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Photocatalytic Degradation of O-nitrophenol using Silver Impregnated TiO_2

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Abstract

Treatment of wastewater containing organic pollutant has always been a problem for industries because of the stringent environmental regulations and recalcitrant nature of the organic pollutants. o-Nitrophenol(o-NP) is a primary pollutant listed by USEPA and found in the waste water discharged from various industries. For the treatment of o-NP, photocatalytic degradation has been conducted under UV irradiation with silver impregnated TiO_2 as a semiconductor photocatalyst. The experiments have been performed under batch and continuous conditions. The effect of photocatalyst dose, o-NP concentration, initial solution pH, light intensity and presence of interfering substances has been studied under the ambient conditions. The decolorization of 2-NP has been ascertained by monitoring remaining fraction of o-NP and mineralization verified by monitoring remaining COD of the o-NP solution.

Keywords: O-Nitrophenol, Photocatalysis, Ag impregnated TiO_2.

1. Introduction

Nitrophenols are stable and soluble in water. The presence of the nitro group on phenolic ring makes it more resistant to chemical and biological degradation. Also, Nitrophenols mostly exist in three isomeric forms namely, o-Nitrophenol, m-Nitrophenol and p-Nitrophenol (Keith and Telliard, 1980; USEPA, 1980). o-Nitrophenol(o-NP) is a light yellow solid with a peculiar sweet smell. It is harmful to aquatic life even in very low concentration. Since o-NP is toxic and bioaccumulative (Ksibi et al., 2003), it has been listed as a primary pollutant by USEPA (Keith and Telliard, 1980; USEPA, 1980).

Photocatalytictreatment is an effective oxidation process for the treatment of toxic and bio-resistant pollutants at a low energy cost (Ksibi et al., 2003). In the Photocatalytictreatment process semiconductor photocatalystinteracts with UV light of sufficient energy,resulting in photo excitation of electrons from valence band to conduction band leaving positive holes. This e^--h^+ pairs take part in producing free radicals ($OH^{\cdot}$, $HO_2^{\cdot}$, O_2^-) on the surface of the photocatalyst(Chun et al., 2000). The end products of photocatalytic treatment are innocuous products: water, CO_2 and some inorganic ions. Recent studies have represented TiO_2 as an excellent semiconductor photocatalyst for complete mineralization of phenol and its derivative in water and wastewater. The properties of TiO_2which makes it extensively used photocatalyst are: non toxicity, chemical and biological inertness, insolubility in water, semiconductivity, high stability, resistance against photo-chemical corrosion, ease in operation and low cost. The work is a part of on-going research in IIT Kharagpur under the supervision of Dr. A.K. Gupta.

2. Materials and Methods

2.1 Materials and Reagents

O-nitrophenol was purchased from LobaChemiePvt. Ltd., India. Titanium dioxide was purchased from Merck India Pvt.Ltd.Potassium dichromate; sulphuric acid and mercuric sulphate used for preparation of digestion solution were purchased from Merck India Pvt. Ltd. Sulphuric acid reagent was prepared using silver sulphate and conc. sulphuric acid. Na_2SO_4, $NaNO_3$, purchased from Merck India Pvt. Ltd. and Na_2CO_3 from Analytical Rasayanand used as interfering substances. All reagents were of analytical grade and were used without further purification. Genesis 20 spectrophotometer of Thermo Spectronic USA (model No: 4001/14) was used to measure COD removal. The decolorization of the o-NP was monitored by UV-vis spectrophotometer (UV-Thermospectronic, England) at 352 nm wavelength.

3. Results and Discussions

3.1 Determination of Photocatalyst Dose

The variation in decolorization and mineralization rate of o-NP against the dose of Ag impregnated TiO_2(Photocatalyst) was ascertained over the range 0.5-4.0 g/L by irradiating the sample solution (50 mg/L) for 2h(Figure 1). Both the decolouration rate and mineralization rate initially increased with the increase in dose of Photocatalyst with a maximal value at 1.5 g/L. This increase in rate may be due to availability of more surface area of photocatalyst to produce hydroxyl radicals. After the maximal value, degradation rate slightly decreased. The decrease in rate can be attributed to lesspenetration of UV light into aqueous solution and scattering oflight due to turbidity caused by excess of photocatalyst. The excessive dose results in agglomeration of photocatalyst particles and hence decreases in surface area to contact with incident radiation and generation of hydroxyl radicals(Ahmed et al., 2010; Chun et al., 2000).

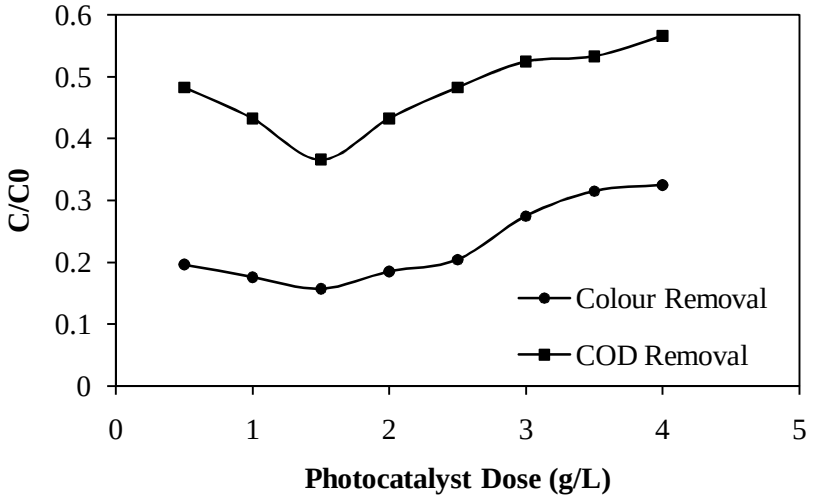


Figure 1: Effect of photocatalytic dose on o-NP decolorization and mineralization rate (o-NP conc. = 50 mg/L, Irradiation time= 2h, Initial pH=6.22, Temperature= 30±2 °C)

3.2 Effect of Irradiation Time

To elucidate the influence of irradiation time on decolorization and mineralization rate, photocatalysis was performed by treating aqueous solution of o-NPof concentration 50 mg/L and photocatalytic dose of 1.5 g/L for 6h(Figure2). Initialdegradation rate is higher that may be due to more contact between photocatalyst surface and o-NP. Lateron the degradation rate is slower that may be due to the availability of less surface active sites on photocatalyst surface.

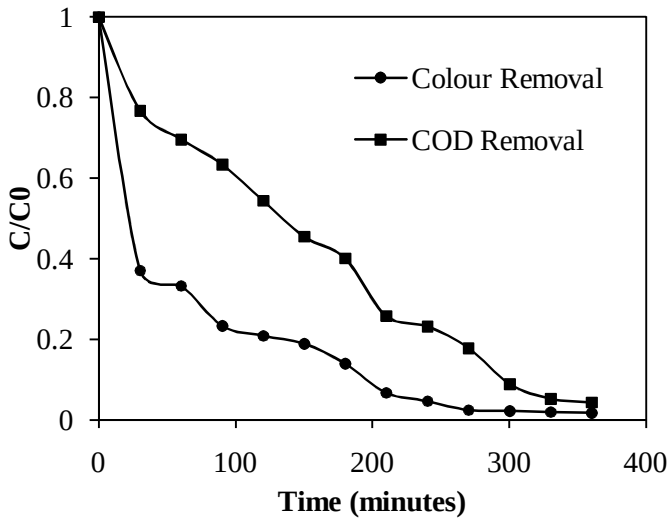


Figure 2: Effect of irradiation time on decolorization rate andmineralization rate of o-NP (o-NP conc. =50 mg/L, Photocatalyticdose= 1.5 g/L, Initial pH=6.22, Temperature= 30±2 °C)

3.3 Effect of Initial pH

Influence of initial pH on mineralization of o-NP was ascertained over a pH range of 2 to 11 for an irradiation time of 2h (Figure 3)**.**The solution pH was adjusted using 0.05N HCl and 0.1N NaOH. In the acidic range, o-NP mineralization rate is higher. The trend could be explained in terms of functional groups ($TiOH_2^+$,TiO^- and TiOH) present on the photocatalystsurface. At $pH<pH_{ZPC}$catalyst surface is positively charged ($TiOH_2^+$,) and at $pH>pH_{ZPC}$ catalyst surface is negatively charged (TiO^- and TiOH) (Sahoo et al., 2005). The zero point of charge (ZPC) of Ag impregnated TiO_2 is 7.4. Below this ZPC, $TiOH_2^+$ functional group is dominated and electrostatic attraction takes place between positively charged catalyst surface and negatively charged hydroxyl group resulting in formation of free hydroxyl radicals. These hydroxyl radicals are highly reactive and later take part in oxidation of o-NP. (Ahmed et al., 2010; Ksibi et al., 2003).

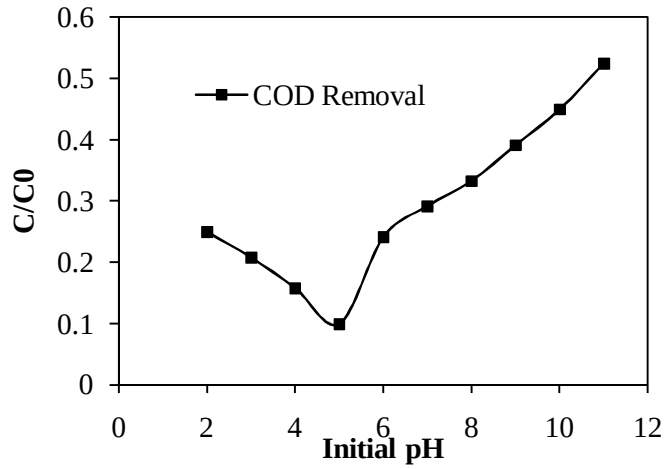


Figure 3: Effect of pH on mineralization of o-NP (o-NP conc. = 50 mg/L, Photocatalytic dose= 1.50 g/L, Irradiation time = 2h, Temperature= 30±2 °C).

3.4 Effect of Light Intensity

Light intensity plays an important role in degradation rate. The effect of UV-light intensity on the degradation of o-NP is shown in Figure 4. It has been observed that the fraction of remaining concentration of o-NP and COD is decreasing with increase in UV light intensity. The decrease of remaining concentration is due to increase in highly reactive hydroxyl radical concentration. At high UV intensity more hydroxyl radicals are produced due to the reaction of H_2O/OH^- with e^--h^+ pairs. (Ahmed et al., 2010)

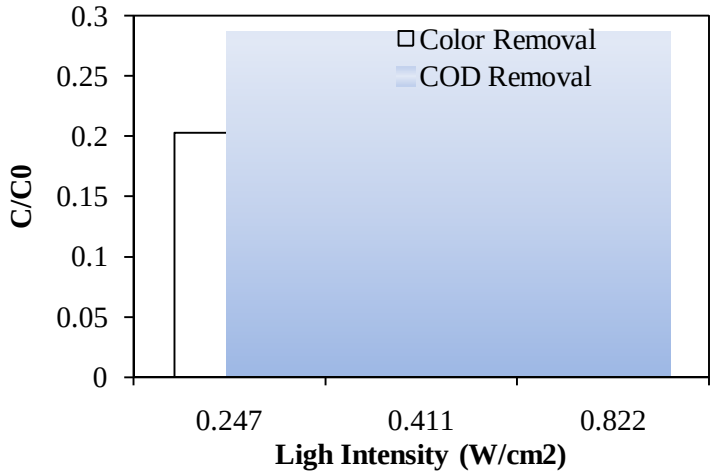
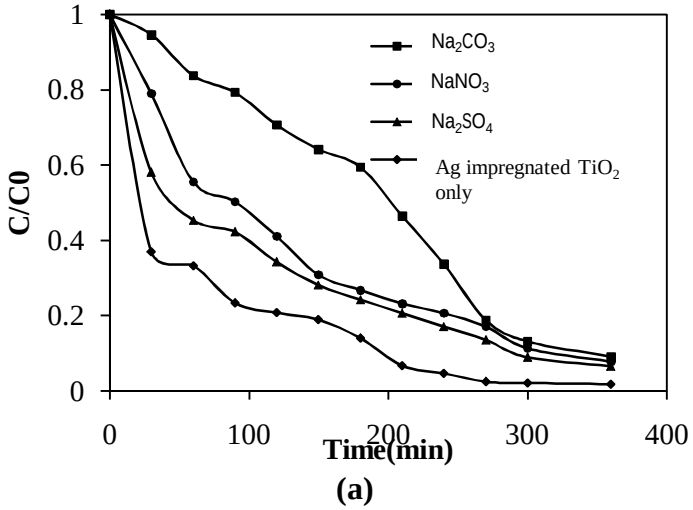


Figure 4: Effect of light intensity on degradation rate of o-NP (o-NP conc.=50 mg/L, Irradiation time= 2h, Photocatalyticdose=1.5 g/L, pH=6.22, Temperature = 30±2 °C)

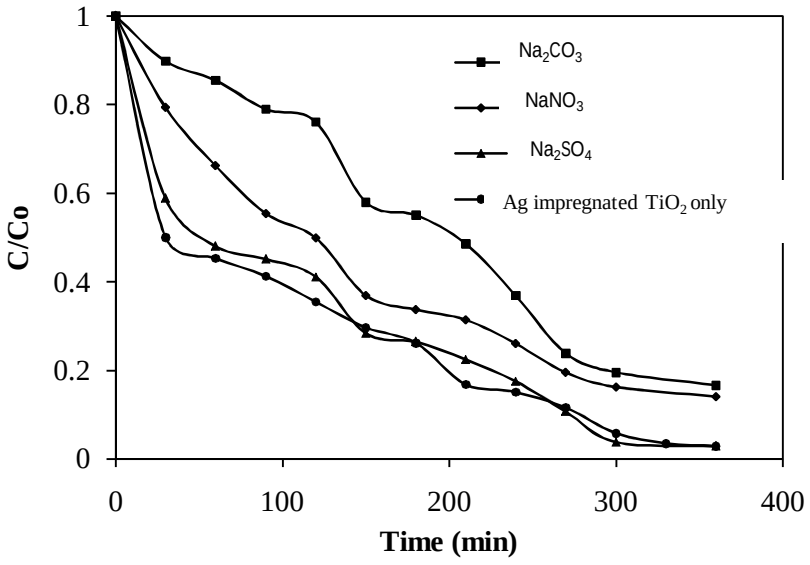
3.5 Interfering Substances

The effect of interfering substances (anion) on decolorization and mineralization rate of o-NP was investigated. The individual anions [CO_3^{-2}(500 mg/L), NO_3^- (500 mg/L), SO_4^{-2}(200 mg/L)] were mixed with aqueous solution of o-NP with 1.5 g/L dose of photocatalyst(Figure 5). The presence of anions in aqueous solution causes significant inhibition in degradation rate. This inhibition can be due to competitive adsorption effect of anions on photocatalyst surface and OH radical scavenging effects of anions. CO_3^{-2} showed the highest OH radicals scavenging effect by the following equations (Ahmed et al., 2010; Sahoo et al., 2005) (Eq. 1):

$$CO_3^{-2} + \cdot OH \rightarrow OH^- + CO_3^{-\cdot} \quad (1)$$



(a)



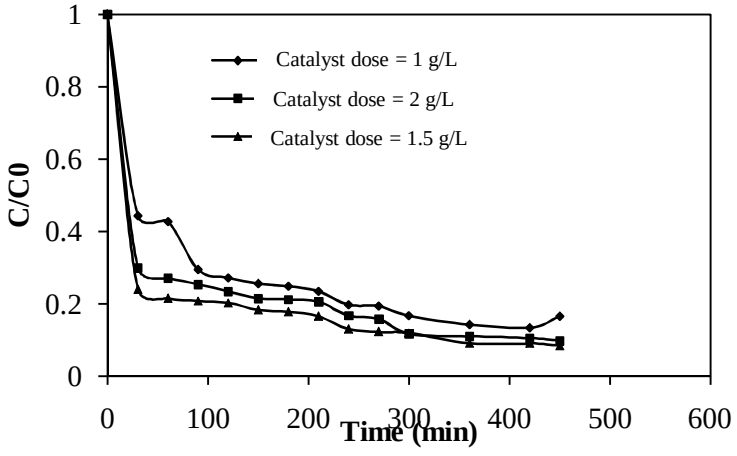
(b)

Figure 5: Effect of anions on (a) decolourisation and (b) COD removal rates of o-NP (o-NP conc. =50 mg/L, Photocatalyticdose= 1.5 g/L, pH=6.22, Temperature = 30±2 °C).

3.6 Application of Continuous Flow Reactor

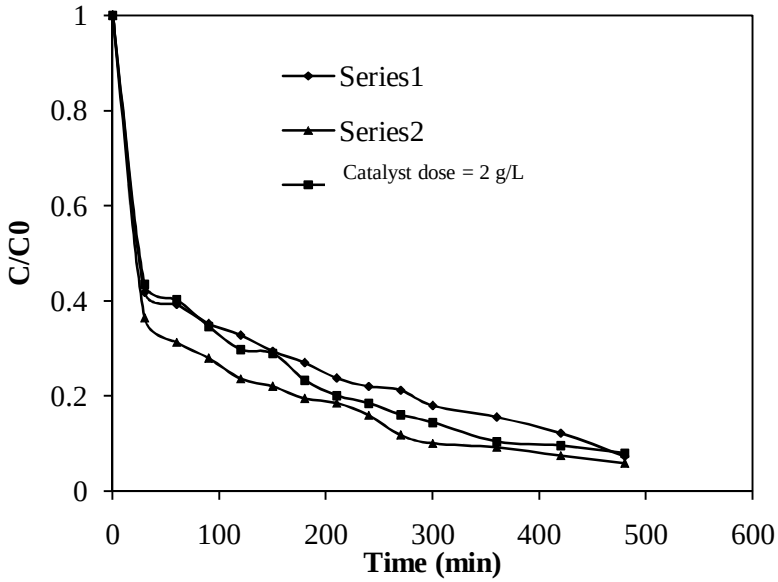
3.6.1 Effect of Photocatalyst Dose

The effect of photocatalyst dose on the decolorization and mineralization was investigated by introducing aqueous solutions of o-NP of 50 mg/L concentration and photocatalytic dose in to the continuous flow reactor at flow rate of 1.5 L/h. From Figure 6a&b it was observed that decolorization and mineralization rates increased with time for a particular photocatalyst dose and were maximal for a dose of 1.5 g/L.



Catalyst dose = 1 g/L

(a)



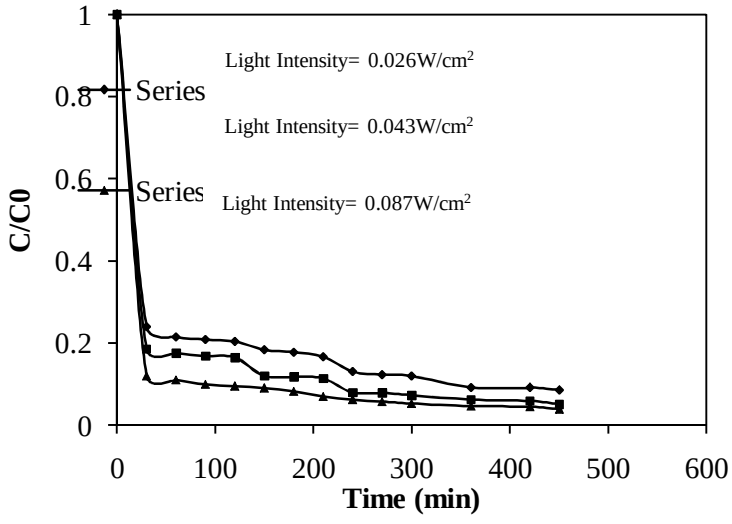
Catalyst dose = 1.5 g/

(b)

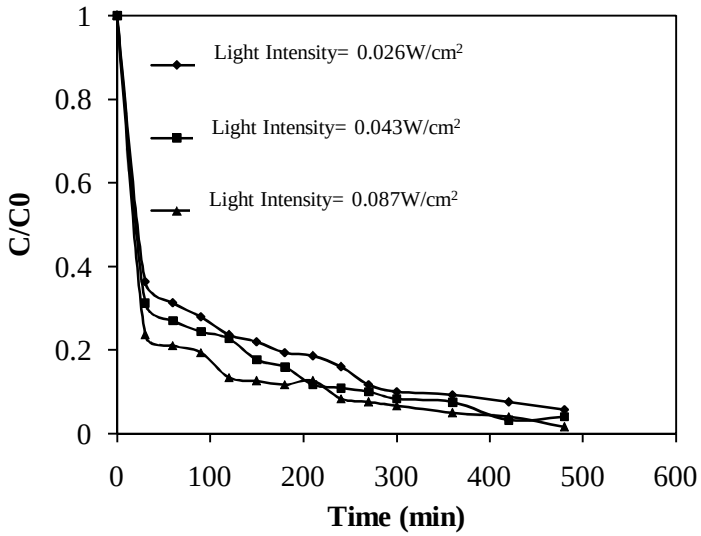
Figure 6: Effect of photocatalyst dose on (a) decolorization rate (b) COD removal rate of o-NP in a continuous flow reactor (o-NP Conc.=50 mg/L, Initial pH=6.22, Temperature = 30±2 °C).

3.6.2 Effect of Intensity of UV Light

The effect of UV light intensity on the decolorization and mineralization of aqueous solution of o-NP was investigated by conducting the experiment with aqueous solution of o-NP (50 mg/L) and photocatalyst (1.5 g/L) in the continuous flow rector under irradiation from 15 W, 25 W and 50 W UV lamps respectively (Figure 7a&b).



(a)



(b)

Figure 7: Effect of UV light intensity on (a) decolorization rate and (b) COD removal rate of o-NP in a continuous flow reactor (o-NP Conc.=50 mg/L , Photocatalytic dose=1.5 g/L, pH=6.22).

From the figure, it is observed that, the decolorization rate and mineralization rate increased with increase in UV light intensity. This may be because, with increase in UV light intensity, number of catalyst particles irradiated increased and number of oxidizing species produced also increased.

4. Conclusion

Photodegradation can be an alternative treatment method for the contaminants which are resistant to conventional methods. Photodegradation can be used for complete mineralization of o-NP. UV/TiO_2 process for o-NP degradation is compatible with the environment. The incorporation of silver on semiconductor surface allowed quicker separation of electron-hole pair and reduced the recombination process. The reaction rates of photocatalytic degradation of o-NP can be influenced by various operating parameters such as initial concentration, catalyst amount, initial pH and the presence of ionic compounds in solution. The influence of these parameters was studied under batch and continuous conditions.

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