to 12. Studies on the reaction mechanism revealed that sulfur dioxide anion radical ($SO_2^{\bullet-}$)) was responsible for the main reduction effect. The main product of nitrobenzene reduction was aniline (>99.9 %). The total cost of purification process was USD $0.77/m^3$. The high efficiency, short process time, low cost, and lack of need for complicated equipment make this developed process potentially widely applicable in the industry. The developed method for the reduction of nitrobenzene to aniline is the first non-catalytic method with such high efficiency and without the formation of intermediate reaction products.

1. Introduction

The wide use of aniline in industry is related to the production of urethane monomers used for polymer production (accounting for over 85% of the world's aniline production). Other applications include rubber production (9%), herbicides (2%), dyes (2%), and others [1]. According to the report "Aniline Market: Global Industry Trends, Share, Size, Growth, Opportunity and Forecast 2023-2028″ [2], the global production of aniline reached 9.4 million tons in 2022. Every ton of produced aniline is associated with the formation of pollutants in the

form of volatile organic compounds (VOCs) and post-process wastewater containing a mixture of aniline and nitrobenzene.

Nitrobenzene ($C_6H_5NO_2$) is the main raw material for the production of aniline ($C_6H_5NH_2$). The global production of nitrobenzene is still increasing with the growing demand for aniline, which is produced over 90% from nitrobenzene by catalytic hydrogenation [3].

Nitrobenzene present in industrial wastewater is a serious pollution, requiring advanced treatment. There are many types of wastewater containing nitrobenzene, for example: municipal wastewater [4], refinery industrial effluents [5], drinking water [6], printing industry

wastewater [7].

Currently known methods of wastewater treatment containing nitrobenzene include zero-valent iron-activated persulfate [8], electrochemical [9], ozonation [10], microbial [11], etc. In the case of AOPs, reactive oxygen species (ROSs) are responsible for the degradation of chemical compounds, which in a chemical reaction with the pollutant lead to the degradation of the compound through oxidation. Among the most common ROSs in AOPs are hydroxyl radicals, which have one of the highest oxidation potentials among ROSs. However, the main disadvantage of the above mentioned processes is the formation of a large number of intermediate products. Their degradation is not always fully possible.

On the other hand, ARPs - a relatively new group of processes - are based on reductive radicals (RRs), and their degradation mechanism involves the reduction of an impurity as a result of reaction with a reductive radical [12,13]. RRs with the highest reduction potential include solvated electrons and hydrogen radicals. Thus, ARPs complement the well-researched Advanced Oxidation Processes (AOPs) and allow for the degradation of substances resistant to oxidation. Based on this classification, the reduction reaction using DTN, both under aqueous conditions and with the application of UV radiation, belongs to ARPs.

The main purpose of this paper was to develop a fast and efficient method for the production and recovery of aniline from nitrobenzene effluents. The developed process can be applied both to the production of aniline from nitrobenzene as well as for treatment of wastewater containing nitrobenzene (including aniline recovery) in the environment of organic matter and anions, which are commonly present in the real wastewater matrix. The method's resistance to the presence of ions and organic matter makes the process applicable to any type of wastewater, even highly saline wastewater and wastewater with a high organic matter load. In our work, the reaction leads unidirectionally to aniline as a main product. Focused recovery of aniline from effluents is possible making overall process sustainable. Other studies have also shown that aniline can be effectively extracted from water using nitrobenzene, which complements the reduction process of nitrobenzene to aniline [14].

2. Materials and methods

2.1. Materials

For the preparation of nitrobenzene solutions, demineralized water (Direct-Q® Water Purification System – Merck Millipore) and nitrobenzene (analytical grade according to ACS, producer POCH S.A., Poland) were used. Acetone (analytical grade according to ACS, POCH S. A., Poland) was used to stabilize the sample after sampling from the reaction system, and DTN (analytical grade, Merck, Germany) was used as a reducer. Aniline (analytical grade according to ACS, POCH S.A., Poland) was used as a reference in the research. Sodium hydroxide solution (analytical grade according to ACS, POCH S.A., Poland) and sulfuric acid (VI) solution (concentration of 99%, POCH S.A., Poland) in demineralized water were used to adjust the pH.

In the catalytic process, titanium dioxide (IV) P25 type with particle size of 10–40 nm (purity of 100 %, Evonik, Germany) was used.

To investigate the influence of ions on the reduction of nitrobenzene, sodium chloride, iron (III) chloride, sodium sulfate, sodium nitrate, sodium carbonate, sodium nitrite, sodium azide, and sodium thiosulfate (purity > 98 %, Merck, Germany) were used.

Humic acid sodium salt (purity of 97 %, Angene, China) was selected to study the effect of dissolved organic matter on nitrobenzene reduction.

Acetonitrile (purity > 99.9 % for HPLC, Fischer Chemical, USA) was used as an eluent component in high-performance liquid chromatography (HPLC) analysis. Prior to chromatographic analysis, all samples were filtered through a syringe filter (hydrophilic PTFE, Alchem,

Poland) with a pore size of 0.45 μm.

2.2. Experimental procedures

2.2.1. Preparation of nitrobenzene solution

A 7.5 L nitrobenzene solution with a concentration of 150 ppm was prepared in demineralized water. The appropriate amount of nitrobenzene was weighed on an analytical balance (model: AS.310.R2, RADWAG, accuracy of 0.1 mg). The mixture was then vigorously stirred using a magnetic stirrer (set model: 06 MSH PRO T, Chemland, Stargard, Poland) in a tightly closed container for 1 h until the nitrobenzene was completely dissolved in water.

2.2.2. Oxygen content analysis

The oxygen content was measured using a conductometer (model CCO-401, Elmetron) equipped with an oxygen sensor (model COG-1, Elmetron). The analysis was based on a two-point calibration: 100 % oxygen content for air and 0 % oxygen content in supersaturated sodium dithionite solution.

2.2.3. Preparation of DTN solution

The mass of DTN corresponding to a given molar ratio (reducer: impurity) was weighed on an analytical balance (model: AS.310.R2, RADWAG) and dissolved in demineralized water. The DTN solution was prepared directly before adding the reducer solution to the reactor.

2.2.4. Post-processing sample stabilization

To stop the nitrobenzene reduction reaction by DTN, 5-mL samples taken from the reduction system were immediately mixed in 10 mL vials with 3 mL of pure acetone followed by 10 s manual shaking.

2.2.5. Process control by HPLC method

Retention time values of compounds in the studied chromatographic system were determined using standard solutions. A 5-point calibration curve (external standard method) was prepared for quantitative determinations. Separation was carried out in a reversed-phase system (RP-HPLC) with ultraviolet visible spectrophotometer (UV–VIS) detection. The study used a model LaChrom chromatograph (MERCK-HITACHI, Germany), consisting of a model D-7000 interface, a model L-7100 pump, a Rheodyne model 7125 injector (IDEX Health & Science, LLC, USA), an Agilent chromatographic column (C-18, 3.5 μm, 4.6 × 150 mm), and a model L-7420 UV–VIS detector. The conditions for analysis of post-processed samples were: eluent 50 % water/50 % acetonitrile (flowrate 1 mL/min, temperature 20 °C), monitored wavelength was 270 nm. Aniline and nitrobenzene retention time was 2.6 and 5.1 min. respectively. The limit of detection (defined as signal to noise level equal to 3; LOD) was 0.1 ppm.

2.2.6. Reduction of nitrobenzene

The reduction of nitrobenzene was carried out in two interconnected reactors. Reactor number 1 was used for sample collection, addition of the reducing agent, and cooling of the reduced mixture – as shown in Fig. 1. Reactor number 2 contained a UV mercury lamp (type UVQ 250Z, 250 W, UV-Technik, Germany), which was turned on or off depending on whether the process was conducted with or without UV. The total volume of the reduced mixture was 7.5 L, and the initial concentration of nitrobenzene at the beginning of each process was 150 ppm.

The temperature in the reaction system was maintained at 20 °C, and the system was hermetically sealed throughout the process. The mixture was circulated between the reactors using a model 505L peristaltic pump (Watson Marlow, UK) with a speed of 220 RPM (flow rate of 1.3 L/min).

2.2.7. Study of the influence of TiO₂ on the activation of dithionite

In order to prepare a catalyst mixture in the form of a TiO_2 suspension with a tested nitrobenzene solution, 0.75 g of titanium (IV) oxide
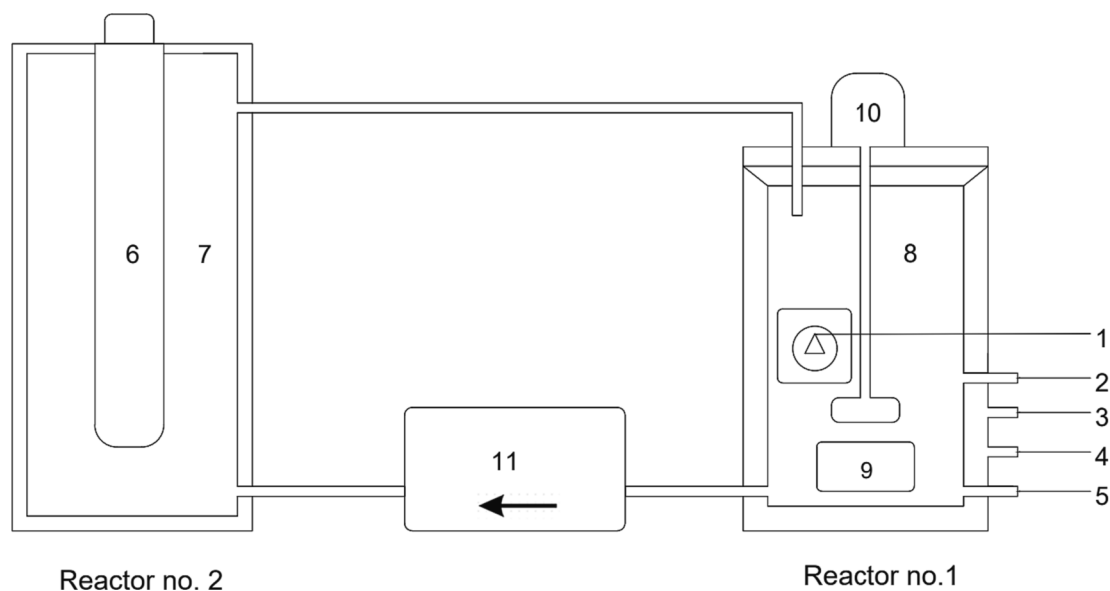
Fig. 1. Experimental setup, 1 – mixer speed regulator, 2 – reductant input, 3 – cooling water output, 4-cooling water input, 5 – sampling place, 6 - UV lamp, 7 – reactor no. 2, 8 – reactor no. 1, 9 – thermometer, 10 – mixer, 11- peristaltic pump.

was mixed with 7.5 L of previously prepared nitrobenzene solution (150 ppm). The whole mixture was stirred until completely homogenized, and then transferred to the reactor system. Prior to adding the catalyst and after preparing the suspension, process samples were collected to evaluate the adsorption of nitrobenzene.

2.2.8. Studies of the effect of anions on the reduction of nitrobenzene

In order to investigate the effect of anions on the reduction of nitrobenzene, the following water-soluble salts were selected: sodium chloride, sodium sulfate, sodium nitrate, sodium carbonate, sodium nitrite, sodium azide, and sodium thiosulfate. A mass corresponding to a mole ratio (nitrobenzene: salt) of 1:30 of each salt was weighed on an analytical balance and added to 7.5 L of nitrobenzene solution. The mixture was then stirred for approximately 30 min, until the salt was completely dissolved in water.

2.2.9. Studies of the effect of organic matter on the reduction of nitrobenzene

To study the effect of organic matter on nitrobenzene reduction, humic acid sodium salt (HASS) was selected. Nitrobenzene: HASS molar ratios of 1:1, 1:5 and 1:30 were selected for the study. Test mixtures were prepared by dissolving a selected amount of HASS in 7.5 L of a 150 ppm nitrobenzene solution on a magnetic stirrer. After 15 min of stirring, sodium dithionite (SDT) was added to the solutions in a molar ratio of nitrobenzene: SDT (1:3). Samples for testing were collected after 15 min of the process, filtered through a syringe filter and analyzed by HPLC.

2.2.10. Radicals scavenging tests

The identification of radicals formed during the decomposition of sodium dithionite was carried out by adding a water-soluble salt, FeCl₃. To this end, a 1 L of 150 ppm solution of nitrobenzene was prepared, into which iron (III) chloride was dissolved in a mole ratio of (nitrobenzene: salt) of 1:30. The mixture was stirred until the salt was completely dissolved. Then, the mass of sodium dithionite corresponding to the mole ratio of (nitrobenzene: dithionite) of 1:3 was weighed and added to the previously prepared solution. Samples for analysis were taken before adding the dithionite and 60 and 120 min after adding the reducing agent to the solution.

2.2.11. Identification of degradation byproducts

The chromatographic analysis was performed using a gas chromatograph coupled with a mass spectrometer (GC–MS, model QP2010SE, Shimadzu, Japan). Samples for analysis were prepared using the dispersive liquid–liquid microextraction (DLLME) technique. The separation conditions were as follows: a capillary column RTX®-100-DHA (100 m x 0.25 mm ID x 0.5 μm df), carrier gas was hydrogen at 1 mL/min, injection port temperature was 280 °C. Samples were separated under temperature programming conditions at initial temperature of 35 °C for 5 min, followed by a temperature ramp at 14.3 °C/min, up to 250 °C, followed by isothermal separation at 250 °C for 20 min. The mass spectrometer ion source temperature was 200 °C, interface temperature was 250 °C. MS operated at mass scan range from 34 m/z to 350 m/z. A detailed description of the methodology is provided in a previous work [15].

3. Results and discussion

3.1. Studies on the effectiveness of DTN reduction of nitrobenzene

Dithionites constitute a very interesting group of compounds with a high reduction potential. The reduction radicals generated in the process of DTN decomposition and the reduction reactions involving these radicals belong to the group of Advanced reduction processes (ARPs). The decomposition of DTN in water to form sulfur dioxide radical anions with reducing properties $(SO_2^{\bullet-})$ is shown in reaction (1). Under aqueous conditions, one mole of DTN produces two moles of $(SO_2^{\bullet-})$ with a SHE reduction potential of −0.66 V [16].

$$S_2O_4^{2-} \leftrightarrow 2SO_2^{\bullet-} \quad (k = 1.4 \bullet 10^9 M^{-1}s^{-1}) \tag{1}$$
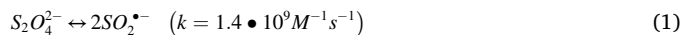
In reaction (1), the main driving force is the consumption of the reaction product $(SO_2^{\bullet-})$ due to the reduction reaction. The decrease in the concentration of the reaction product in the solution shifts the equilibrium of the reaction to the right, in accordance with the Le Châtelier-Braun principle. The bond between sulfur atoms in DTN is very unstable and susceptible to breaking, as shown in Fig. 2.

The instability of the bond between sulfur atoms is mainly due to the bond length and molecular structure. The bond between sulfur atoms is the longest (2.389 Å) in the entire DTN molecule, which is why it is the least stable [17]. The bond lengths in DTN are shown in Fig. 3a.
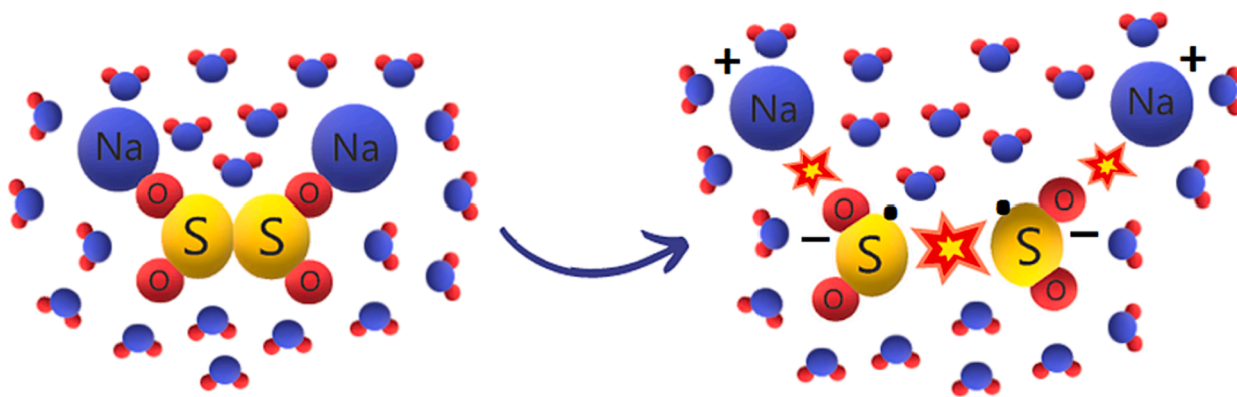
Fig. 2. DTN hydrolysis with formation of reducing radicals ($SO_2^{\bullet-}$).

Therefore, DTN belongs to compounds that are ideal for generating reducing conditions in a process and for reducing oxidation-resistant compounds that cannot participate in AOPs.

However, the structure of sodium dithionite is not planar due to the rotation of the -SO₂ groups about the S-S bond axis resulting from the molecular structure. The bonds between sulfur and oxygen are graphically represented as single and double bonds, but according to crystallographic studies, both of these bonds (S-O) can be classified as "one and a half bonds", which is evident from the bond lengths shown in Fig. 3 [18]. Therefore, the difference in the lengths of both bonds results solely from the spatial shape of the DTN molecule – Fig. 3b, rather than from a division of the bonds into single or double bonds.

3.1.1. The effect of dissolved oxygen in the treated medium on the reduction conditions

In each of the investigated solutions under normal conditions at a temperature of 20 °C, there is approximately 1.3×10^{-3} mol/L of dissolved oxygen [19], the content of which drastically decreases at the beginning of the process due to its reaction with ($SO_2^{\bullet-}$) – reaction (2) [20].

$$SO_2^{\bullet-} + O_2 \rightarrow SO_2 + O_2^{\bullet-} \tag{2}$$
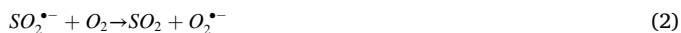
The graph showing the dependence of concentration of dissolved oxygen in water after the addition of 1 g DTN per 1 L of water is shown in Fig. 4.

The higher the oxygen concentration in the solution, the more reducing agent will be consumed in the process of removing oxygen. However, these are not significant amounts, equivalent to 1.3 mM of the reducing agent. Therefore, various methods of deoxygenating the reduced mixture are worth considering. Such methods include sonication, purging with inert gas, or intense heating [21,22]. For practical reasons, deoxygenation of wastewater undergoing treatment in quantities of several tens of m³/h is often not feasible. For this reason, the research in this study was conducted without deoxygenating the water.

During the experiment, it was noted that when DTN is added to the mixture, the oxygen concentration rapidly decreases in 1st minute of the process, the oxygen concentration was measured using an oxygen-
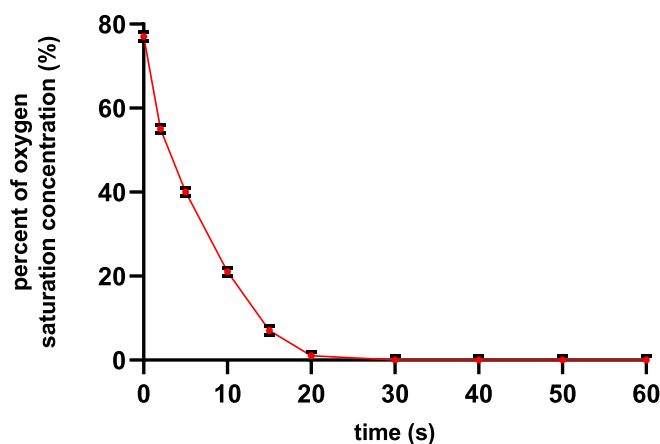

Fig. 4. Oxygen concentration change during the process after adding 1 g of DTN to 1L of water at 20 °C with stirring. Oxygen initial concentration: 0,0013 mol/L.

selective electrode. After one minute of treatment the oxygen content was below 1 % of the maximum solubility (saturation) under normal conditions. The complete deoxygenation of the mixture at the beginning of the reduction process is beneficial to the process, as it intensifies the reducing conditions of the process.

3.1.2. Studies on the activation of dithionite by UV radiation

The generation of radicals from various substances using UV radiation is widely known and described in the literature [23–26]. In the case of AOPs, a great improvement in the efficiency of generation of oxidative radicals under UV radiation conditions has been demonstrated with catalysts such as titanium (IV) dioxide [27,28]. The topic of generation of reducing radicals under UV radiation conditions without catalysts is definitely less explored in the case of ARPs than AOPs. The most common source of UV radiation is the sun, but in terms of energy units, UV radiation accounts for only 7 % [29]. Increasing the proportion of UV radiation in the unit of delivered radiation energy is possible by using an artificial UV radiation source, such as a UV lamp.

The mercury lamp used in the study generates radiation across the entire UV spectrum, but as presented in Fig. S1, the highest proportion consists of UV type C radiation, which is radiation with the shortest wavelength and highest energy.

In the case of DTN, as shown in the study [30], the greatest reduction effect of chlorates by UV radiation was achieved for wavelengths between 280 and 320 nm, which corresponds to the UV type B radiation range. However, the effectiveness of other types of UV radiation (type A and C) should not be disregarded, as their effectiveness has also been demonstrated (DTN/UV-A chlorate reduction efficiency is about 25 %
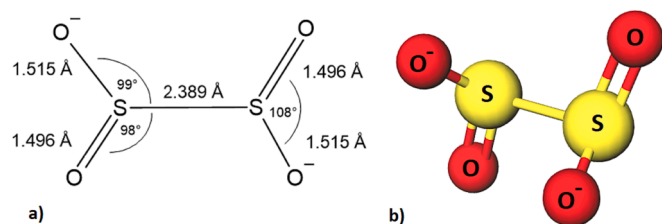

Fig. 3. Molecular structure of DTN a) DTN bonds lengths [17], b) three-dimensional DTN molecule visualization using Molview.org software.

lower than DTN/UV-B, and DTN/UV-C chlorate reduction efficiency is about 35 % lower than DTN/UV-B). In the process, it is therefore possible to achieve effective degradation with the application of lamps of other types, but it is crucial that the highest possible percentage of radiation should be generated in the B-type UV range.

Under the influence of the energy of radiation from a mercury lamp in a solution, reactions occur that lead to the formation of radicals with a higher reduction potential than radicals $(SO_2^{\bullet-})$, for example, hydrogen radicals $(H^{\bullet})$ and hydrated electrons $(e_{aq.}^-)$. For the reduction of nitrobenzene to aniline, radicals such as $H^{\bullet}$ or e_{aq}^- with a reduction potential > 1.0 [V] are not required, and the sufficient efficiency is ensured by radicals $(SO_2^{\bullet-})$ with a SHE reduction potential of -0.66 V [25]. The effectiveness of $(SO_2^{\bullet-})$ radicals results from the amount in which they are formed during the process, and that their generation requires significantly lower energy than the generation of hydrated electrons or hydrogen radicals from dithionite.

The UV radiation is advantageous in the reduction process, especially when most of the DTN has undergone hydrolysis, and the number of generated radicals $(SO_2^{\bullet-})$ drastically decreases. It is precisely then that UV radiation should allow for the generation of other types of reducing radicals $(S_2O_3^{\bullet-}, SO_3^{\bullet-}, H^{\bullet})$ from the remaining products of DTN hydrolysis in the solution. Examples of such products may include the formation of hydrogen sulfate and thiosulfate ions resulting from reaction (3), which undergo further phototransformation to yield reducing radicals in reactions (4) and (5). Reaction (4) leads to the formation of hydrated electrons, which are radical species with one of the highest known reducing potential value of -2.9 [V] [31], while in the case of reaction (5), the reaction product is hydrogen radicals with a similarly high reducing potential of -2.1 [V] [32]. Some DTN will also remain in an undissociated form, which, when subjected to ultraviolet radiation, leads to the formation of dithionite radicals and hydrated electrons in reaction (6) [33].

$$2S_2O_4^{2-} + H_2O \longrightarrow 2HSO_3^- + S_2O_3^{2-} \tag{3}$$

$$S_2O_3^{2-} + h\nu \longrightarrow e_{aq.}^- + S_2O_3^{\bullet-} \tag{4}$$

$$HSO_3^- + h\nu \longrightarrow SO_3^{\bullet-} + H^{\bullet} \tag{5}$$

$$S_2O_4^{2-} + UV \longrightarrow S_2O_4^{\bullet-} + e_{aq.}^- \tag{6}$$

The process of radical formation in the ARP/UV process is therefore a very complex issue, as the formation of radicals is dependent on many process parameters that constantly change over time.

The study on the reduction of nitrobenzene in the DTN system with the participation of a mercury UV lamp, whose radiation activated dithionite to form a radical species with a high reducing potential, proved that UV radiation increases the efficiency of nitrobenzene degradation at the same mole ration of pollutant to reductant. The study examined the mole ratios of 1:1, 1:2, 1:2.5, and 1:3, and the results are presented in Table 1.

In each of the cases, the process conducted with the UV lamp turned on proved to be more efficient than the analogous process carried out without the UV lamp. Therefore, the use of UV radiation in reduction

processes employing DTN is effective and allows for an increase in the overall reduction effect of organic pollutants when dithionites are used. The use of UV radiation also results in a reduction in the consumption of the reducing agent. All aspects of the use of UV radiation in the reduction process of nitrobenzene by dithionites are therefore positive and worth extending to other DTN/UV/ARP processes.

The studies on the optimization of the DTN dose showed a linear correlation between the maximum degradation of nitrobenzene after 60 min of the process and the molar ratio of pollutant to reducing agent, as presented in Fig. 5.

Based on the determined trend lines presented in Fig. 5, the following equations were derived to predict the degradation effectiveness of nitrobenzene by DTN at a temperature of 20 °C depending on the conditions: MIX – mixing, MIX + UV – mixing under UV radiation.

$$SD : \frac{C}{C_o} = -0.3383 \bullet r_{red} + 0.9893 \left(R^2 = 0.9946\right) \tag{7}$$

$$SD + UV : \frac{C}{C_o} = -0.3329 \bullet r_{red} + 0.8891 \left(R^2 = 0.9979\right) \tag{8}$$

Where: C – concentration of nitrobenzene after 60 min of the process:
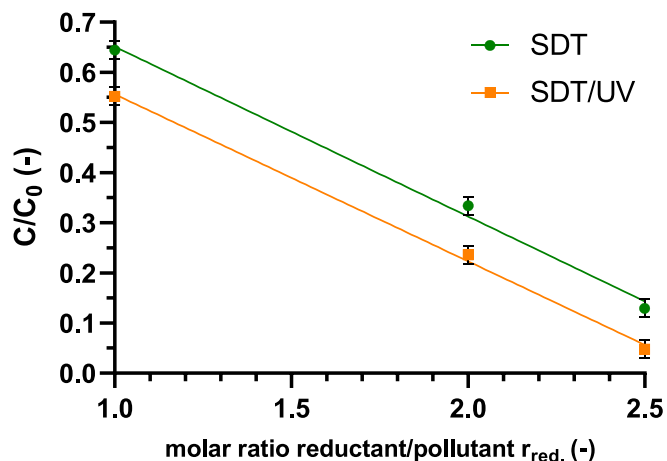
C_0 – initial nitrobenzene concentration;

r_{red} – the number of moles of sodium dithionite per mole (molar ratio) of nitrobenzene in initial solution.

Based on Eqs. (7) and (8), the optimal values of r_{red} for 100 % degradation of nitrobenzene were calculated, and then the degradation effect was examined for the predicted mole ratios. The results are presented in Table S1.

The study revealed a high agreement between the predicted and experimental results of nitrobenzene reduction. Therefore, determining such linear relationships for the industrial scale process can be applied for online optimization of wastewater treatment process under ARP conditions. In the case of treatment of wastewater with a simple matrix, the current concentration of nitrobenzene in the influent stream to the reactor can be monitored online using a flow UV spectrophotometric analyzer.

Although the process was carried out for 60 min, the data presented in Fig. 6 reveal that the process occurs most rapidly during the first stage of degradation, i.e., between 1 and 5 min (the steepest slope of the degradation curve). Then, the process gradually slows down due to the decreasing concentration of nitrobenzene and the reductant in the reactor. With the duration of the process, the probability of encountering radicals $(SO_2^{\bullet-})$ formed in reaction (1) with nitrobenzene molecules decreases, which reduces the rate of the reduction reaction.

During the stage between 5 and 60 min of the process, the dominant

Table 1
Nitrobenzene degradation after 60 min of the process at 20 °C.

Molar ratio (NB:SD)	Nitrobenzene degradation [%]	
	UV lamp on	UV lamp off
1:1	39.3	31.5
1:2	76.4	66.7
1:2.5	95.2	87.1
1:3	100.0	100.0
without DTN	0.0	0.0

NB – nitrobenzene, SD – sodium dithionite.

Fig. 5. Degradation of 150 ppm solution of nitrobenzene by SDT under different conditions during 60 min of treatment at 20 °C.
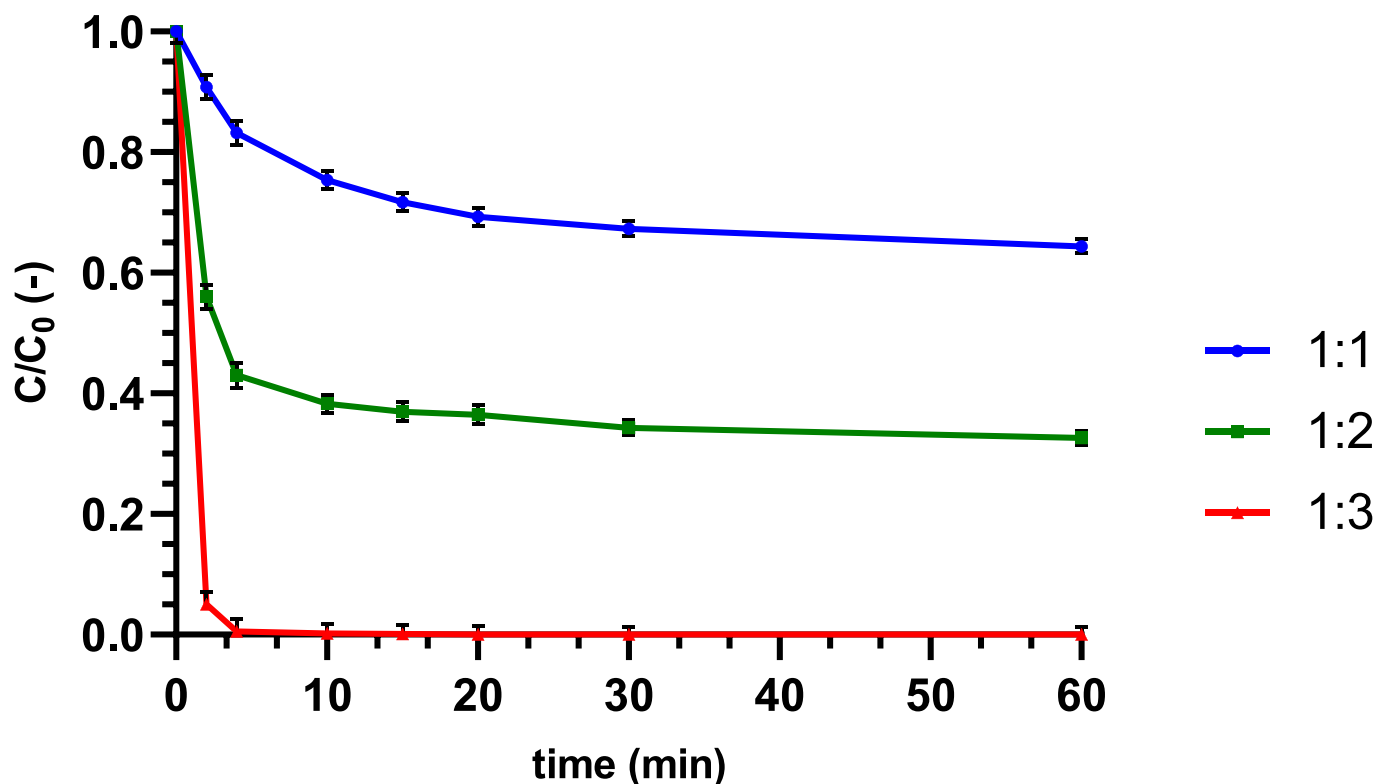
Fig. 6. Degradation of 150 ppm solution of nitrobenzene by SDT under neutral conditions for molar ratios NB:SDT 1:1, 1:2 and 1:3 at 20 °C.

reduction effect is taken over by the remaining unreacted DTN molecules, whose slow dissociation leads to the reduction of nitrobenzene molecules remaining in the solution at very low concentrations (below 1 ppm). In the case of the process carried out with UV radiation, this stage between 5 and 60 min is crucial for improving the effectiveness of nitrobenzene reduction. During this stage, the remaining ions in the solution are activated by UV radiation into reducing species with a higher reduction potential. As a result, reactive radicals (*e.g.,* $S_2O_4^{\bullet-}$, $H^{\bullet}$, $e_{aq.}^{-}$ and $S_2O_3^{\bullet-}$) can be formed, which can reduce nitrobenzene in a similar way to the ($SO_2^{-\bullet}$) radical.

The minimum process time required to achieve 99.5 % reduction of nitrobenzene is 5 min at a molar ratio of (NB: DTN) 1:3. The high rate of the reduction reaction and the resulting short time for near quantitative conversion make this process applicable to a wide range of technological processes and organic syntheses.

3.1.3. pH of a mixture

The pH level of treated wastewater is crucial for the effectiveness of the process. Determining the impact of different pH values of the aqueous phase on the effectiveness of nitrobenzene reduction reaction with dithionite is important for the practical application of the process, as the pH values of wastewater can vary significantly depending on its origin. The study was conducted at neutral pH (pH = 7), acidic pH (pH = 3), and alkaline pH (pH = 12), with a 1:1 M ratio of pollutant to reducing agent under UV and non-UV irradiation conditions. The stoichiometric amount of the reducing agent was used to capture subtle differences in efficiency that may not have been noticeable with an excess of the reducing agent and immediate near-quantitative conversion. In addition, a study was carried out on the effect of UV radiation alone on the concentration of nitrobenzene, which did not show any progress in the reaction (0 % reduction after 60 min of the process). The results are presented in Fig. 7.

Based on the data presented in Fig. 7, it can be concluded that the change in pH of nitrobenzene solution compared to neutral pH (pH =
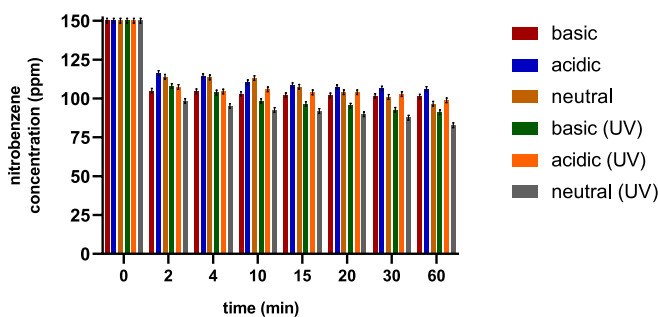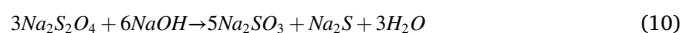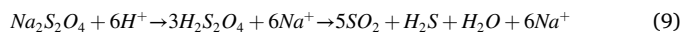

Fig. 7. Dependence of the 150 ppm nitrobenzene solution reduction on the pH of the solution (NB:SD ratio 1:1), at 20 °C.

7.0) is unfavorable in terms of the effectiveness of the reduction process, both under DTN conditions alone and under UV-assisted conditions. However, the differences are not large. The negative effect of acidic and alkaline pH is due to the reaction of protons (reaction (9)) or reactions of hydroxide ions (reaction (10)) with dithionite anion [34].

$$Na_2S_2O_4 + 6H^+ \rightarrow 3H_2S_2O_4 + 6Na^+ \rightarrow 5SO_2 + H_2S + H_2O + 6Na^+ \qquad (9)$$

$$3Na_2S_2O_4 + 6NaOH \rightarrow 5Na_2SO_3 + Na_2S + 3H_2O \qquad (10)$$

Side reactions (8) and (9) under acidic and basic pH conditions have a negative impact on the overall effectiveness of nitrobenzene degradation, as they result in the formation of ions that do not exhibit reducing properties, and the reactions themselves lead to the consumption of the reducing agent (DTN) in the reaction system.

Wastewater containing nitrobenzene can vary in pH, thus it is crucial to ensure a high efficiency of the reduction process regardless of the pH in acceptable range. Nitrobenzene reduction with DTN shows the highest effectiveness at pH = 7. DTN also effectively reduces nitrobenzene at acidic (pH = 3) and alkaline (pH = 12), and the effect of pH on

the process only leads to deviations from maximum reduction efficiency by ± 5 %. The final degree of reduction can be easily increased by using a small excess of the reducing agent, as described in the paper.

3.1.4. The effect of addition of TiO₂ catalyst

Under UV radiation, TiO₂ can reach excited state (in the electron hole-electron system). Excited TiO₂ is commonly used in AOPs as a catalyst for the activation of oxidants such as ozone (O_3) or hydrogen peroxide (H_2O_2) under UV radiation [31] for degradation of contaminants present in wastewater via AOP mechanism. There are also reports in the literature on its use in ARPs as a catalyst for the decomposition of formic acid (HCOOH) under UV radiation to produce carboxyl radical anions $CO_2^{\bullet-}$ with a reduction potential of −2.1 V [32,33]. In this study the effect of TiO₂ on the decomposition of DTN into reducing radicals under UV radiation was examined as an additional aspect, considering this option in the context of further process intensification.

Based on the data presented in Fig. 8, it can be concluded that the addition of titanium(IV) oxide as a catalyst does not affect the activation of DTN under UV radiation. Additionally, it is evident that the efficiency of nitrobenzene reduction was lower compared to the DTN/UV process but higher than for DTN alone. The observed differences are due to the partial absorption of UV radiation by the titanium (IV) oxide suspension, which does not contribute to the photocatalytic activation of DTN or the degradation of nitrobenzene, thus reducing the amount of UV light available for DTN activation.

The fact that TiO₂ is not effective in the DTN/UV/ARP process can be explained by the rate of DTN hydrolysis, which, due to the high rate of reaction of $SO_2^{\bullet-}$ radicals with nitrobenzene (consuming the hydrolysis product), dominates over catalytic processes on the surface of TiO₂.

3.1.5. The effect of the presence of anions on the reduction of nitrobenzene

Substances with ionic character, particularly inorganic ions, are an integral component of wastewater. Therefore, any reduction process in the aqueous medium must ensure effectiveness and selectivity for the degradation of target pollutants in the presence of ionic substances, especially inorganic anions. The application of the reduction process under real conditions (in wastewater and water) requires high efficiency in the presence of ions such as chlorides, nitrates, sulfates, thiosulfates, and azides as well as organic matter. In this study, their influence was examined at concentrations corresponding to a molar ratio of nitrobenzene to anion of 1:30, equivalent to a molar concentration of anions at 37 mM. The research conducted under optimal process conditions ($r_{red} = 3$, pH = 7, and nitrobenzene concentration of 150 ppm) revealed that the presence of excess azide, thiosulfate, and nitrite ions in the nitrobenzene solution has a negligible effect on the reduction of

nitrobenzene by sodium dithionite. Chloride and sulfate ions decreased the reduction effect by only about 2 % compared to the control sample, nitrate ions by 6 %, and carbonate ions by 22 % (Fig. 9). The slight decrease in the efficiency of nitrobenzene reduction is caused by the reaction of the reducing radicals with these ions, as presented in reactions (11)–(13). The result of reactions (11)–(13) is the formation of radicals with a positive potential, thus belonging to the group of weak oxidants, which is detrimental for the reduction process. In conclusion, the conducted research showed that the presence of additional ions in the solution has a minor impact on the overall effect of nitrobenzene reduction in the developed ARP process.

$$NO_3^- + SO_2^{\bullet-} \rightarrow NO_2^- + SO_3^{\bullet-} \tag{11}$$

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \tag{12}$$

$$HCO_3^- + SO_2^{\bullet-} \rightarrow CO_2 + HSO_3^{\bullet\, 2-} \tag{13}$$

The fact that the DTN/UV system shows low sensitivity to the presence of inorganic ions is a significant advantage compared to AOP (Advanced Oxidation Processes) methods. For many AOPs, the degradation efficiency of pollutants in real matrices significantly decreases compared to studies conducted with model solutions [35]. Therefore, many efficient processes, such as based on persulfate, do not perform well in the presence of inorganic ions.

3.1.6. The effect of the presence of dissolved organic matter on the reduction of nitrobenzene

Organic matter is present in most types of municipal and industrial wastewater, so assessing its effect on nitrobenzene reduction in organic matter environment is crucial for the application of this process in wastewater treatment. Humic acid sodium salts (HASS) were used to simulate the controlled organic matter content of nitrobenzene solution. The study was conducted at 20 °C, the initial concentration of nitrobenzene 150 ppm, the molar ratios of nitrobenzene: HASS of 1:1, 1:5 and 1:30 showed 100 %, 99.2 % and 87.2 % reduction of nitrobenzene, respectively. The obtained results revealed that nitrobenzene can be effectively reduced even when organic matter is present in solution.

3.1.7. Identification of reductive radical species

The degradation of nitrobenzene under ARPs can occur in several ways, mainly depending on the kind of radical species generated in the treated medium. The influence of individual types of radicals can be determined based on changes in the reduction efficiency in the presence of selective radical scavengers. Based on the chemistry of dithionite ions, the reaction system can be expected to contain primarily $SO_2^{\bullet-}$ radicals as well as hydrated electrons and hydrogen radicals. Ions, such as NO_2^-,
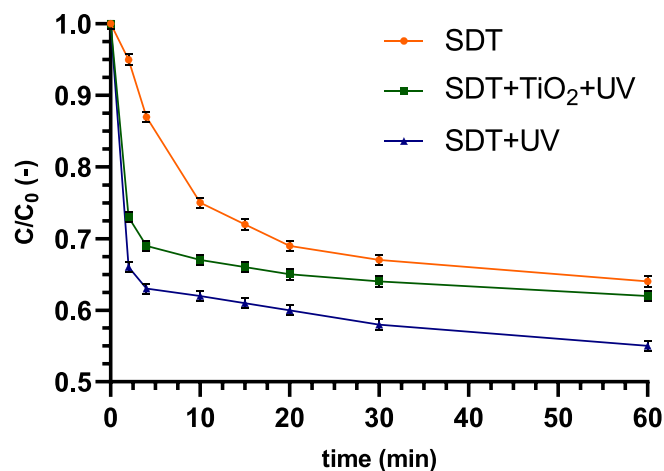

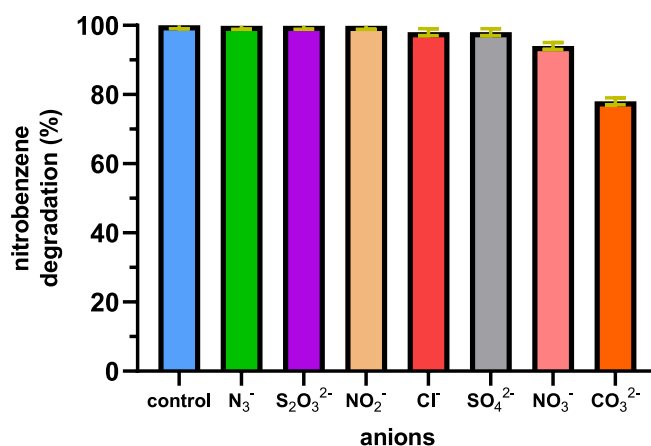**Fig. 8.** Dependence of the 150 ppm nitrobenzene solution reduction on time in the presence of a TiO₂ catalyst at 20 °C.

Fig. 9. The effect of anions presence (nitrobenzene: anions molar ratio 1:30) on the reduction of 150 ppm nitrobenzene solution at 20 °C.

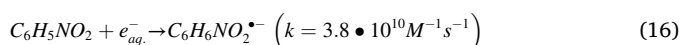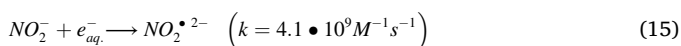NO_3^-, and Fe^{3+}, were used for their identification.

The assessment of the impact of $(SO_2^{\bullet-})$ radicals on pollutant degradation can be achieved by using iron(III) cations, which effectively eliminate this type of radicals according to reaction (14).
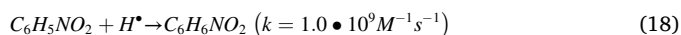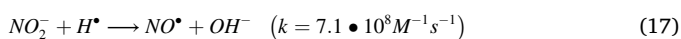
$$Fe^{3+} + SO_2^{\bullet-} \rightarrow Fe^{2+} + SO_2 \quad (k = 5 \bullet 10^6 M^{-1} s^{-1}) \tag{14}$$
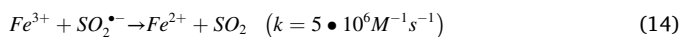
Research performer during this study has revealed that in the presence of iron(III) ions, the reduction of nitrobenzene using DTN does not occur until all Fe^{3+} ions in the solution are depleted. The depletion of iron(III) ions in the solution is easily observable because the yellow-colored iron (III) ions transform into colorless iron(II) ions upon reaction with DTN, resulting in the decolorization of the solution. The high reaction rate between iron(III) ions and the radical $(SO_2^{\bullet-})$ makes it an effective and easily applicable indicator of the presence of this radical.
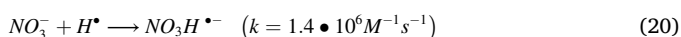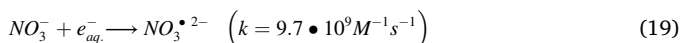
The presence of hydrated electrons and hydrogen radicals in the DTN reduction process under UV radiation and DTN itself can be confirmed by adding nitrite and nitrate ions to the solution. For nitrobenzene solutions in the presence of nitrite ions, the reduction of nitrobenzene occurred with nearly 100 % efficiency. Considering that the rate constants of reactions (15) and (16) are at comparable levels, it was expected that both reactions would compete with each other, leading to a decrease in the efficiency of nitrobenzene reduction in the presence of hydrated electrons in the solution. The lack of significant change in efficiency indicates a negligible impact of hydrated electrons on the mechanism of nitrobenzene reduction using DTN.

$$NO_2^- + e_{aq.}^- \longrightarrow NO_2^{\bullet\, 2-} \quad \left(k = 4.1 \bullet 10^9 M^{-1} s^{-1} \right) \tag{15}$$

$$C_6H_5NO_2 + e_{aq.}^- \rightarrow C_6H_6NO_2^{\bullet-} \quad \left(k = 3.8 \bullet 10^{10} M^{-1} s^{-1} \right) \tag{16}$$

Similarly, by comparing the rate constants of reactions (17) and (18), the presence of hydrogen radicals $(H^{\bullet})$ as the reducing radicals responsible for nitrobenzene reduction can be eliminated [36].

$$NO_2^- + H^{\bullet} \longrightarrow NO^{\bullet} + OH^- \quad \left(k = 7.1 \bullet 10^8 M^{-1} s^{-1} \right) \tag{17}$$

$$C_6H_5NO_2 + H^{\bullet} \rightarrow C_6H_6NO_2 \quad \left(k = 1.0 \bullet 10^9 M^{-1} s^{-1} \right) \tag{18}$$

Additionally, the study of nitrobenzene reduction in the presence of nitrate ions showed a slight decrease of 6 % in the efficiency of nitrobenzene reduction to aniline, which is caused by the direct reaction of nitrate ions with the radical $(SO_2^{\bullet-})$. However, the 6 % decrease in nitrobenzene reduction efficiency is small enough that, considering the previously determined rate constant for the reaction of $(SO_2^{\bullet-})$ radicals being lower than $k = 5 \bullet 10^6 M^{-1} s^{-1}$, and the significantly higher rate constants of reactions (19) and (20), the presence of hydrated electrons and reducing radicals can once again be eliminated as the main species responsible for nitrobenzene reduction [37].

$$NO_3^- + e_{aq.}^- \longrightarrow NO_3^{\bullet\, 2-} \quad \left(k = 9.7 \bullet 10^9 M^{-1} s^{-1} \right) \tag{19}$$

$$NO_3^- + H^{\bullet} \longrightarrow NO_3H^{\bullet-} \quad \left(k = 1.4 \bullet 10^6 M^{-1} s^{-1} \right) \tag{20}$$

The conducted research confirmed the dominant role of $SO_2^{\bullet-}$ radicals in the nitrobenzene reduction process. The obtained result is consistent with the predictions regarding the chemistry of DTN, which serves as an excellent substrate for the production of reducing radicals $SO_2^{\bullet-}$.

3.1.8. The effect of nitrobenzene concentration on reduction efficiency

The efficiency of the process over a wide range of nitrobenzene concentrations is a crucial aspect in the context of implementing the developed technology under real conditions. The pollutant stream subjected to purification may contain nitrobenzene at concentrations ranging from a few ppm to as high as 2000 ppm (the solubility limit of nitrobenzene in water), depending on its origin.

The research carried out under $r_{red} = 3$ conditions (where the initial nitrobenzene concentration was increased proportionally with the DTN dose to maintain a constant molar ratio) at a temperature of 20 °C, in the absence of UV radiation, showed that the reducing radicals in the form of sulfur dioxide anion radical $(SO_2^{\bullet-})$ efficiently and rapidly led to nitrobenzene reduction over a wide range of nitrobenzene concentrations, ranging from a few ppm up to 1000 ppm (100 % reduction in 10 min).. The obtained results confirm the high applicability of the developed process. However, for concentrations above 1000 ppm, the economic justification for using ARP for nitrobenzene reduction seems questionable. In such cases, methods based on adsorption processes should be applied to enable nitrobenzene recovery. An additional advantage of the reduction process using DTN is its high water solubility, which is 182 g/L, ensuring the effective reduction of nitrobenzene even in wastewater containing nitrobenzene at the solubility limit of 2 g/L. The efficiency of the developed process confirms another advantage of ARP over AOP. In many cases, AOPs exhibit high degradation efficiency for concentrations at the single ppm level, but a tenfold increase in the pollutant concentration often leads to a drastic decrease in degradation efficiency. Frequently, even significantly extending the treatment time does not ensure complete degradation. In the method described in this study, a 200-fold increase in pollutant and reduction product concentrations does not negatively affect the efficiency or time required for complete nitrobenzene reduction. The previously demonstrated strong correlation between degradation efficiency and reducing agent dose can be utilized for automatic control of the reduction process. The use of a flow-through UV spectrophotometer, monitoring the nitrobenzene content in the treated wastewater, enables precise dosing of the reducing agent.

3.2. Product of nitrobenzene reduction by dithionite

As a result of dithionite decomposition, highly reactive radicals $(SO_2^{\bullet-})$ with a reduction potential of -0.64 V are formed. The reduction potential value is significantly lower compared to hydrated electrons (-2.9 V) or hydrogen radicals (-2.1 V) but sufficient to reduce the nitro group to an amino group. The main advantage of using dithionites in ARPs is the abundance of generated radicals $(SO_2^{\bullet-})$, which, despite their relatively low reduction potential, have been proven to rapidly and effectively reduce nitrobenzene. Each reduction process of a nitrobenzene solution in water within the concentration range of 500–1000 ppm leads to the formation of the main product, in this case aniline, as well as intermediate products that should also be reduced to the main product during the process. In the case of nitrobenzene reduction using DTN, the amount of intermediate products formed during the process is trace-level and practically negligible after 60 min, as confirmed by high-performance liquid chromatography with UV diode-array detection (HPLC-UV-DAD) studies. To further identify the intermediate products formed during the process, a gas chromatography-mass spectrometry (GC–MS) analysis was carried out on the reaction mixture collected at 2, 5, 10, 30, and 60 min.

Fig. 10 illustrates alternative transformation pathways of nitrobenzene to aniline. Pathway a) represents the reduction of nitrobenzene (I) to nitrosobenzene (II), which is further reduced to phenylhydroxylamine (III), and then directly to aniline (VII). Alternative pathway b) leads to the formation of nitrosobenzene (II) from nitrobenzene (I), followed by the formation of azoxybenzene (IV), which undergoes further reduction to azobenzene (V), and subsequent reduction of azobenzene yields hydrazobenzene (VI). The last-mentioned intermediate product can undergo decomposition, resulting in the formation of two molecules of aniline.

Trace amounts of nitrosobenzene (II) were detected in samples collected at 2, 5, and 10 min, but no other intermediate products of pathway b) were detected. Additionally, the absence of intermediate product (III) – phenylhydroxylamine, in the sample, can be explained by
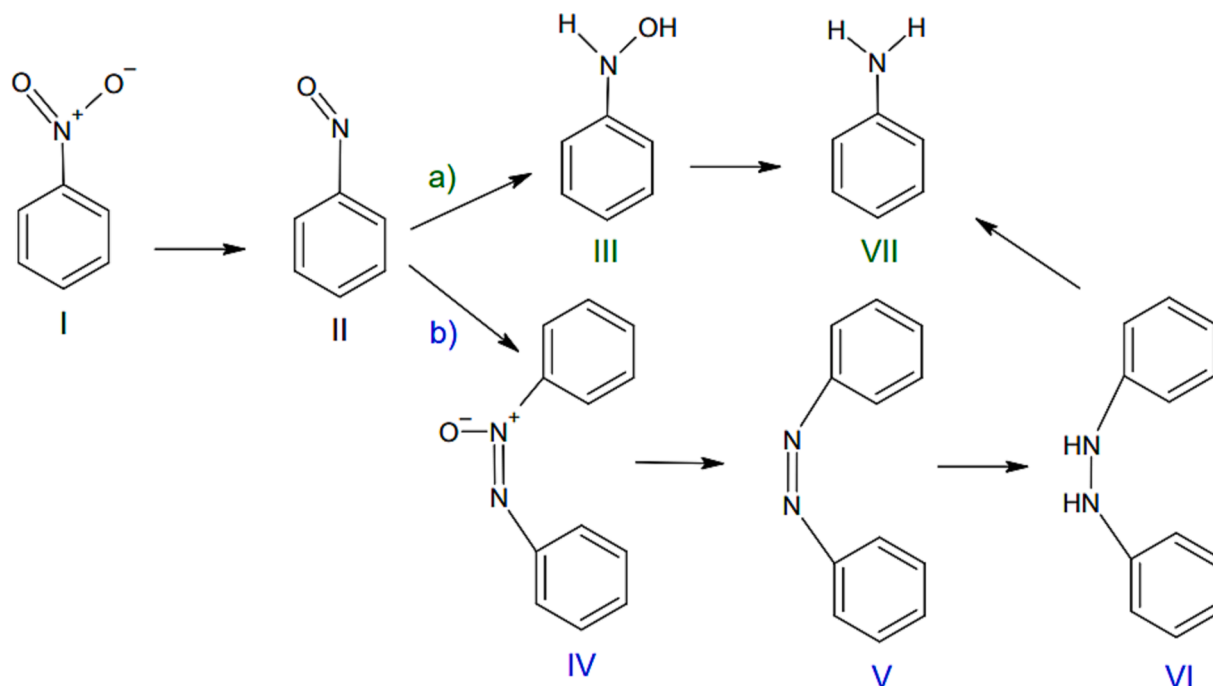
Fig. 10. Nitrobenzene reducing pathways: a) primary pathway, b) secondary pathway. I–nitrobenzene, II-nitrosobenzene, III-phenylhydroxylamine, IV-azoxybenzene, V-azobenzene, VI-hydrazobenzene, VII-aniline. Based on [39].

the highly unstable nature of this compound [38].

Taking into account the absence of transitional products IV, V, and VI in the samples, it was determined that the main reduction pathway was the one shown in Fig. 10 as pathway a), which is also indicated in the literature as the primary pathway for the reduction of nitrobenzene to aniline [40]. In the presence of radicals ($SO_2^{\bullet-}$), this reaction occurs at a very rapid rate.

The detailed course of the reaction is presented in Fig. 11. In the first step, the radical ($SO_2^{\bullet-}$) gives up an electron to the nitrogen atom of the nitro group in nitrobenzene. Subsequently, the radical is released in the form of the SO$_2$, which is soluble in water. In the next step, exactly the same electron transfer occurs, followed by the double attachment of the proton H$^+$, resulting in the formation of nitrosobenzene after the release of the water molecule. Nitrobenzene is then protonated, and another electron is attached from the reducing radical ($SO_2^{\bullet-}$). Subsequent protonation of the molecule thus formed leads to phenylhydroxyamine. Subsequently, two protonations and the acceptance by phenylhydroxy-amine of two electrons from the reducing radicals ($SO_2^{\bullet-}$) lead to the final product of the reaction, aniline.

3.3. Concept of wastewater treatment with the removal of aniline from water

As a result of the reduction reaction of nitrobenzene in an aqueous solution, pure aniline is produced, and its recovery from water can be carried out using various methods such as liquid membrane separation [41], pervaporation [42], or nitrobenzene extraction combined with salting out. All the above-mentioned methods of separating aniline from water are applied as the second stage of wastewater treatment for the removal of nitrobenzene, in combination with the solution described in this paper.

This concept aligns with the idea of sustainable development. In addition to the benefits associated with the reduction of nitrobenzene in wastewater, the process enables the production of a valuable product in the form of aniline, which is a commodity.

4. Economic analysis

The economic analysis was performed based on the data obtained during the experiments described in this paper (volume of treated medium: 7.5 L) for the treatment process recalculated for 1 m^3 of wastewater with a concentration of 150 ppm of nitrobenzene, with and without UV irradiation.

Based on current market prices, the purchase cost of 1 ton of DTN is $1000. To treat 7.5 L of 150 ppm solution, approximately 4.8 g with a value of $0.0048 was used. Considering the energy cost for stirring with a 6 W mixer for one hour at $0.17/kWh, the cost is $0.001. Therefore, the total cost of treating 7.5 L of 150 ppm nitrobenzene solution without UV irradiation is approximately $0.0058, which translates to a cost of $0.77/m^3.

Performing the process additionally with a 250 W UV lamp and a peristaltic pump with 100 W power operating at 50 % efficiency for 1 h results in an energy consumption of 0.3 kWh, with a cost of $0.051. Taking into account the cost of DTN and stirring, the total amount is $0.057. Thus, the total cost of treating the nitrobenzene solution with UV irradiation is $7.6/m^3.

In summary, the costs of employing UV irradiation in the process are more than ten times higher than the equivalent process without UV irradiation. Therefore, considering only a 10 % increase in process efficiency with UV, from an economic standpoint, the use of UV irradiation in the process is not cost-effective. The process without UV irradiation appears to be economically justified.

The economic analysis presented above was done for model conditions. In the real wastewater, certain process costs may be increased. According to the study, the efficiency of the process in the presence of dissolved organic matter (DOM) and anions at the levels present in the wastewater has minor (less than 10 %) impact on the efficiency of the treatment process. Therefore, according to the prediction of the economic analysis, the cost of treating real wastewater will be about 10 % higher than the model wastewater.

The advantages of the developed method for the production of aniline are the lower investment costs comparing to catalytic hydrogenation processes. The catalytic hydrogenation process requires constant
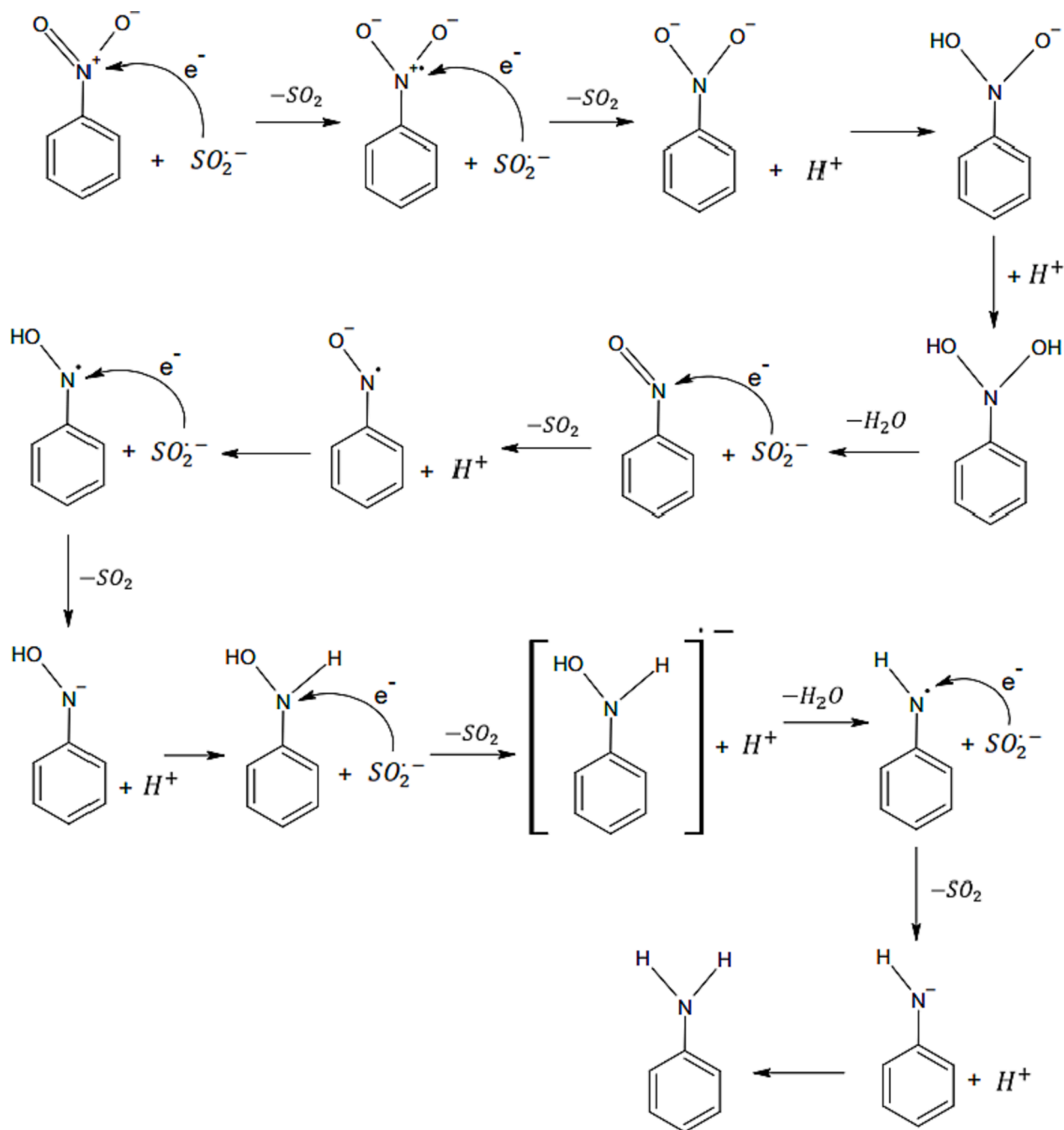
Fig. 11. Nitrobenzene reduction mechanism by sulfur dioxide radical anions.

access to high-purity hydrogen, the storage and transportation of which is virtually impossible on an industrial scale, so there is a need to produce hydrogen at the site of the catalytic reduction process. The process of industrial hydrogen production is commonly carried out by means of steam reforming of natural gas or light hydrocarbons. This demands to have a constant access to such a feedstock (i.e. pipeline delivery system) or pressurized storage tanks. In case of reducing nitrobenzene using DTN, the setup is relatively simple in and low cost.

Also noteworthy is the ability to extract aniline from water and then recover it in a pure form suitable for industrial and laboratory applications [43].

5. Conclusions

The research described in this paper has shown that DTN is a highly

reactive and efficient reductant in the aqueous phase and can be effectively activated using UV radiation. A molar ratio of 3:1 of DTN to nitrobenzene in the aqueous phase ensures 100 % degradation of nitrobenzene within 60 min, with pure aniline as the final product. It is also possible to achieve 100 % degradation of nitrobenzene within 60 min using a smaller amount of reductant under UV irradiation. The developed method for the reduction of nitrobenzene to aniline is the first non-catalytic method with such high efficiency and without the formation of intermediate reaction products. The application of this method for water purification from nitrobenzene with simultaneous aniline production is advantageous from an industrial perspective, especially in the production processes of aniline from nitrobenzene, where an additional increase in the overall conversion of nitrobenzene is possible through efficient reaction in wastewater (post-process water). The developed process does not require the use of catalysts, pure

hydrogen, or specialized equipment, which is undoubtedly a significant advantage. Additionally, the study showed that the process works effectively across the pH range from 3 to 12.

The economic analysis of the process is also favorable, as the total cost of reducing 1 m^3 of a 150-ppm nitrobenzene solution was $0.77/m^3 for the process without UV and $7.6/m^3 for the process with UV. Therefore, the presented process serves as an introduction to the potential reduction of other compounds containing the nitro group and has great potential for application in various reduction processes in industry and organic synthesis.

CRediT authorship contribution statement

Łukasz Cichocki: Conceptualization, Investigation, Visualization, Writing – original draft, Writing – review & editing. **Lingshuai Kong:** Writing – review & editing. **Chongqing Wang:** Writing – review & editing. **Andrzej Przyjazny:** Writing – original draft, Writing – review & editing. **Grzegorz Boczkaj:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2023.147878.

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