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Study of the Effect of Nickel Nano Particles and pH on the Photo-degradation of Congo Red

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Abstract Nickel nano particles were synthesized by chemical reduction method using nickel chloride as precursor, hydrazine as reducing agent in a basic medium in presence of surfactant sodium dodecylsulphonate (SDS) and polymer polyvinylpyrolidone (PVP). Titanium dioxide conventionally used as a photo-catalyst for the degradation of Congo red – water pollutant largely used as a dye in textile industries [the line is not match]. Synthesized nickel nano particles of different sizes were mechanically [need specific mechanical process] mixed with titanium dioxide. Measuring the absorbance of congo red solution, congo red solution mixed with titanium dioxide and titanium dioxide with nickel nano particles of different sizes using UV-Vis spectrophotometer, it was found that nickel nano particles accelerate the rate of photo degradation of congo red when it was mixed with titanium dioxide [this sentence is to large]. It was found that with decreasing the size of the nickel nano particles the rate of degradation increases [Need some hypothetical logic for decreasing the size of the nickel nano particles the rate of degradation increases]. Experimental results also show that there is an effect of pH of the solution. The rate of degradation is higher in acidic medium (pH 5.7) instead of basic medium (pH 8) [These two sentences may be merged].

Keywords: *Photo catalyst, absorbance, degradation, UV-Vis, Titanium dioxide, Nickel nanoparticles*

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1. Introduction

A versatile class of colored organic compounds that have extensively been used in industrial appliations such as textiles, paper, leathers, additives and analytical chemistry are azodyes [change the sentence] [1]. From these industries a large quantity of waste water containing dyestuffs with intensive colours and toxicity enter in to the aquatic system [not is only aquatic system but also aquatic biota, geology and also in aquatic environment] [2]. So it is necessary to find an effective method of waste water treatment in order to remove color from effluents. Photo degradation of pollutants in textile and other industrial wastewater has been regarded to be one of the main aims in controlling environmental pollution [water environment pollution] all over the world [3]. Physical and chemical techniques such as coagulation, [settling with long retention time], adsorption on activated carbon, ultra filtration, and reverse osmosis are generally used efficiently to remove dyes from textile waste-water. However, these processes are considered as non-destructive since they merely transfer the dye from liquid to solid wastes.

Consequently, the regeneration of the adsorbent material and post-treatment of solid wastes, which are expensive operations, are needed [4,5]. Advanced oxidation processes (AOPs) are alternative techniques of destruction of dyes and many other organic pollutants in wastewaters and effluents. These processes generally involve UV/H_2O_2, UV/O_3 or UV/Fenton's reagent for the oxidative degradation of contaminants [6]. Among the various AOPs, semiconductor-mediated photo-catalysis has been given great credit over the past few years due to its potential to destroy [please specific "the pollutants is not destroy, it may be changed to another form of eco-friendly materials] a wide range of organic and inorganic pollutants at ambient [it may be "normal exiting"] temperatures and pressures, with no harmful by-products [7]. The commonly studied photo catalysts are TiO_2, ZnO, Fe_2O_3, ZnS, WO_3 and CdS [8] [change this sentence]. In order to achieve more effective photo-catalytic degradation, it is necessary to consider the surface charge property of semi-conductors and the nature of dye molecules [the term semi-conductor is change to metal nano-particle?]. It is known that pH affects the surface charge of semiconductors [metal nano –particle] and can also lead to aggregation phenomenon in dye solutions [9]. Aggregation is one of the features of dyes in solution and ionic dyes tend to aggregate in diluted solutions, leading to dimmer formation and sometimes even higher [higher is omitted and put the term "extension"] order [of] aggregates. In most cases titanium oxide TiO_2 was used as photo catalyst [10,11]. It shows great photo degradation

activity toward many pollutants like organic dyes. UV irradiation is found to be necessary to achieve such decomposition. Many experiments have been carried out to improve the catalyst in order to substitute the UV irradiation by visible light. Titania (TiO_2) [please check] doped with various metals as well as non-metals were found to be active in visible light [12,13,14]. In general, TiO_2 activity depends on many factors: (1) Crystalline phase, anatase was found to be photo catalytically active over the two other forms rutile and brookite [15]. (2) The purity of the phase - commercialized mixture of anatase and rutile (Degussa P25) exhibited much superior photo catalytic activity compared to pure-anatase and rutile [16,17]. (3) The size of the particles, which were very fine particles (a few nanometers in width) showed decrease in photocatalytic activity although the surface area was higher; this is explained by recombination of e−/h+ (electron–hole pairs), which could be high in extremely small particles [18]. (4) The shape of titanium oxide particles: for instance, nanorod shape anatase was found to be less active for Congo red photo degradation than dot shape anatase [19]. In general, titanium oxide, TiO_2, can be prepared by several methods. Many of them require special apparatus, or they are using highly costly starting required especially if it leads to a reactive material. Recently, the interest has grown to improve the optical response of TiO_2 from UV spectrum to the visible range to increase photo-catalysis efficiency for TiO_2. Since the treatment costs can be further reduced by efficiently utilizing solar light as the source of excitation, extensive efforts are currently underway to develop TiO_2 based photo-catalysts that are not only capable of supporting visible light activated photodegradation, but also possess improved photo catalytic reactivity as compared to that of the pure material. The band gap of titanium dioxide would be decreased and visible light absorption would be increased owing to the incorporation of metals into the dioxide structure [20,21,22]. Various studies reported that doped TiO_2 with transition metal ions such as V, Cr, Mn, Fe, Ni or Au extends light absorption into the visible region. The role of loaded metal is trapping and subsequently transferring of photo-excited electron onto the photo-catalyst surface and decreasing the recombination of hole-electron pairs [23]. But very little information is available in the literature related to the effect of metals such as Ni, Cu and Zn depositing on the surface of TiO_2 by means of photo reduction on optical absorption capability [24]. The loaded metals on TiO_2 should be chemically stable during the photo catalytic oxidation reaction or storage in atmospheric condition. Dopage with metals is one of the most efficient strategies to change the intrinsic structure of the gap of TiO_2, which can promote the photocatalytic activity increasing solar light sensitivity. Doping TiO_2 structure modified its crystalline size and/or surface due the presence of metallic nano-compounds deposited over the surface. Several methods such as sol-gel, impregnation (organo-metallic complex, commercial materials, etc.), co-precipitation, implantation, photo deposition, etc. are used for catalyst dopaginge. The aim of this study is to evaluate the effects of doping of TiO_2 with Ni, Cu and Zn via mechanical procedure and wet impregnation during CR photo catalytic de-colorization at acidic (pH=5.7) and alkaline (pH=8.0) conditions.

2. Materials and Method

2.1. Materials

Congo red (M.W.696.67 g mol/l, $C_{32}H_{22}N_6O_6Na_2S_2$), sodium hydroxide, hydrochloric acid, titanium dioxide (TiO_2), nickel nanoparticles (particles prepared in this research). Solutions were prepared by using deionized and distilled water.

2.2. Equipment

Computer controlled photoreactor (CCP-4V) supplied by Luzchem [reference number is needed here], Canada, which uses four set of lamps has been used for the photocatlytic degradation of congo red. Photoreactor enclose irradiation chambers that are about 32 cm (w) x 33 cm (D) x 21 cm (H). Lamps are located at the top and sides. There are different kinds of lamps used in this instrument- UVA lamp, UVB lamp and UVC lamp. CE2041 UV/Vis spectrophotometer was used for optical characterization of the congo red solution titanium di oxide and nanao nickel particles before and after irradiation UV-Vis using Computer controlled photoreactor (CCP-4V). The working rang of this instrument was 190-1000 nm wavelength range with a narrow 1.8 nm optical bandwidth. With straylight of 0.01%, wavelength precision of 0.1nm and baseline stability of better than ±0.001A/hr, the most demanding analytical work may be undertaken.

2.3. Method

Congo red solutions were prepared by using the appropriate amount of congo red in deionized and distilled water. The pH of the congo red solution was controlled by using hydrochloric acid and sodium hydroxide solution of very low concentration. Photo catalytic experiments were performed in an open 100ml Pyrex beaker. This beaker containing congo red solution and 0.05 g TiO_2 was kept inside the photocatalytic reactor (CCP-4V, Luzchem, Canada.). The mixture was stirred for 10 minutes then the lamp was switched on for the irradiation of UVC. Samples were collected after different time periods; the collected samples were analyzed using a UV-Vis spectrophotometer. Experiments were carried out using only congo red solution, congo red solution with TiO_2 and TiO_2 with mechanically mixed nano nickel. The pH of congo red solution was maintained at [by] 8. To study the effect of pH on photo degradation of congo red using TiO_2 as photo catalyst experiments [with Ni, Cu and Zn] and were completed at different pH. To study the effect of concentrations of congo red solution experiments were carried out with different concentrations of congo red solution [please check it].

3. Results and Discussion

Congo red solution of different concentration were prepared. Sodium hydroxide was used to maintain the pH at 5.7 and 8 respectively. Absorbance of the congo red solution of different concentration i.e. 30 ppm, 40 ppm, 50 ppm, 60 ppm, 70 ppm, 80 ppm, 90 ppm, 100 ppm were measured using a UV-Visible spectrophotometer. A plot

of absorbance versus wavelength is shown in Figure 1 for the congo red solution at pH 5.7. Another plot of absorbance versus wavelength is shown in Figure 2 for the congo red solutions at pH 8. Maximum absorbance for the congo red solution determined using the plots shown in Figure 1 and Figure 2, was found to be at 500 nm. This finding is agreement with previous authors [25,26,27] who have also found this to be 500 nm.

Figure 3 shows the standard curve for blank in which absorbance versus concentration of the congo red solution are plotted. The graph shows that the absorbance increases in a linear fashion as the concentration was increased from 30-90 ppm. By using different catalysts for example TiO_2, TiO_2 mechanically mixed with nano nickel, changes in the concentration of congo red after irradiation of UVC could be found using a similar plot as shown in Figure 3. The absorbance of the congo red solution after irradiation with UVC for different time with titanium oxide photo catalyst and titanium oxide with mechanically mixed nickel nanoparticles was determined.

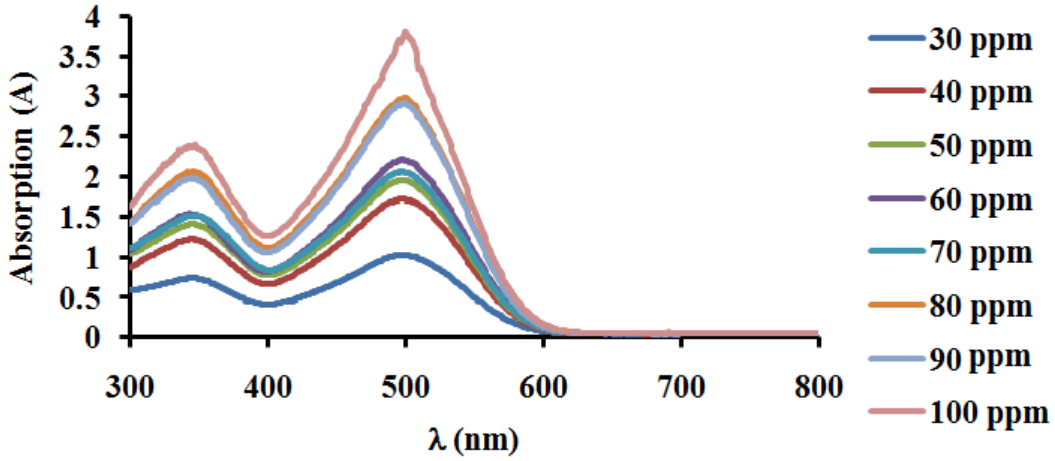

Figure 1. Absorbance versus wavelength for different concentration of congo red solution at pH 5.7

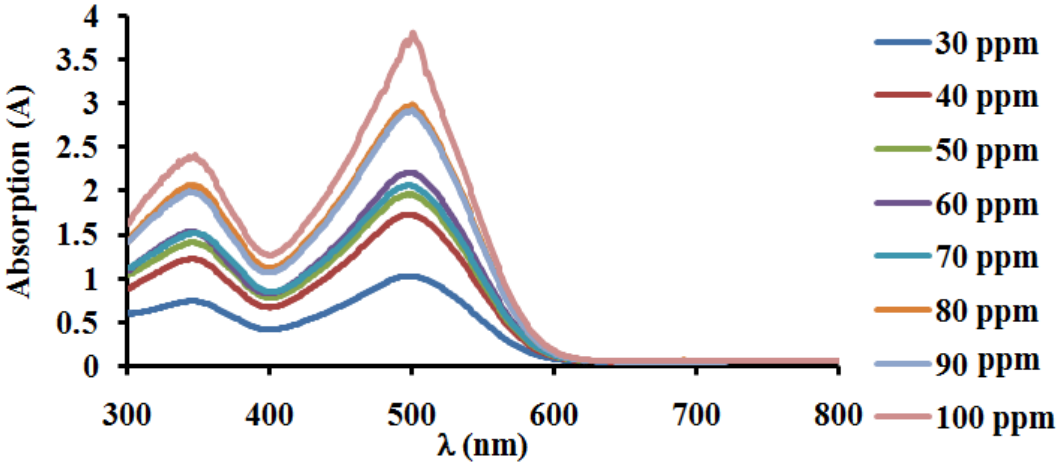

Figure 2. Absorbance versus wavelength for different concentration of congo red solution at pH 8

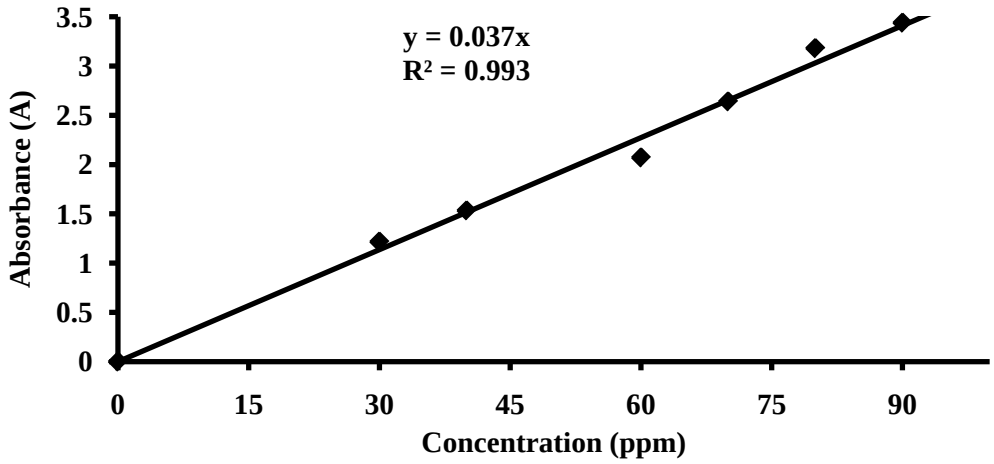

Figure 3. Standard curve (Concentration versus absorption) for blank i.e. after irradiation of UVC on 30ppm congo red solution at pH 8

Figure 4 shows the changes in absorbance of the congo red dye with time of exposure to UVC on 30 ppm congo red solution containing 0.5 g/l TiO_2 photocatalyst at pH 8. Figure 5 shows the change in absorbance of the congo red solution with time of exposure of UVC on 30 ppm congo red solution containing 0.5g/l TiO_2 with mechanically mixed nickel nanoparticles (1) photo catalyst at pH 8. Figure 6 shows the change in absorbance of the congo red solution with time of exposure of UVC on 30 ppm congo red solution containing 0.5g/l TiO_2 with mechanically mixed nickel nanoparticles (2) photo catalyst at pH 8. Figure 4, Figure 5 and Figure 6 shows that the photo catalytic activity of TiO_2 for the photo degradation of congo red is higher than that of the mechanical mixture of TiO_2 with nickel nano particles in the basic medium i.e. at pH 8. Figure 7 shows the comparative study of the degradation using TiO_2, TiO_2 with MNT1 and TiO_2 with MNT2 which also similar to the earlier statement.

Figure 8 shows absorbance at different time after irradiation with UVC on 30 ppm congo red solution at pH 5.7 without any TiO_2 or TiO_2 mixed with nickel nanoparticles. Figure 9 shows the change in absorbance of congo red solution with time of exposure of UVC on 30 ppm congo red solution containing 0.5g/l TiO_2 with photo catalyst at pH 5.7. Figure 10 shows the change in absorbance of the congo red dye with time of exposure of UVC on 30 ppm congo red solution containing 0.5 g/l TiO_2 mixed with nickel nano particles (1) as photo catalyst at pH5.7. Figure 11 shows the change in absorbance of the congo red solution with time of exposure to UVC for the 30 ppm congo red solution containing 0.5g/l TiO_2 mixed with nickel nano particles (2) as photo catalyst at pH-5.7. Figure 12 shows the comparative study of these three sample at pH 5.9. The experimental plots show that the photocatalytic activity of nickel nano particles mechanically mixed with TiO_2 is higher than that of the TiO_2 only in an acidic medium with pH5.7. From these experimental results it can be stated that nickel nano particles are very efficient in removing congo red from the industrial waste water at pH5.7. The rate of decomposition of congo red increase with decrease in the size of the nano nickel particles. Hence, the application of nickel nano particles in the removal of congo red is much better than those conventionally used photo catalyst. Congo red is itself an acidic compound, based on the experimental results obtained in this research it can be recommended that this dye should be removed from industrial waste water in acidic medium using nickel nano particles. Using the same procedure it would be possible to remove other organic dyes from the industrial waste water by using nickel nano particles as a photo catalyst with titanium di oxide which will help to keep water safer for human consumption and other living creatures that depend on the environment for water.

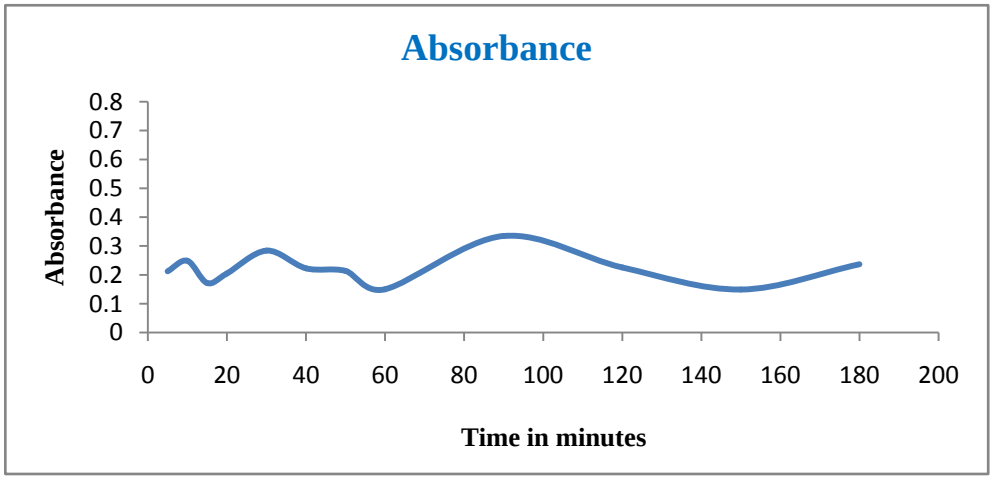

Figure 4. Plot of absorbance versus time (minutes) for the TiO_2

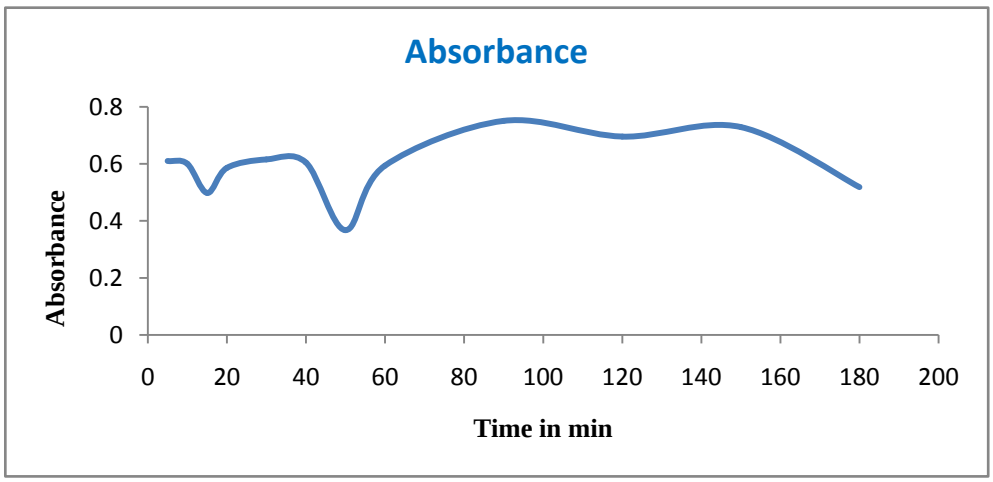

Figure 5. Plot of absorbance versus time in minutes for the TiO_2 mechanically mixed nickel nanoparticles (1) at pH 8. (MNT1)

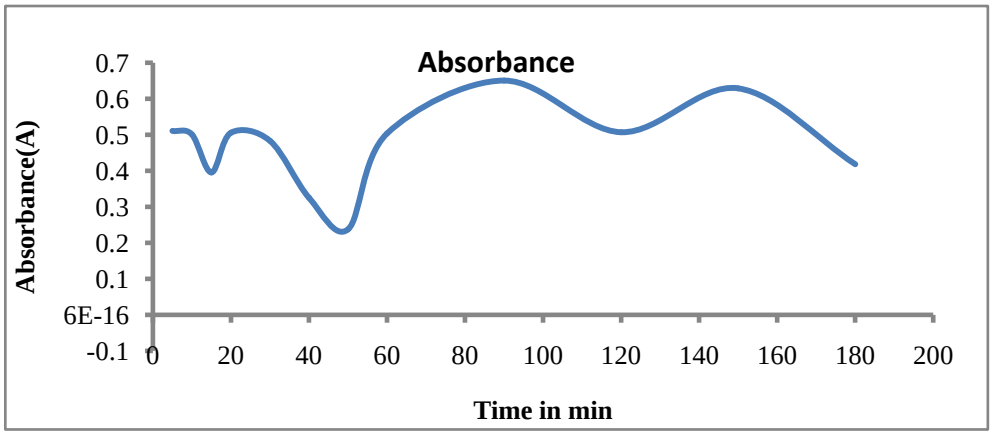

Figure 6. Plot of absorbance versus time in minutes for the TiO_2 mechanically mixed nickel nanoparticles (2) at pH 8. (MNT2)

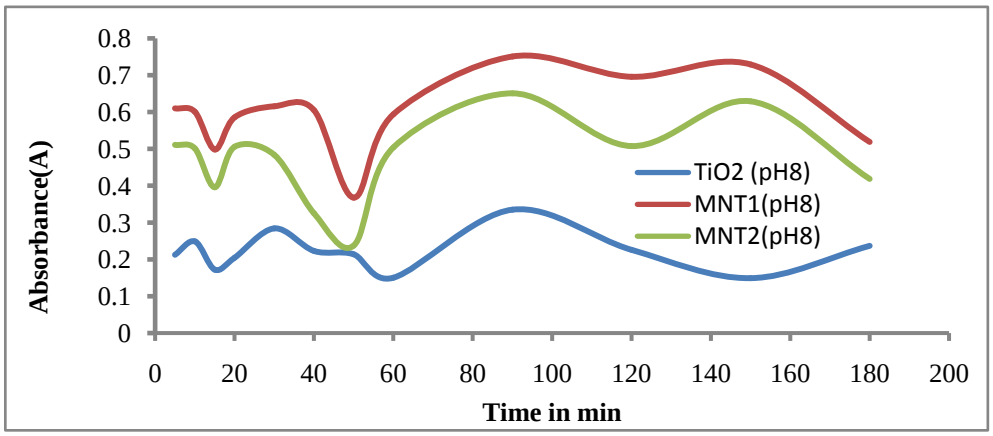

Figure 7. Plot of absorbance versus time in minutes for the three samples at pH 8

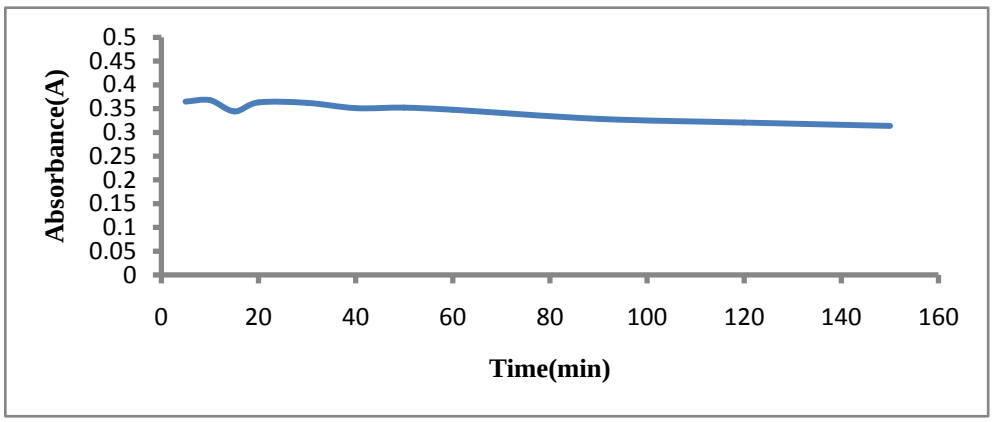

Figure 8. Absorbance at different time after irradiation of UVC on 30ppm congo red solution at pH5.7

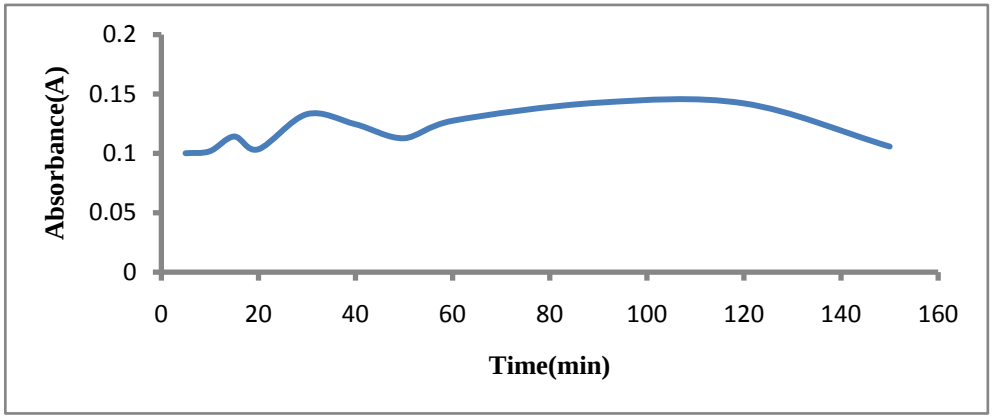

Figure 9. Absorbance at different time after irradiation of UVC on 30ppm congo red solution at pH 5.7 in presence of TiO_2

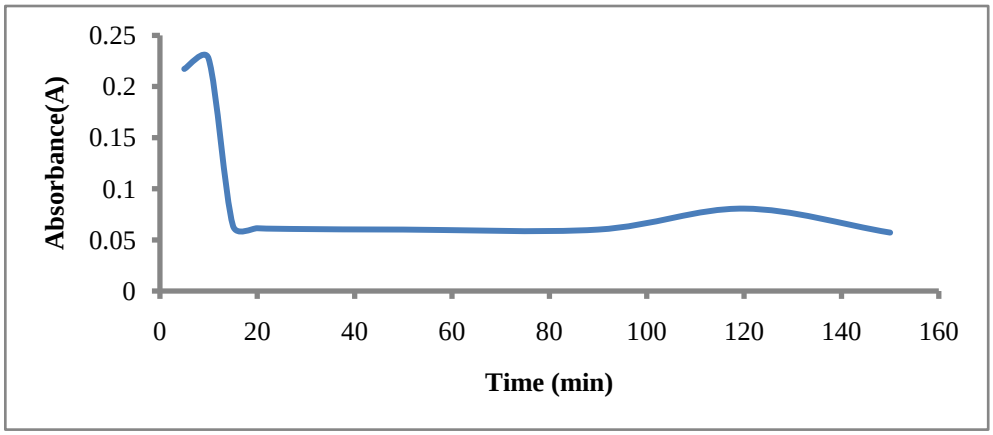

Figure 10. Absorbance at different time after irradiation of UVC on 30ppm congo red solution at pH 5.7 in presence of TiO_2 (sample MNT1)

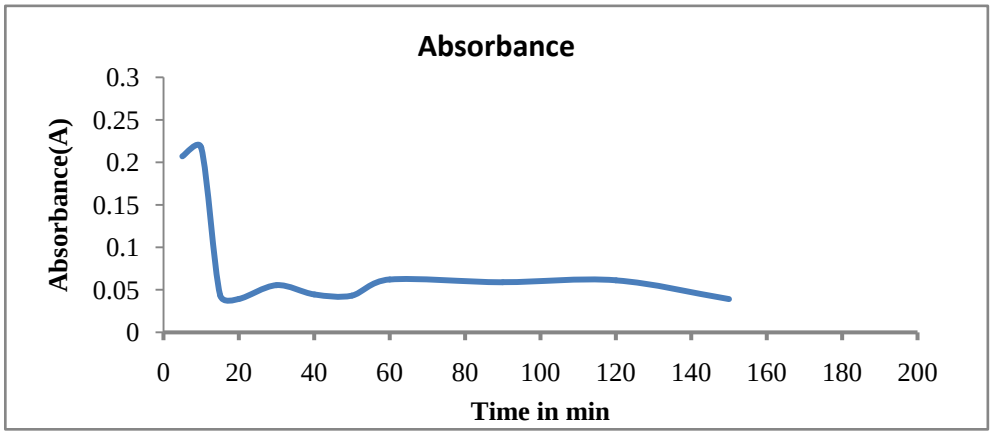

Figure 11. Absorbance at different time after irradiation of UVC on 30 ppm congo red solution at pH 5.7 in presence of TiO_2 (MNT2)

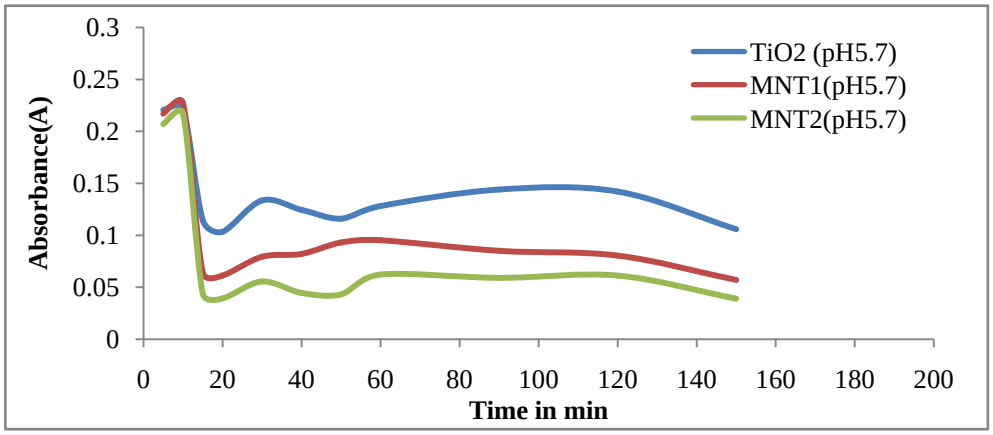

Figure 12. Absorbance at different time after irradiation of UVC on 30ppm congo red solution at pH5.7

4. Conclusion

In this research work nano nickel particles have been synthesized and photo-degradation of congo red by using TiO_2 in presence and absence of nickel nano particles was investigated. Photo degradation dependent on the pH of the congo red solution. Absorbance results shows that presence of nickel nano particles accelerate the rate of photo-degradation of congo red solution. Results also shows that size of the nickel nano particles plays an important rule on the rate of photo-degradation of congo red. Decreasing the particle size of nickel nano particles the rate of photo-degradation of congo red increases [why please explain here].

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