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Preparation of iron–nitrogen doped titanium dioxide nanoparticles and its application for photocatalytic degradation of phenol under UV and visible light

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ABSTRACT

Phenol is one of the most persistent organic pollutants which is toxic for human and its degradability is slow in the environment. The purpose of this study was to evaluate the photocatalytic process efficiency of iron–nitrogen doped titanium dioxide nanoparticles immobilized on a glass bed in removal of phenol from the aqueous medium. This experimental study was carried out on a laboratory scale using a reactor equipped with five UV lamps (6 W). Moreover in order to investigate the effect of visible light, five xenon (6 W) lamps were used as a visible light source. Operating parameters including pH, nanoparticle dosage, source of light, and initial phenol concentration as a function of contact time were investigated. Material characterization was carried out by X-ray diffraction, scanning electron microscope, X-ray microanalysis, and Fourier-transform infrared spectroscopy. The results showed that optimal conditions for phenol degradation under UV light included pH = 5, catalyst dose = 2 g m^{-2}, initial concentration of phenol = 25 mg L^{-1}, and contact time = 90 min. Phenol removal of 88% and COD removal of 65% were reached at the optimal condition. However, the efficiency for visible light was three times less than UV light.

Keywords: Photocatalyst; Phenol; Titanium dioxide; Nitrogen; Iron

1. Introduction

Environmental pollution is one of the major issues that we face in developed and developing countries. In recent years, the world faces many problems regarding shortage of drinking water due to natural disaster, population growth, and water pollution. According to reports, 1.2 billion people do not access to drinking water; approximately 3 billion do not access to water treatment technologies, millions of people die from illnesses associated with contaminated water every year [1]. According to the United States, by 2025, two thirds of the world's population is facing water scarcity. Therefore, the importance of recycling and water treatment becomes more apparent. Resistant organic pollutants are one of the important water contaminants. Phenol and phenolic compounds are the most prominent examples of pollutants, which have been considered as a leading environmental issue by the scientific community due to their resistant to environmental degradation through chemical, biological, and photolytic processes.

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The United States environmental protection agency (USEPA) has classified these compounds as priority pollutants [2]. The European Union has set the maximum acceptable concentration of total phenol in drinking water, 0.5 μg L^{-1}, and the concentration of each individual phenol compound is 0.1 μg L^{-1} [3]. The EPA has set the initial phenol standard for discharge in surface water less than 1 ppb [4]. Phenolic compounds are very important due to toxicity, salinity, high COD, and low biodegradability. These compounds are abundant in sewage, surface water, and underground water and even drinking water, as well as in factory effluents such as coal refinery, phenol production, pharmaceutical industry, resin paints, petrochemicals, pulp, and paper industries [5–7]. Conventional methods that have been used to remove or reduce the concentration of phenols in water have low efficiency, due to the formation of secondary toxic substances, incomplete removal, high consumption of chemicals and time consuming [8,9]. Biological method also cannot decompose a high percentage of organic pollutants [10,11]. While advanced oxidation processes can be used to decompose many organic pollutants into harmless compounds such as water and carbon dioxide [12,13]. The basis of photocatalytic processes is the emission of light into semiconductors and the production of hydroxyl radicals and the decomposition of pollutants through these radicals [14]. Due to high photocatalytic activity, availability, low toxicity, low cost, high stability and environmentally friendly, TiO_2 has proven to be a favorite among the other semiconductors [15]. Despite many advantages, TiO_2 has limitations, such as recombination of electron–hole and large band gap energy which are further excited by UV light. This led to the TiO_2 not being activated by sunlight since UV light is only a small part of sunlight. The recombination of light-emitting electron pairs is one of the main reasons for the low photocatalytic activity of TiO_2. Structural imperfections in the TiO_2 network create traps that act as centers for trapping electrons and holes and thus will lead to reduction of performance. Heretofore, several solutions have been proposed to solve this problem that doping by metals and nonmetal is one of these ways. Among the various elements, Fe^{3+} is most used due to the half-jump electron structure [16]. In addition, ionic radius of Fe^{3+} is very close to TiO_2 (ionic radius of Fe^{3+} and Ti are 0.64 and 0.68 angstroms, respectively). It prevents the combining of electrons and holes and increases the activity of TiO_2 [17]. Doping of TiO_2 with nonmetals such as nitrogen, limit the band gap through a new compound energy band, which is slightly upper than the TiO_2 capacity band [18,19]. It has been shown that the photocatalytic activity of doped TiO_2 by Fe is greater than that of TiO_2 alone, this is due to the smaller size of the crystals and the ability to absorb more light in the doped TiO_2 [20]. Whereas in most of the studies, the removal efficiency has been investigated in suspended form, here the photocatalytic efficiency of iron–nitrogen doped titania nanoparticles supported on glass in removal of phenol from an aqueous media under UV and visible light has been evaluated.

2. Materials and methods

2.1. Preparation of titanium dioxide

2 g TiO_2, Degussa P25 TiO_2 (Evonik Industries, Germany), was combined with 70 mL of 10 M NaOH, and then heated for 24 h in a teflon autoclave at 160°C. The resulting product was washed with distilled water to reach a pH of 7. Subsequently, the nanoparticles were stored for 24 h in a solution of HCl at pH = 1 at free-air temperature to protonate the surface of nanoparticles. It was then washed with deionized water to obtain a pH = 7. Finally, by centrifuging and drying the product in an oven at 80°C for 12 h and followed by calcination at 400°C for 2 h, titanium nanoparticles were obtained.

2.2. Iron–nitrogen doped titania nanoparticles preparation

To synthesize iron–nitrogen doped titania nanoparticles, 0.75 g urea was added to the initial solution during the synthesis process, while other details were retained for the preparation of N–TiO_2 nanoparticles. Doping iron onto TiO_2, N–TiO_2 nanoparticles were immersed in 30 mL of $FeN_3O_9.9H_2O$ solution. After stirring for 24 h, the mentioned combination was dried at 80°C for 12 h and then calcined at 400°C for 2 h.

2.3. Coating of iron-nitrogen doped titania nanoparticles on a glass

First, the sandblasted glass was placed in a concentrated NaOH solution for 24 h and then washed with much plenty of water, Then, to dissipate the Fe–N–TiO_2 nanoparticles, dissolve it in a deionized water, spread it on a glass, leave it at room temperature for 24 h and then at a temperature of 80°C for 12 h and finally calcined in 400°C for 2 h [19].

2.4. Photocatalytic activity experiment

Phenol decomposition was analyzed using synthesized catalyst. Initially, the stock solution of phenol was prepared with a concentration of 1,000 ppm. Phenol concentration was analyzed using UV–Visible T 80 spectrophotometer based on standard methods for the examination of water and wastewater [21]. The concentration of phenol solutions was obtained using a computer program and a calibration curve. In each stage, by changing one parameter and maintaining the other parameters, the phenol removal efficiency at different operation parameters was investigated. Experiments were conducted in a Plexiglass reactor equipped with five xenon lamps (6 W, Philips, the Netherlands) as shown in Fig. 1. Moreover, a peristaltic pump was used for recirculation of solution.

3. Results and discussion

3.1. Properties of nanophotocatalyst (XRD, SEM, EDX and FTIR analysis)

Fig. 2 shows the X-ray diffraction (XRD) patterns of prepared nanophotocatalyst, according to the data presented, TiO_2 samples are crystallized in anatase phase, and their crystallization network is tetragonal. In TiO_2 nanoparticles that are doped with nitrogen, nitrogen atoms replace oxygen atoms in the TiO_2 structure, and because the radius of N and O are nearly close, the defect in the network is not significant. In Fig. 2, the peak appearing in the 50, 29, 44, 48, and 56 degrees' regions associated with the anatase TiO_2 phase and other peak are related to iron oxides.

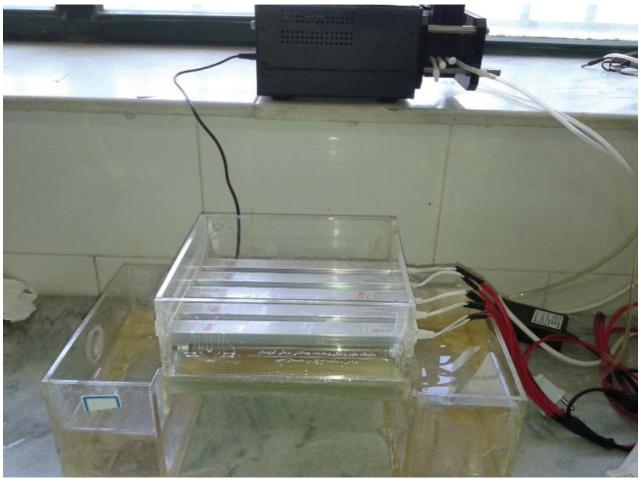

Fig. 1. Plexiglass reactor equipped with five xenon lamps (6 W).

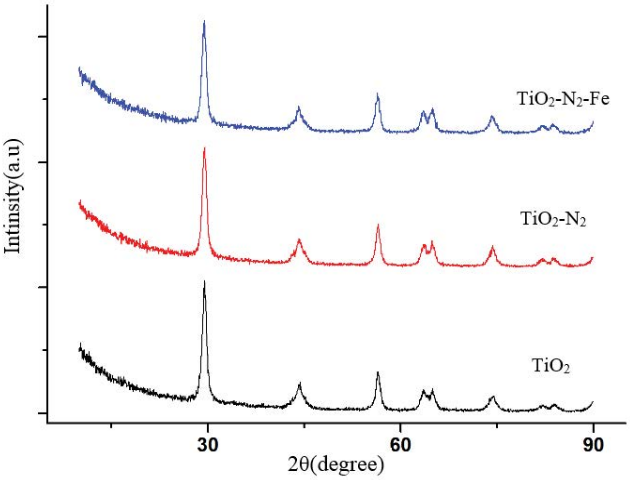

Fig. 2. XRD patterns of iron–nitrogen doped titanium dioxide nanoparticle.

The size of the crystals was calculated by using the X-ray patterns obtained with this formula.

$$D = \frac{(K \times \lambda)}{\beta \cos \theta} \tag{1}$$

The K value of the above equation depends on the shape of the particles, which is considered to be 0.9 for spherical particles, λ is considered as the radiation wavelength of 0.154 nm, and θ is the angle of the peak diffraction and β is equal to the full width of the fractional line at half the highest intensity expressed in radians.

3.2. Fourier-transform infrared spectroscopy

Fourier-transform infrared spectroscopy (FTIR) for Fe–N–TiO_2 is illustrated in Fig. 3. The band located at 3,438 cm^{-1} is attributed to hydroxyl group. The observed peaks at 455 and 484 cm^{-1} indicate the vibrational Fe–O bond, the observed peak in 811 cm^{-1}, indicating the Ti–O vibration band and the observed band of 655 cm^{-1} is a tensile strength band associated with TiO–Ti. The symmetric the peak appeared in 455 cm^{-1} is due to the vibrational Fe–C and it is in 2,000–1,000 cm^{-1} due to the C–N tensile band. The spectrum peak at 989 and 1,037 cm^{-1} is, respectively, due to the tensile bonding of C–N (aliphatic amines) and the C–H bond in the alkenes. Given that during the hydrothermal synthesis method, urea has been added as a precursor, the peak is much wider in the 3,000 cm^{-1} range. The absorption band in the area of 2,900–3,600 cm^{-1} is related to the O–H tensile bond. The peaks in the regions of 3,420–3,450 and 1,630–1,640 are corresponded to tensile vibrations [22]. As can be seen, one of the main peaks in the absorption spectra of the samples is at a range of 3,300–3,500 cm^{-1}, which is due to the presence of water and hydroxyl groups [23]. Also, the peak presented in 2,345 cm^{-1} is because of the presence of CO_2 adsorbed on the surface [24].

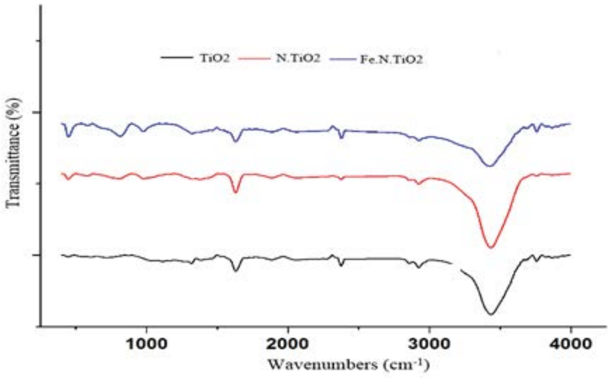

Fig. 3. FTIR of iron–nitrogen doped titanium dioxide nanoparticle.

3.3. Scanning electron microscope and X-ray microanalysis

Figs. 4a and b are scanning electron microscope (SEM) photographs of TiO_2 and Fe–N–TiO_2, respectively. The average particle diameter in pure TiO_2 is 51.6 and in Fe–N–TiO_2 is 45.95 nm, it is observed that pure TiO_2 nanoparticles do not have a specific shape and they are not uniform in size. Figs. 5a and b are X-ray microanalysis (EDX) of Figs. 4a and b, respectively. As shown in Figs. 5a and b, the energy dispersive X-ray microanalysis of pure TiO_2 shows the peak for titanium and oxygen elements and does not show any other impurity in detecting EDX spectrum. It is also seen in Fig. 5b which shows peaks for titanium, iron, nitrogen, and oxygen.

3.4. Photocatalytic activity

The variation of photocatalytic activity of prepared catalyst for phenol degradation at different operational condition was investigated; the results are presented in this part.

3.4.1. Effect of pH

Fig. 6 shows the phenol removal efficiency at various pH values (3, 5, 7, 9, and 11), the constant concentration of

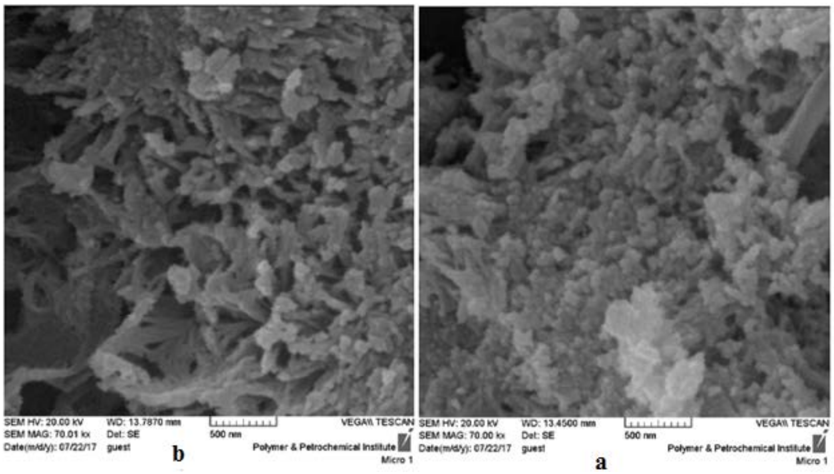

Fig. 4. SEM photographs of TiO_2 (a) and Fe–N–TiO_2 (b).

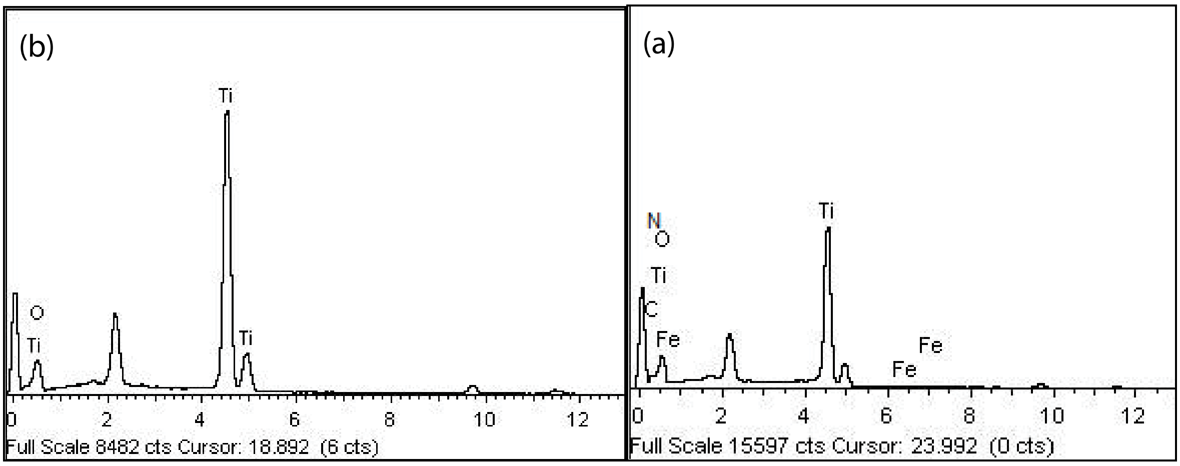

Fig. 5. EDX of TiO_2 (a) and Fe–N–TiO_2 (b).

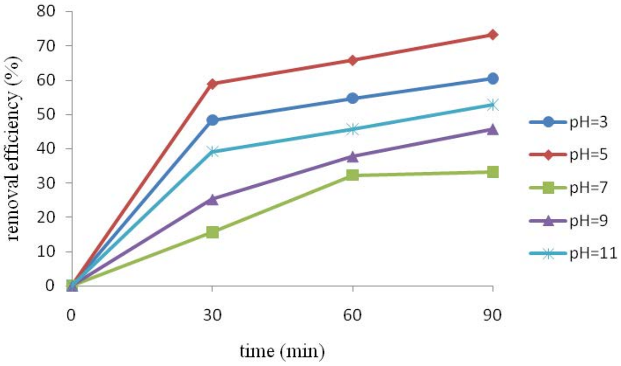

Fig. 6. pH effect on the efficiency of phenol removal (phenol = 50 mg L^{-1}, TiO_2 = 2 g m^{-2}).

phenol (50 mg L^{-1}) and the amount of 2 g of doped titanium dioxide nanoparticles with iron and nitrogen under UV light. As can be seen, the highest percentage of photocatalytic degradation of phenol reached at pH 5 with a yield of 73% and the lowest removal rate was related to pH 7 with a yield of about 33% after 90 min. Results related to the effect of pH on the efficiency of phenol removal indicate that pH is a very important factor in photocatalytic processes. The higher efficiency in acidic pH is due to the fact that at pH values lower than pH_{zpc}, surface of TiO_2 has a positive charge [25] while at this pH organic compounds have a negative charge [26,27]. Therefore, low pH values facilitate the absorption of organic compounds and enhance the photocatalytic degradation efficiency [28]. In addition, the electrostatic reactions between the semiconductor surface, solvent molecules, substrates and formed radicals are strongly influenced by the pH of solution. Protonation of organic compounds also depend on the pH of the solution. However, higher phenol degradation efficiency at alkaline pH than neutral pH is due to the presence of phenol molecules as negatively charged phenolate species, which are more reactive than phenol molecules. Also, in alkaline conditions, the concentration of OH radicals increases [29]. Although this increase can lead to further degradation of the phenol in alkaline conditions compared with neutral conditions, but when the concentration of OH radicals in the solution goes up, it prevents UV light penetration to the catalyst level, and also high pH causes formation of carbonate ions, which can be an OH scavenger and reduce decomposition rates [30,31]. This leads to less phenol degradation efficiency in alkaline pH compared with acidic pH. In the current study, the solution was colorless at the start of the reaction, but after a few minutes of radiation, pink color appears, and some time later, a bright red color appears, then color is dimmed and eventually becomes colorless. This indicates the phenol breakdown to intermediates in the early stages of reaction. Laoufi et al. [32] obtained similar results in a photocatalytic analysis of phenol in water by TiO_2 in a helical reactor that is consistent with the present study [32]. Akbal and Onar [31] examined the effect of pH 3 to 8 in photocatalytic analysis of phenol. The results showed that at low pH, the rate of photocatalytic degradation was high and the highest removal efficiency of phenol was reached at pH 5 [31].

3.4.2. Effect of nanocatalyst dose

The effect of nanocatalyst content (0.5, 1, 2, and 3 g m^{-2}) on photocatalytic degradation of phenol under UV lamp is shown in Fig. 7. The phenol removal efficiency was enhanced with increasing of nanocatalyst content. It is clear that higher activity is because of higher number of active sites of absorption, then the number of absorbed photons increased and eventually the number of phenol-adsorbed molecules increased [33]. The removal efficiency was increased with nanocatalyst increasing from 0.5 to 3 g m^{-2}, while at doses higher than 3 g m^{-2} reduced due to bulk catalyst formation which leads to reduction of light absorption and photocatalytic activity [34,35]. Selvam et al. [36] showed that the 4-fluorophenol degradation constant increased (from 0.0152 to 0.0358 min^{-1}) by increasing the dose of TiO_2 (50–150 mg L^{-1}), while a further increase in the catalyst dose (150–250 mg L^{-1}) resulted in reduction of the rate constant from 0.0358 to 0.0296 min^{-1} [36].

3.4.3. Effect of the initial concentration of phenol

The effect of the initial concentration of phenol on the process efficiency is shown in Fig. 8. It is observed that with increasing concentrations, the efficiency of the process has decreased. After 90 min, with increasing initial concentration of phenol from 25 to 100 mg L^{-1}, phenol removal efficiency decreased from 88.35% to 48.9%. The reduction in efficiency at higher concentrations is due to the fact that the light absorbed by the phenol is greater than the light absorbed by the TiO_2 nanoparticles doped by iron and nitrogen. Therefore, absorbed light is not sufficient for photocatalytic degradation reaction [37,38]. In fact, with the advancement of the decomposition process, especially in the initial concentrations, some of the intermediate products are formed and competitively absorbed on the surface of the catalyst and reacts with active species in a competitive manner [38–40]. In addition, oxidative intermediate products can also react with active substances such as electrons, and eventually lead to a reduction in the rate of decomposition of the substrate [41]. Parida and Parija [42] investigated the effect of the initial concentration of substrate on the photocatalytic degradation of phenol under sunlight, UV light, and visible light. It has been found that by increasing the substrate concentration, under sunlight, the degradation efficiency decreased from 100% to 60%, under UV light from 94% to 52%, and under visible light from 95% to 50% [42].

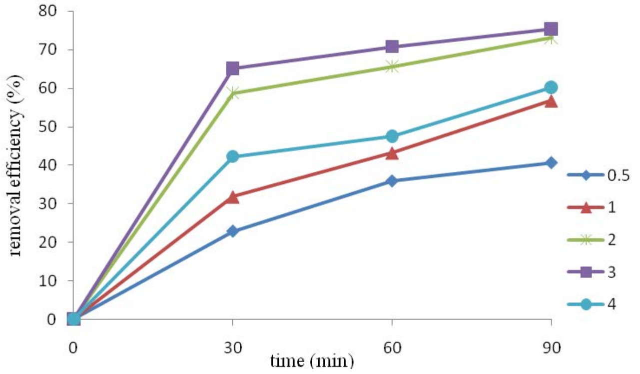

Fig. 7. Effect of the amount of nanoparticles on the removal of phenol (phenol = 50 mg L^{-1}, pH = 5).

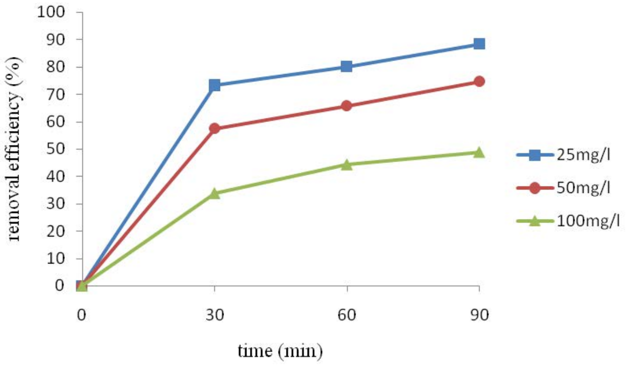

Fig. 8. Effect of initial concentration on the removal of phenol (TiO_2 = 2 g m^{-2}, pH = 5).

3.4.4. Effect of UV and visible light

In order to determine the effect of the visible light and UV on the photocatalytic activity, the optimal condition for removal efficiency under UV light was considered and the experiment was carried out under visible light using xenon

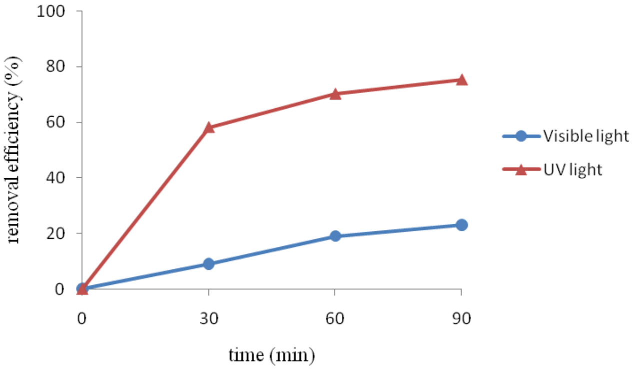

Fig. 9. Effect of the number of lamps on removal of phenol (phenol = 50 mg L^{-1}, pH = 5, TiO_2 = 2 g m^{-2}).

light as a light source. Fig. 9 presents the differences between two light sources. As is observed, the efficiency for visible light was approximately three times less than UV light. Light intensity plays a key role in the photochemical reactions required to form electron–hole pairs [43]. It has been found that the oxidation rate of 95% was achieved within 3 h using a 330 W lamp while this efficiency by a 1,600 W lamp was obtained within 4 h [44]. The low efficiency of phenol degradation in this study may correspond to the low intensity of applied xenon lamp as a visible light source.

4. Conclusion

In this study, phenol photocatalytic degradation using iron–nitrogen doped titanium dioxide nanoparticles immobilized on glass was investigated. The results showed that optimal conditions for phenol degradation under UV light included pH = 5, catalyst dose = 2 g m^{-2}, initial concentration of phenol = 25 mg L^{-1}, and contact time = 90 min. However, the efficiency for visible light was three times less than UV light. Results related to the effect of pH on the efficiency of phenol removal indicate that pH is a very important factor in photocatalytic processes. The higher efficiency in acidic pH is due to the fact that at pH values lower than pH_{zpc}, surface of TiO_2 has a positive charge. The removal efficiency was increased with nanocatalyst increasing from 0.5 to 3 g m^{-2}, while at doses higher than 3 g m^{-2} reduced due to bulk catalyst formation which leads to reduction of light absorption and photocatalytic activity. With increasing initial concentration of phenol from 25 to 100 mg L^{-1}, phenol removal efficiency decreased from 88.35% to 48.9%. The reduction in efficiency at higher concentrations is due to the fact that the light absorbed by phenol is greater than the light absorbed by the TiO_2 nanoparticles doped by iron and nitrogen. The prepared catalyst can be activated under visible light. The low efficiency of phenol degradation in this study may correspond to the low intensity of applied xenon lamp as a visible light source.

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