



Synthesis, characterization, and photocatalytic application of Pd/ZrO₂ and Pt/ZrO₂

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Received: 8 June 2017 / Accepted: 10 April 2018 / Published online: 19 April 2018
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Abstract

Zirconia-supported palladium (Pd/ZrO₂) and Zirconia-supported platinum (Pt/ZrO₂) nanoparticles (NPs) are synthesized from their precursors via impregnation technique. The Pd/ZrO₂ and Pt/ZrO₂ NPs were analyzed via SEM and EDX, while the study of indigo disulfonate dye degradation was carried out by UV/VIS spectrophotometer. The SEM micrographs illustrated that the Pd and Pt NPs were well placed on ZrO₂ surface. The Pd/ZrO₂ and Pt/ZrO₂ NPs were also employed as photocatalysts for the photodegradation of indigo disulfonate in an aqueous medium under UV-light irradiation. The photodegradation study presented that Pd/ZrO₂ and Pt/ZrO₂ NPs degraded 96 and 94% of indigo disulfonate in 14 h, respectively. The effect of pH of medium and catalyst dosage and efficiency of recovered Pd/ZrO₂ and Pt/ZrO₂ NPs on the photocatalytic degradation were also studied. It was also found that the maximum degradation of dye was found at pH 10 (95–97%) and at 0.02 g weight (40.28%).

Keywords Indigo disulphonate · Photodegradation · Nanoparticles · Scanning electron microscopy

Introduction

Industries are considered not only as a backbone for country development but also responsible as the major source for discarding toxic wastes into aquatic systems (Shah et al. 2016). Their growth has increased the generation and accumulation of waste by-products (Mital and Manoj 2011). These industries discharge their effluents containing water pollutants such as dyes and pigments (Saeed et al. 2015). Synthetic dyes have been increasingly used in textiles, plastic, rubber, cosmetics, foods, and pharmaceutical industries (Sharma and Sharma 2013). About 10–15% of all dyes are directly lost to waste water during the dyeing process (Tolia et al. 2012). Synthetic dyes significantly cause an environmental pollution because of stability and toxicity and result in severe health risk (Reza et al. 2015). Most of these dyes

are non-biodegradable, toxic, and carcinogenic because of complex structures and large size (Xu et al. 2008). Various chemical, biological, and physical techniques are used for its elimination like adsorption, precipitation, ozonization, membrane separation, ultrafiltration, and flocculation. Most of these treatment techniques are non-destructive and convert them into other products which are considered as secondary pollutants that need further treatment (Saeed et al. 2015). Recently, semiconductor photocatalysis has attracted much attention for waste water treatment due to its potential of scavenging large range of toxic pollutants (organic and inorganic) at ambient pressure and temperature with no harmful by-products (Saeed et al. 2015). This technology provides a simple route for conversion of solar energy into chemical energy used for water splitting and other purposes (Ayodhya et al. 2016). In photocatalysis, semiconductors are used as photocatalysts (Kumar et al. 2008). Photocatalysts are semiconducting materials that are activated via adsorbing high-energy photon and have the ability of accelerate photodegradation reaction without being consumed (Saeed et al. 2016; Fox 1988). Various photocatalysts are reported for the photodegradation of organic pollutants such as Zn²⁺-Ni²⁺-Fe³⁺-CO₃²⁻ LDHs for methyl orange (Dang et al. 2017), PAN/CNT-TiO₂ for methylene blue and indigo carmine (Mohamed et al. 2016), Ag/OM-PAN nanofiber for

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methyl orange (Saeed et al. 2015), graphene-supported Sn-Pt bimetallic nanoparticles Basic Green 5 (Saeed et al. 2016), TiO₂ nanoparticles for methyl orange (Su et al. 2013), Mg doped TiO₂ for methyl orange (Avasarala et al. 2016), TiO₂/Pt and TiO₂/Pd photocatalysts for methyl violet dye (Saeed et al. 2017), and chitosan conjugated magnetic nanoparticles used for of bromophenol blue (Khan et al. 2016).

In the present study, Pd- and Pt-deposited zirconia nanoparticles were synthesized by impregnation technique and were used as photocatalysts for photodegradation of indigo disulfonate in aqueous medium. ZrO₂ is the main material of ceramics industry and is currently used as heterogeneous photocatalyst because of its n-type semiconductor nature (Botta et al. 1999). In this work, we use ZrO₂ as a support for the better dispersion of Pt and Pd nanoparticles. The Pd and Pt were selected because they have high melting point, less toxicity, efficiently recycled, and highly catalytic ability (Emsley 2011; Golunski 2007). However, the indigo is selected because it is an oldest and most importantly used dye. Its production is 3% of the total dye production. The major industrial application of indigo is the dyeing of clothes (blue jeans) and other blue denim products. Its melting point is 390–392 °C and has very poor solubility because of the existence of strong intermolecular hydrogen bond (Vautier et al. 2001). The morphological and elemental compositions of the prepared photocatalysts were studied. The photodegradation study was carried out by UV/VIS spectrophotometer. The recycle abilities of Pd/ZrO₂ and Pt/ZrO₂ photocatalysts were also investigated.

Experimental work

Materials

The NaOH and HNO₃ were purchased from Scharlau chemicals and Sigma Aldrich. Zirconium oxide dichloride octahydrate (ZrOCl₂·8H₂O), PtCl₄, and PdCl₂ are supplied by BDH. Indigo disulfonate was purchased from Merck.

Preparation of Pd/ZrO₂ and Pt/ZrO₂ photocatalysts

First of all, monoclinic zirconia was prepared from their precursors ZrOCl₂·8H₂O by ammonolysis and then calcined at 750 °C in the furnace at a heat ramp of 5 °C/min for 3 h. Pd/ZrO₂ and Pt/ZrO₂ were prepared separately by the impregnation method by addition of 0.01% solution of PdCl₂ and PtCl₄, respectively. The paste of the prepared samples was dried overnight in an oven at 110 °C. Pd/ZrO₂ and Pt/ZrO₂ were thus obtained after calcination at 750 °C at a rate of 3 °C/min for 3 h.

Photodegradation of indigo disulfonate

10 mL of indigo disulfonate (100 ppm) and 0.02 g of Pd/ZrO₂ and Pt/ZrO₂ were separately taken in vials and placed in UV-light (254 nm, 15 W) with constant stirring. The catalyst from each vial is separated by centrifugation (1200 rpm) after specific irradiation time, while the indigo disulfonate degradation was calculated by UV–VIS spectrophotometry (UV-1800, Shimadzu, Japan). The following equation was used for the calculation of %degradation of indigo disulfonate in aqueous medium (Saeed et al. 2015).

$$\text{Degradation rate(\%)} = \left(\frac{C_0 - C}{C_0} \right) \times 100$$

$$\text{Degradation rate(\%)} = \left(\frac{A_0 - A}{A_0} \right) \times 100,$$

where C_0 is the initial dye concentration, C is the dye concentration after UV irradiation, A_0 shows the initial absorbance, and A shows the dye absorbance after UV irradiation.

Results and discussion

SEM and EDX study

Figure 1a and b shows the SEM micrographs of Pd/ZrO₂ and Pt/ZrO₂, respectively. The micrographs presented that Pd and Pt NPs are formed on the surface of ZrO₂. Micrographs show that at some points Pd and Pt form agglomerates, while also appear in dispersed form at some points. The images also presented that the size of NPs was below 100 nm, while the size of agglomerates is in the range of 100–700 nm. The formation of Pd and Pt was also confirmed by EDX analyses (Fig. 2a, b for Pd/ZrO₂ and Pt/ZrO₂, respectively). The figures illustrated that about 0.04 and 0.16 %weights of Pd and Pt NPs are deposited on ZrO₂. The presence of oxygen also confirms that the TiO₂ has been prepared from their precursor.

Photodegradation study of indigo disulfonate

The photocatalytic activities of Pd/ZrO₂ and Pt/ZrO₂ were examined against indigo disulfonate under UV-light irradiation. Figure 3a and b shows the UV–Visible spectra of indigo disulfonate dye before and after UV-light irradiation photodegraded by Pd/ZrO₂ and Pt/ZrO₂, respectively, in aqueous medium. The photodegradation of indigo disulfonate dye was obtained from its relative intensity of UV/VIS spectra which give the maximum absorbance peak at 611 nm. The comparison of %degradation of dye in the

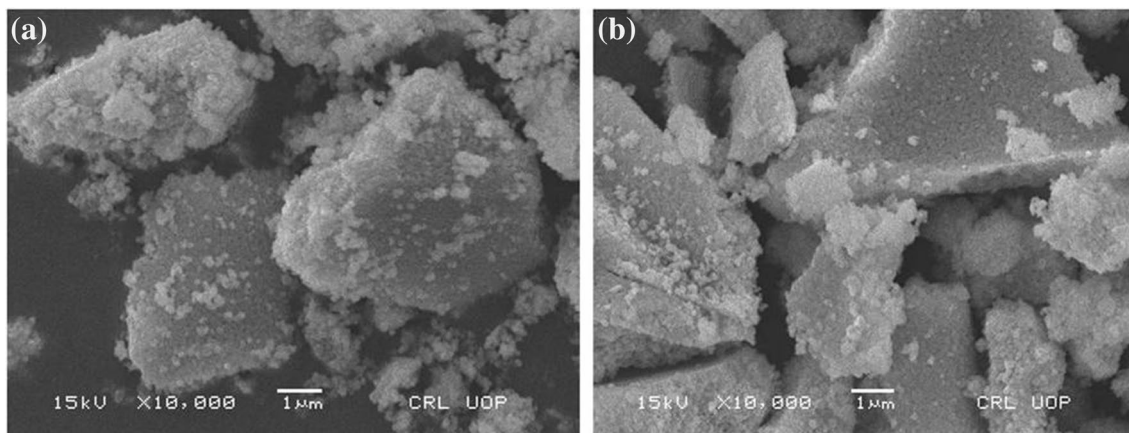


Fig. 1 SEM images of a Pd/ZrO₂ b Pt/ZrO₂

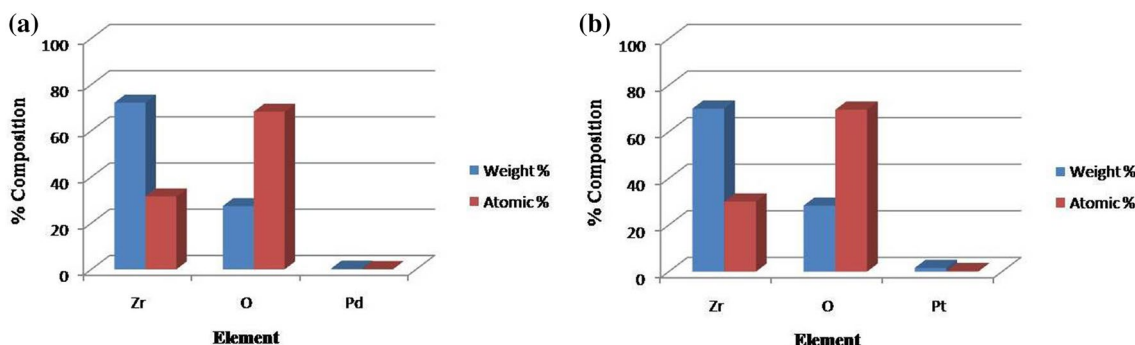
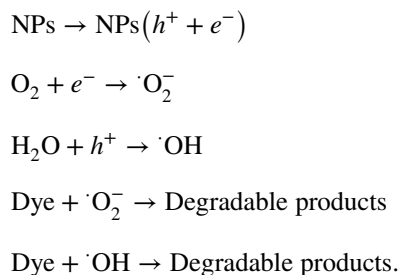


Fig. 2 EDX study of a Pd/ZrO₂ b Pt/ZrO₂

presence of Pd/ZrO₂ and Pt/ZrO₂ is shown in Fig. 3c. Figure 3a–c shows that dye degradation increased by increasing the irradiation time to their optimum. Figure also shows that Pd/ZrO₂ is more active in dye degradation as compared to Pt/ZrO₂ under the same experimental conditions. The result data revealed that Pd/ZrO₂ degraded about 10.26% of dye within 30 min, and the degradation increased up to 96.61% by increasing UV-light irradiation time up to 14 h. Similarly, the Pt/ZrO₂ degraded about 6.04% of dye within 30 min, and the degradation increased up to 94.46% by increasing UV-light irradiation time up to 14 h. The effect of recycle catalyst was also investigated by washing and using it again as photocatalysts under the same experimental conditions. The recycle catalysts were also active against dye degradation. However, the recycle catalysts show less activity as compared to the originals, which might be due to photosensitive hydroxide deposition on the photocatalysts surface, and that might block active site of the catalyst (Saeed et al. 2016).

The proposed mechanism is that when UV-light falls upon the NPs, the valence electrons (e⁻) get excited toward the conduction band and result in the formation of positive hole (h⁺) in the valence band. The e⁻ and h⁺ play important

role in the generation of reactive radicals. For example, the h⁺ and e⁻ react with water and O₂ molecules, which results in hydroxyl radicals (·OH) and superoxide radical ion (O₂^{-·}), respectively. These reactive radicals are responsible for the photodegradation of dye. The major reaction mechanism under sunlight irradiation is summarized in the following equations:



Effect of photocatalysts dosage

The effect of photocatalyst amount was also tested on the photodegradation of dye by applying different amounts (0.010, 0.015, 0.020, 0.025, and 0.030 g) of photocatalysts

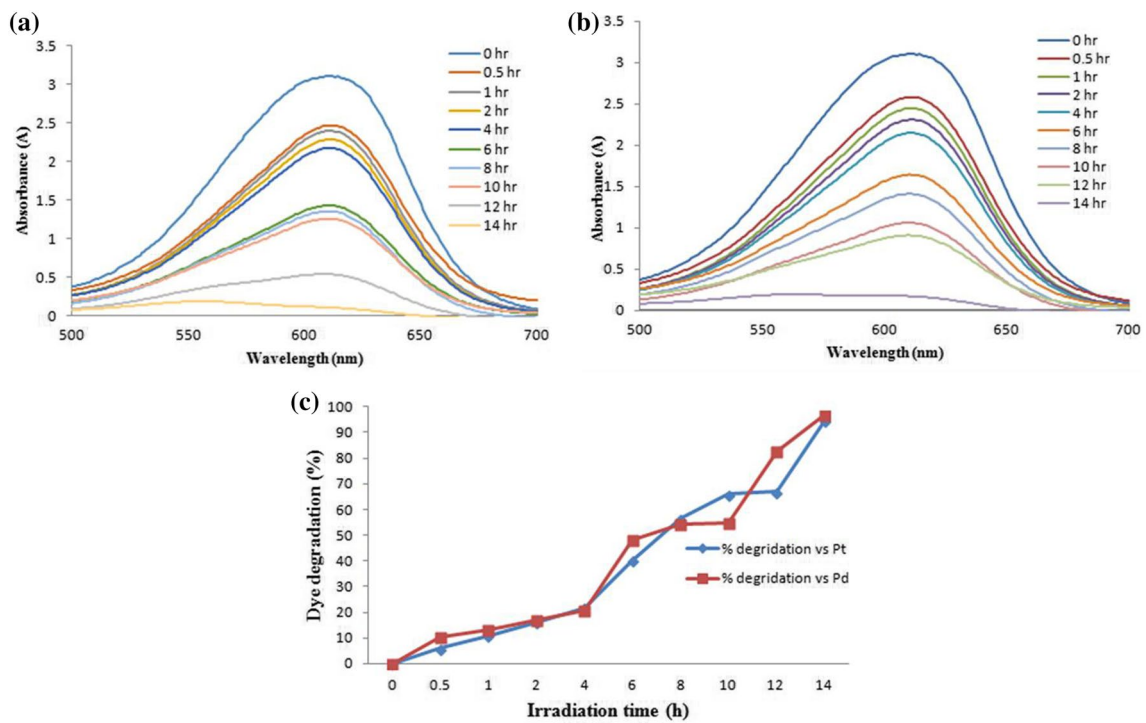


Fig. 3 **a** UV–VIS absorbance spectra of indigo disulfonate degraded by Pd/ZrO₂, **b** UV–VIS absorbance spectra of indigo disulfonate degraded by Pt/ZrO₂, **c** comparison of % degradation by both photocatalysts

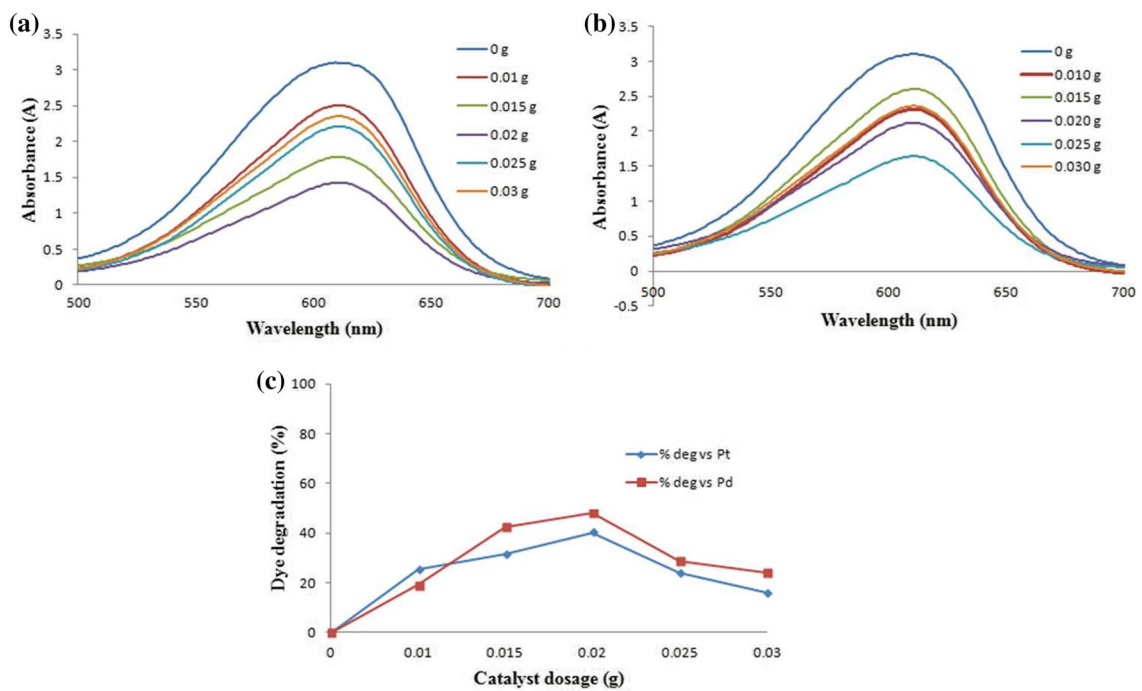


Fig. 4 **a** UV–VIS absorbance spectra of indigo disulfonate degraded at different catalyst dosages of Pd/ZrO₂ and **b** Pt/ZrO₂; **c** comparison of % degradation by different catalyst dosages

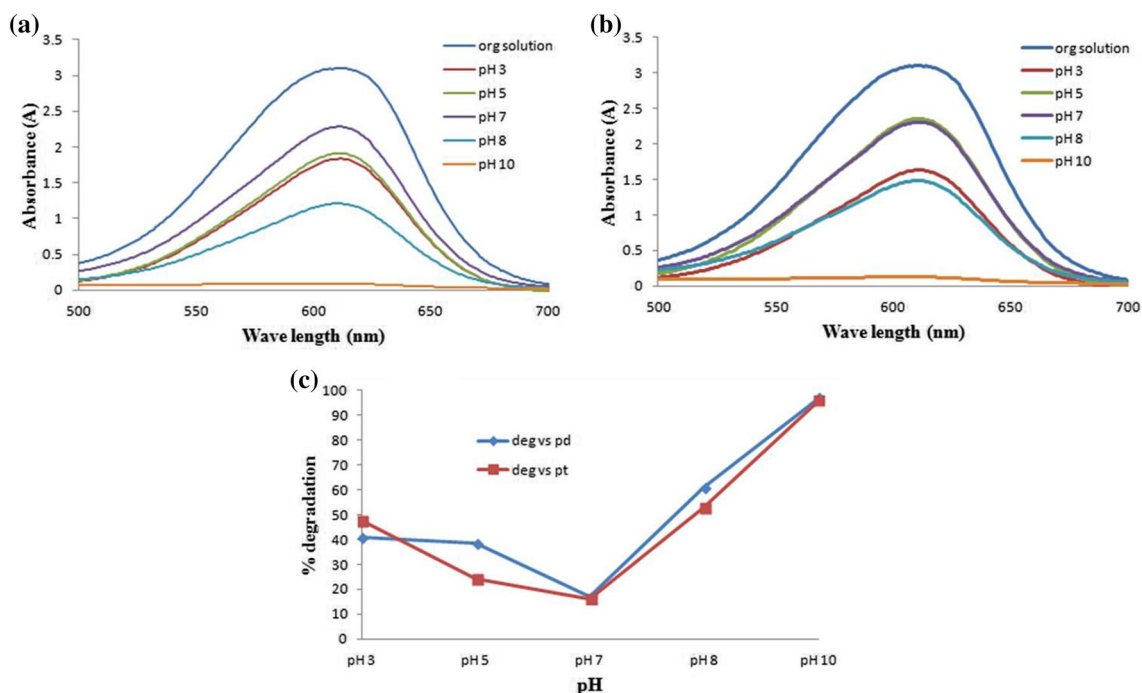


Fig. 5 a UV–VIS absorbance spectra of indigo disulfonate degraded at different pH mediums by Pd/ZrO₂ and b Pt/ZrO₂; c comparison of % degradation at different pH values

under constant experimental conditions (time = 6 h). Figure 4a and b shows the UV/Visible spectra of indigo disulfonate dye before and after UV-light irradiation in the presence of different amounts of Pd/ZrO₂ and Pt/ZrO₂, respectively. Figure 4c shows the comparison of % degradation of indigo disulfonate dye photodegraded by Pd/ZrO₂ and Pt/ZrO₂. Figure 4a–c shows that as catalyst amount increases photocatalytic degradation of dye also increases. The result revealed that 0.01 g of Pd/ZrO₂ photocatalyst degraded 19.11% dye which gradually increased to 48.1% with the increasing catalyst amount to 0.02 g and any addition beyond 0.02 g of catalyst dosage causes decrease in degradation of dye. The 0.03 g of photocatalyst degraded 16.14% of dye which is very low as compared to degradation of 0.02 g of Pd/ZrO₂ photocatalyst. Similarly, 0.01 g of Pt/ZrO₂ catalyst degraded 25.36% of dye which is gradually increased with the increasing amount of catalyst, and 0.02 g of catalyst degraded about 40.28% of dye, and then increasing Pt/ZrO₂ catalyst dosage further decreases degradation of dye. The 0.03 g of photocatalyst degraded 16.14% of dye which is very low as compared to degradation of 0.02 g of the Pt/ZrO₂ photocatalyst. The result indicates that 0.02 g is the optimal dosage for both photocatalysts for dye degradation, and the increasing catalyst causes decrease in dye degradation. This decrease in dye degradation might be due to the interception of light by suspension and agglomeration of catalyst particles due to which surface for photon absorption becomes

unavailable due to the increased catalyst dosage beyond optimal limit (Akpan and Hameed 2009).

Effect of pH on indigo disulfonate degradation

pH is an important parameters in photodegradation as it plays a vital role in the release of proton and hydroxyl radicals' production. The mechanism of pollutant (dyes) degradation involves the attack of hydroxyl radical, direct reduction by electron in the conduction band, and direct oxidation by the positive holes (Saeed et al. 2016). Different industries such as dyes, textile, and surface coating release their effluents to water reservoirs at various levels. Hence, it is important to evaluate the function of pH on photodegradation of pollutants (Saeed et al. 2015). The effect of pH on the rate of photodegradation of indigo disulfonate is shown in Fig. 5. Figure 5a and b shows UV–Visible spectra of indigo disulfonate before and after UV-light irradiation photodegraded at various pH values in the presence of Pd/ZrO₂ and Pt/ZrO₂. Figure 5c shows the comparison of % degradation of indigo disulfonate photodegraded by Pd/ZrO₂ and Pt/ZrO₂. The results illustrated that the photodegradation of dye increased as by increasing the pH of medium. The maximum degradation is achieved in the basic medium, which might be due to the highest formation of hydroxyl radicals (Saeed et al. 2015). Results show that at pH 3 Pd/ZrO₂ degraded 40.86% dye which decreased to 16.92% at pH 7, while by adjusting pH to 10, the maximum degradation of

97.03% was achieved. Similarly, Pt/ZrO₂ catalyst degraded about 47.47% dye at pH 3 and then degradation decreased to 16.04% by adjusting pH to 7. The photodegradation increased in basic medium and the maximum degradation of 95.93% was achieved at pH 10.

Conclusion

Both Pd/ZrO₂ and Pt/ZrO₂ NPs are effective for photodegradation of indigo disulfonate dye in aqueous medium. The Pd/ZrO₂ NPs were more efficient than Pt/ZrO₂ NPs. It was concluded that indigo disulfonate degradation rate increased as catalyst dosage and irradiation time increased. Both the recovered catalysts also significantly degraded indigo disulfonate dye in aqueous medium but present lower activity than unused catalyst. It was also reported that basic medium is favorable for photodegradation of indigo disulfonate in aqueous medium and Pd/ZrO₂ degraded 97% and Pt/ZrO₂ 95% within 2 h at pH 10.

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