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Influence of Inorganic Salts during the Photooxidative Process of Nitrobenzene

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Abstract: Into the photooxidation process, several factors such as pH, time of irradiation, dose of UV light, lamp power, contaminant concentration, turbidity of the solution and the presence of salts can interfere with the photodegradation of pollutants. This research aims to evaluate the influence of salts: NaCl, $MgCl_2$, $CaCl_2$, $BaCl_2$, $CuCl_2$, Na_2SO_4, $MgSO_4$, $MnSO_4$, $FeSO_4$, $CuSO_4$, Na_3PO_4, K_2CrO_4 and $K_2Cr_2O_7$ in concentrations of 0.0005 M, 0.005 M and 0.05 M during photodegradation of aqueous solution of 59.5 mg/L of nitrobenzene at a pH of 2.5. It was observed that the presence of salts such as $CuCl_2$, $CuSO_4$, $FeSO_4$, K_2CrO_4 and $K_2Cr_2O_7$ interfere negatively in the system UV/H_2O_2 applied for degradation of nitrobenzene; possibly by oxidation of Fe^{2+} to Fe^{3+} and Cu^{+} to Cu^{2+} in the Cr case, due to the difficulty of transforming the Cr^{6+} to Cr^{3+} or because these solutions have color and act as radiation absorbing filter.

Key words: AOPs, nitrobenzene photooxidation, influence by salts.

1. Introduction

The majority of wastewater discharges are organic compounds that are very stable and thus persistent in the environment, and are unchanged in water, soils and bioaccumulate in living organisms without being degraded or processed at least compounds toxic [1]. This wastewater also contains inorganic substances which can interfere in natural photodegradation organic contaminants. This is the case of wastewater contaminated with nitrobenzene, which is an aromatic organic chemical compound, used in various industries such as raw material or solvent.

Nitrobenzene has been classified as a priority contaminant, due its toxicity to the central nervous system, and its refractory nature to conventional chemical oxidation. A small quantity of nitrobenzene may cause slight irritation on direct contact with eyes or skin. Continuous exposure to a high concentration of nitrobenzene cause methemoglobinemia, this condition reduces the blood capacity to transport oxygen. The maximum allowable level in water bodies recommended by the EPA is 17 ppm, thus avoiding possible health effects [2].

Nitrobenzene found in several industrial effluent in chemical and plastics in higher concentrations to 3.8 g/m^3 in pulp and paper industries in concentrations greater than 0.12 g/m^3, explosives factories concentrations greater than 0.05 g/m^3. Also in municipal wastewater, concentrations are between 0.02 g/m^3 and 0.1 g/m^3 [3, 4]. Its low volatility and weak adsorption in soil suggest that surface water and groundwater could be a route of exposure to this pollutant for the general population.

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Overall conventional treatment methods for these organic compounds present in the wastewater are chemical oxidation, air flotation, liquid-liquid extraction, adsorption, reverse osmosis, ultrafiltration or biological treatment [5].

AOPs (advanced oxidation processes) are modern methods based on physicochemical processes which can produce profound changes in the chemical structure of pollutants because they involve the generation and use of transient species with high oxidizing power as the ·OH (hydroxyl radical). This radical can be generated by various means and is highly effective for oxidation of organic material, especially the one which is not biodegradable and recalcitrant [6, 7]. These processes are usually applied to small or medium scale, especially where conventional methods lose their efficiency. This is the case of water with concentration of toxic contaminants. The AOPs (UV/H_2O_2, UV/O_3 and UV/H_2O_2/O_3) generally may be used alone or in combination with them [7].

A research has been conducted to the degradation of nitrobenzene studying the influence of the initial pH onto the degradation performance of nitrobenzene in aqueous solution, the experiments was developed with a semicontinuous batch reactor in the processes of ozone alone, ozone/ceramic honeycomb, and adsorption of ceramic honeycomb. The results indicate that the initial pH affects significantly both the residual ozone concentrations and the efficiency of the ozone utilization. The total organic carbon elimination and the formation, or evolution, of intermediate products, at different initial pH parameters, was detected during the catalytic ceramic honeycomb ozonation process [8]. Other study investigated the role of the bandgap, superface area and the phase composition on the photocatalityc activity of the nanocrystalline Ti_2O [9]. This study investigated the photocatalytic degradation of nitrobenzene solution (50 ppm) using TiO_2 nanocrystals with different band-gap values compared to TiO_2 Degussa P-25. Degradation rate of nitrobenzene in each case was calculated to evaluate the photocatalytic activity of each sample. The nitrobenzene mineralization in aqueous solution was confirmed by the COD (chemical oxygen demand) analysis [10]. Comparative studies of nitrobenzene and nitroaromatic degradation performance have been realized adding pure and cupper doped iron shavings, proving that iron chips without Cu dopant exhibit a very low reactivity at high pH compared whit Cu doped chips [11]. Another study investigated the effect of initial pH, reaction time and the influence of different concentrations of HCO_3^- and CO_3^{2-} on the sodium acetate [12] and nitrobenzene [13] removal efficiency, using ozone as oxidant [12] natural pollutants of water which react rapidly with the ·OH radical, due to its reaction constants: 7.9×10^7 L/mol·s and 4.2×10^8 L/mol·s, respectively, having a significant influence over the oxidation process [14]. Because the nature and residual water usually contains more than one pollutant. Such additional contaminants may affect the photooxidation process in a positive or in most cases be negative form. A review of the effects of some salts to analyze the secondary reactions that occur between organic free radicals (·OH), inorganic species hydroxyl radicals and other transient intermediates, was published by Zafiriou et al. [15]. This research aims to determine the influence of the presence of different species of inorganic salts in different concentrations of nitrobenzene photooxidative process.

2. Substances and Reagents

Nitrobenzene (J.T. Baker), 99% sulfuric acid (Karal), 98% by volume phosphoric acid (Mercury), 85% by volume hydrochloric acid (Fermont) at 37.2% by volume hydrogen peroxide 50% by volume. (Medina Farmadroguería Puebla), anhydrous sodium sulfate (J. T. Baker), magnesium sulfate heptahydrate (J. T. Baker), manganese II sulfate monohydrate (Baker), cupric sulfate pentahydrate (J. T. Baker), ferrous sulfate heptahydrate (J.T. Baker), phosphate sodium dodecahydrate (J. T. Baker), sodium chloride (J.T. Baker), calcium chloride (J.T. Baker), magnesium chloride (Merck-Schuchardt), barium chloride dihydrate (J.T. Baker), cupric chloride dihydrate (J.T. Baker), dichromate potassium (J.T. Baker), and potassium chromate (J.T. Baker).

Table 1 shows the amount in grams of the salt necessary to form the different solutions used in this investigation.

Table 1 Amount in grams of the salts used to form the solutions.

Salt	0.0005 M	0.005 M	0.05 M
Na_2SO_4	0.056	0.560	5.600
$MgSO_4 \cdot 7H_2O$	0.098	0.986	9.860
$MnSO_4 \cdot H_2O$	0.067	0.676	6.76
$FeSO_4 \cdot 7H_2O$	0.111	1.112	11.122
$CuSO_4 \cdot 5H_2O$	0.093	0.934	9.342
NaCl	0.023	0.233	2.336
$MgCl_2$	0.038	0.380	3.808
$CaCl_2$	0.044	0.443	4.430
$BaCl_2 \cdot 2H_2O$	0.097	0.976	9.769
$CuCl_2 \cdot 2H_2O$	0.068	0.681	6.819
$Na_3PO_4 \cdot 12H_2O$	0.113	1.134	11.344
K_2CrO_4	0.077	0.776	7.768
$K_2Cr_2O_7$	0.117	1.176	11.767

3. Materials and Methods

The photochemical experiments were carried out in a batch-type photoreactor with a maximum capacity of one liter, consisting of a mercury vapor lamp medium pressure PUV-1,022 model of 110 mm in length 1,000 W, 145 V voltage and current of 7.5 A. The photoreactor comprises a recirculation system with demineralised water in order to regulate the temperature of the equipment. The outside of the reactor vessel is a cylindrical Pyrex glass which has two inputs the frosted top 15/30 and at the bottom where it enters an inlet air stream.

The lamp has the highest emission of radiation in wavelengths between 200 nm and 460 nm same region that absorbs most of organic functional groups and which performs the formation of the radical ·OH. The air for agitation and O_2 supply is provided by a compressor at the rate of 801 Elite 2,000 mL/min, which corresponds to the supply of 400 mL/min of O_2. Spectra were determined using a Uv-visible spectrophotometer Uv-Vis Perkin Elmer Lambda 20. The cells used are plastibrand plastic disposable cuvettes were used Uv micro cuvettes with a fill volume of 1.5 mL to 3.0 mL.

Into the batch, reactor was added the solution of nitrobenzene, three experiments were performed varying the pH to find optimal conditions for degradation. The variation of the pH is performed by adding 30% sulfuric acid. As ·OH radical source, 0.1 mL of hydrogen peroxide 50% was added. To generate turbulence and add O_2 into the reaction, the system was injected with an airstream. The lamp was heated for 3 min reaching its stability at full power and aliquot was taken into two time intervals (30 min and 60 min). After that the Uv-Vis spectra and the optimum pH nitrobenzene degradation was determined, contemplating the addition of salts in the experiments.

To evaluate the influence of the inorganic salts in the photodegradation of nitrobenzene were calculated amounts of salts to make solutions with concentrations from 0.0005 M, 0.005 M and 0.05 M, these amounts calculated were added to the aqueous solution of nitrobenzene. The pH was changed by adding sulfuric acid, hydrochloric acid or phosphoric acid to 30% depending on the salt. The determination of the Uv-Vis spectra was carried after irradiating the sample for 30 min and 60 min. It can measure the influence of the salts in the photooxidative process of nitrobenzene.

4. Results and Discussion

Experiments were performed with varying the solution pH of nitrobenzene and the irradiation time in order to find the optimum degradation regimen. Table 2 shows the results.

It observed that at pH of 2.5 and 60 min of irradiation, is reached the 100% degradation. This

Table 2 Percentages nitrobenzene photodegradation at different pH values.

Initial pH	t_{irrad} (min)	Abs (300 nm)	Degradation (%)
2.50	30	1.07	23.57
	60	0	100
3.75	30	1.00	28.57
	60	0.95	32.14
5.43	30	1.20	14.28
	60	0.30	78.57

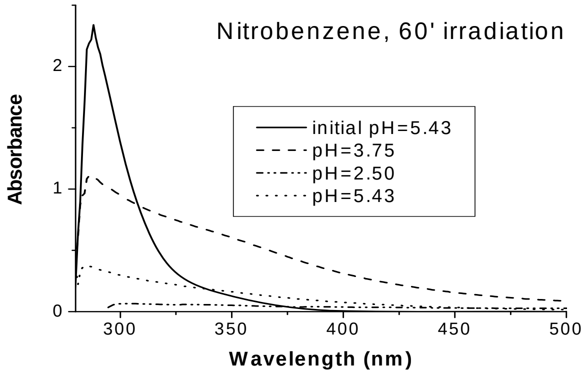


Fig. 1 UV-Vis spectra obtained at different pH and 60 minutes of irradiation.

condition was used for the experiments in which inorganic salt is added. Fig. 1 shows the Uv-vis spectra obtained.

According to the data of Table 3, the addition of sodium chloride, magnesium, calcium and barium conditioned at acid pH or in the initial pH conditions do not show interference in the photooxidative process of nitrobenzene added regardless of the concentration is achieved at 100% degradation. Except with copper chloride, in this case there is no negative interference and increase efficiency achieved degradation of nitrobenzene.

Figs. 2a and 2b show the Uv-vis spectra obtained at pH = 2.5 and initial pH, respectively after irradiating a solution of nitrobenzene contaminated with copper chloride is observed that the addition of salt treatment photooxidative degradation efficiency decreases pH unconditioned.

Table 4 shows the results obtained when the photo-oxidative treatment of nitrobenzene was added sodium sulfate, manganese and magnesium. A decrease of the photodegradation of nitrobenzene is observed with increasing salt concentration.

Table 4 shows that the degradation process is efficient for sodium sulfate, For magnesium sulphate (Figs. 3a and 3b) degradation decreases when the pH is 6.09 and photodegradation increases to pH 2.5. Table 4 observed that adding manganese sulfate II at low concentrations there is no negative interference on photodegradation whereas at high concentrations (0.05 M) interference is minimal.

Table 5 shows the results obtained by adding iron salts and copper sulfate. It can be seen that by adding these heavy metals that are found more frequently and in greater concentration in the wastewater, prove to be a limiting factor for the photodegradation of nitrobenzene, since one can not achieve complete mineralization of the contaminant organic. Uv-vis spectra are shown in Figs. 4a and 4b.

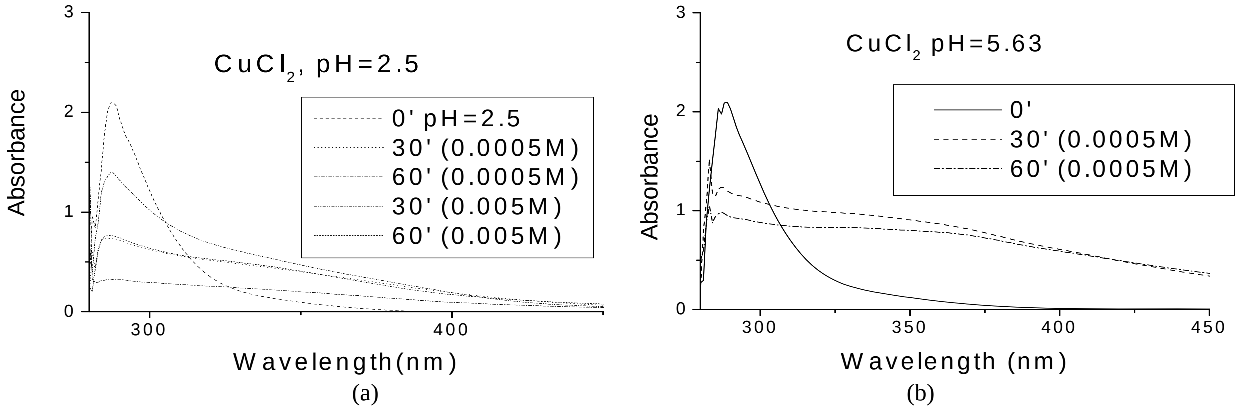
Figs. 4a and 4b note the formation of intermediate compounds which absorb in the same region as

Table 3 Results obtained when adding NaCl, $MgCl_2$, $CaCl_2$, $BaCl_2 \cdot 2H_2O$ and $CuCl_2 \cdot 2H_2O$, pH = 2.5 and initial pH conditions.

Salt	Initial pH	M (mol/L)	t_{irrad} (min)	Abs (300 nm)	Degradatión (%)	Initial pH	t_{irrad} (min)	Abs (300 nm)	Degradatión （%）
NaCl	2.50	0.0005	0	1.38	0	6.52	0	1.19	0
			30	0.18	86.96		30	0.20	83.19
			60	0	100		60	0.05	95.79
		0.005	0	1.36	0	5.98	0	1.28	0
			30	0.10	92.65		30	0.09	92.96
			60	0	100		60	0.05	96.09
		0.05	0	1.37	0	6.22	0	1.20	0
			30	0.20	85.40		30	0.38	68.33
			60	0	100		60	0	100

Table 3 continued

Salt	Initial pH	M (mol/L)	t_{irrad} (min)	Abs (300 nm)	Degradatión (%)	Initial pH	t_{irrad} (min)	Abs (300 nm)	Degradatión (%)
$MgCl_2$	2.50	0.0005	0	1.25	0	6.03	0	1.18	0
			30	0.13	89.60		30	0.22	81.36
			60	0	100		60	0.01	99.15
		0.005	0	1.28	0	5.83	0	1.28	0
			30	0.25	80.47		30	0.28	78.13
			60	0.09	92.97		60	0.01	99.22
		0.05	0	1.25	0	8.73	0	1.28	0
			30	0.60	52		30	0.38	70.31
			60	0	100		60	0.03	97.66
$CaCl_2$	2.50	0.0005	0	1.30	0	6.43	0	1.38	0
			30	0.03	97.69		30	0.03	97.83
			60	0.01	99.23		60	0.01	99.28
		0.005	0	1.30	0	6.95	0	1.38	0
			30	0.11	91.54		30	0.08	94.20
			60	0	100		60	0.01	99.28
		0.05	0	1.30	0	8.14	0	1.25	0
			30	0.50	61.54		30	0.65	48
			60	0.24	81.54		60	0.45	64
$BaCl_2 \cdot 2H_2O$	2.50	0.0005	0	1.20	0	6.01	0	1.20	0
			30	0.15	87.50		30	0.40	66.67
			60	0	100		60	0.01	99.17
		0.005	0	1.20	0	6.17	0	1.20	0
			30	0.40	66.67		30	0.59	50.83
			60	0.06	95		60	0.05	95.83
		0.05	0	1.20	0	5.74	0	1.20	0
			30	0.48	60		30	0.62	48.33
			60	0.36	70		60	0.06	95
$CuCl_2 \cdot 2H_2O$	2.50	0.0005	0	1.26	0	5.63	0	1.25	0
			30	0.63	50		30	1.10	12
			60	0.28	77.78		60	0.88	29.60
		0.005	0	1.26	0				
			30	1.10	12.69				
			60	0.64	49.21				

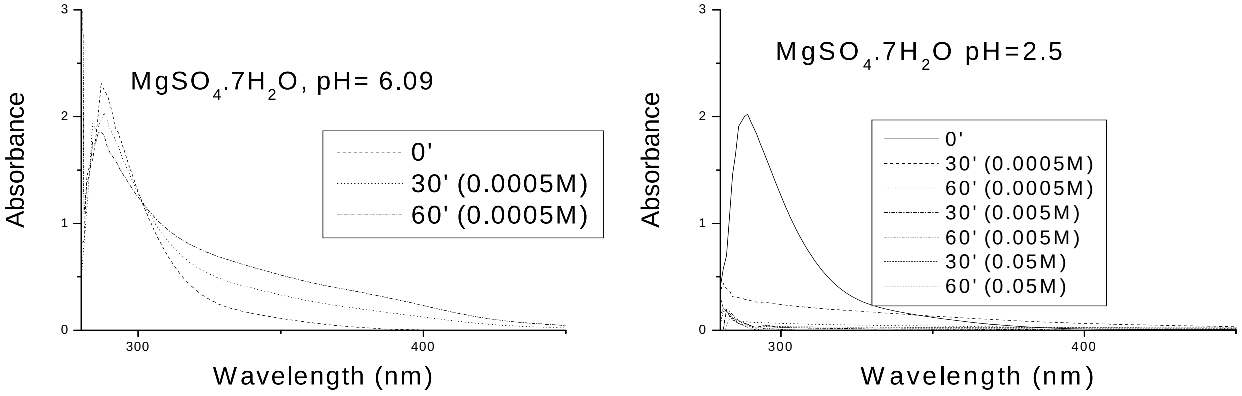


(a) (b)

Fig. 2 UV-vis spectra obtained from the photooxidation of nitrobenzene with $CuCl_2$ ((a) pH = 2.5 and (b) pH = 5.63).

Table 4 Results obtained when added Na_2SO_4, $MnSO_4$, and $MgSO_4 \cdot 7H_2O$, pH = 2.5 and initial pH conditions.

Salt	pH initial	M (mol/L)	t_{irrad} (min)	Abs (300 nm)	Degradatión (%)	pH initial	Abs (300 nm)	Degradatión (%)
Na_2SO_4	2.50	0.0005	0	1.40	0	7.12	1.35	0
			30	0.03	97.86		0.83	38.52
			60	0	100		0	100
		0.005	0	1.40	0	7.33	1.35	0
			30	0.03	97.86		0.68	49.63
			60	0	100		0	100
		0.05	0	1.40	0	7.72	1.40	0
			30	0.04	97.14		1.39	0.71
			60	0	100		1.28	8.57
$MnSO_4 \cdot H_2O$	2.50	0.0005	0	1.23	0	5.60	1.20	0
			30	0.02	98.37		0.45	62.50
			60	0.02	98.37		0	100
		0.005	0	1.28	0	5.67	1.17	0
			30	0.01	99.22		0.45	61.54
			60	0.01	99.22		0.10	91.45
		0.05	0	1.20	0	6.52	0.83	0
			30	0.40	66.67		0.40	51.81
			60	0.10	91.67		0.10	87.95
$MgSO_4 \cdot 7H_2O$	2.50	0.0005	0	1.33	0	6.09	1.31	0
			30	0.23	82.71		1.24	5.34
			60	0.08	93.98		1.21	7.63
		0.005	0	1.21	0			
			30	0.03	97.52			
			60	0.01	99.17			
		0.05	0	1.20	0			
			30	0.03	97.50			
			60	0.01	99.16			



(a) (b)

Fig. 3 UV-vis spectra obtained from the photooxidation of nitrobenzene with $MgSO_4 \cdot 7H_2O$: ((a), pH = 2.5 and (b), pH = 6.09).

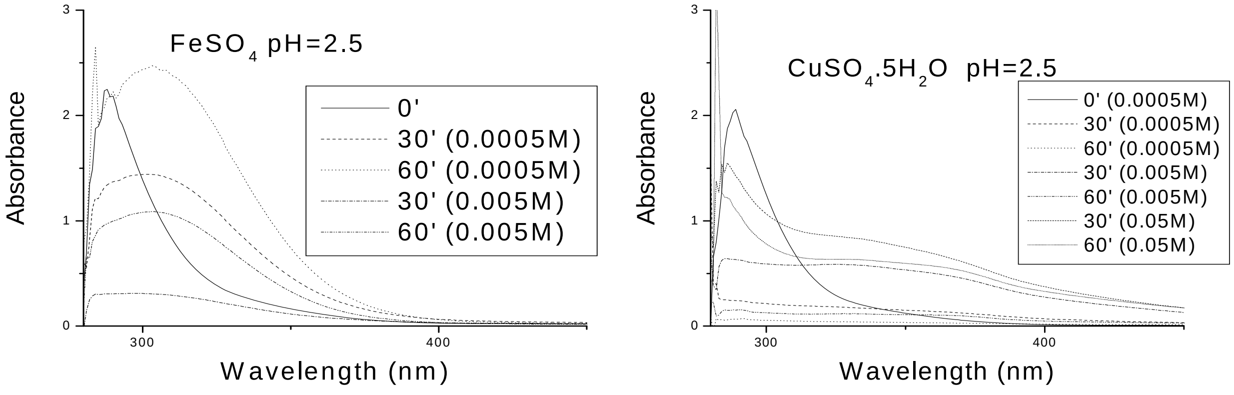
nitrobenzene, making reading difficult degradation was therefore not determined the percentage of degradation for iron sulfate. Possibly the Fe^{2+} is oxidized to Fe^{3+} and Cu^{+} to Cu^{2+} absorption bands shown in Fig. 4 are altered by the absorption bands is caused by oxidation.

Table 6 lists a comparison of the results at pH 2.5 and without conditioning the initial pH when added

Table 5 Results obtained when and $CuSO_4{\cdot}5H_2O$ added to pH = 2.5.

Salt	pH initial	M (mol/L)	t_{irrad} (min)	Abs (300 nm)	Degradation (%)
$FeSO_4{\cdot}7H_2O$	2.50	0.0005	0	1.28	0
			30	0.31	n.d.
			60	1.18	n.d.
		0.005	0	1.38	0
			30	1.45	n.d.
			60	2.45	n.d.
$CuSO_4{\cdot}5H_2O$	2.50	0.0005	0	1.38	0
			30	0.20	85.51
			60	0.09	93.48
		0.005	0	1.45	0
			30	0.68	53.10
			60	0.76	47.58
		0.05	0	1.45	0
			30	1.11	23.45
			60	0.77	46.89

n.d. = not determined



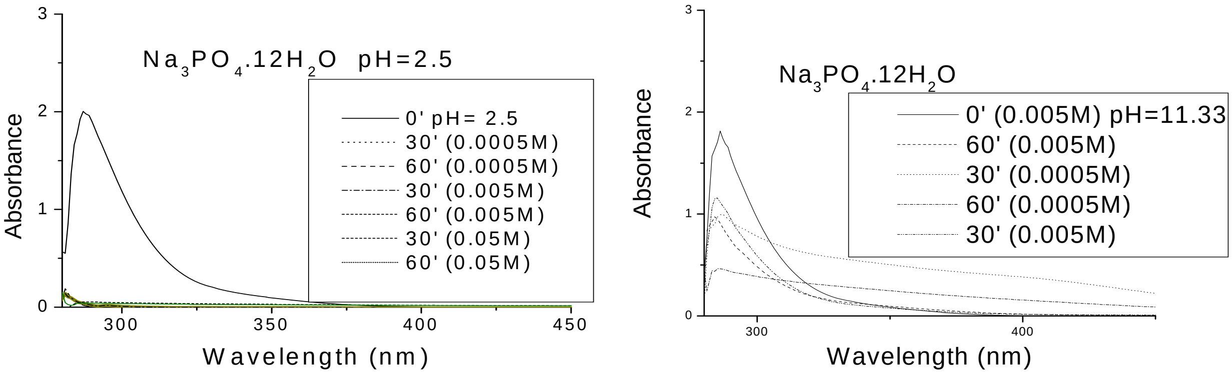
(a) (b)

Fig. 4 UV-Vis spectra obtained from the photooxidation of nitrobenzene with $FeSO_4{\cdot}7H_2O$ (a) and $CuSO_4{\cdot}5H_2O$ (b) at pH = 2.5.

Table 6 Results obtained when $Na_3PO_4{\cdot}12H_2O$ was added to pH = 2.5 and initial pH.

Salt	pH initial	M (mol/L)	t_{irrad} (min)	Abs (300 nm)	Degradatión (%)	pH initial	Abs (300 nm)	Degradactón (%)
$Na_3PO_4{\cdot}12H_2O$	2.50	0.0005	0	1.20	0	10.43	1.24	0
			30	0	100		0.78	37.09
			60	0	100		0.40	67.74
		0.005	0	1.28	0	11.33	1.00	0
			30	0	100		0.63	37
			60	0	100		0.49	51
		0.05	0	1.25	0			
			30	0.03	97.60			
			60	0.02	98.40			

sodium phosphate. Importantly, the presence of phosphate in acidic media has improved efficiency, without encouraging the formation of intermediaries. However, when there is no variation of pH performs absorbance spectra (Figs. 5a and 5b) to a concentration of 0.0005 M, there is a slight slope,

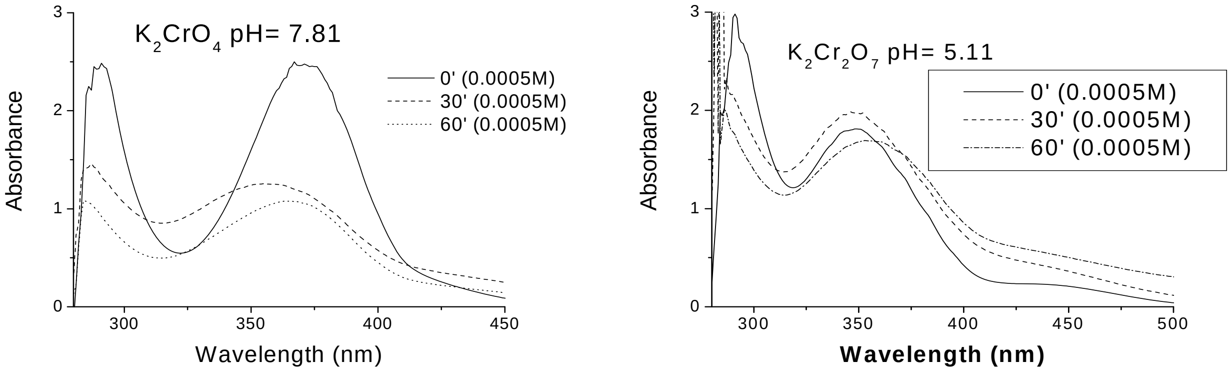


(a) (b)

Fig. 5 Uv-vis spectra obtained from the photooxidation of nitrobenzene with $Na_3PO_4{\cdot}12H_2O$ to pH = 2.5 (a) and initial pH condition (b).

Table 7 Results obtained when $K_2Cr_2O_7$ and K_2CrO_4 was added.

Salt	pH initial	M (mol/L)	t_{irrad} (min)	Abs (300 nm)	Degradation (%)
K_2CrO_4	7.81	0.0005	0	1.50	0
			30	1.10	26.67
			60	0.60	60
$K_2Cr_2O_7$	5.11	0.0005	0	2.50	0
			30	1.28	14.67
			60	1.25	50



(a) (b)

Fig. 6 UV-Vis spectra obtained from the photooxidation of nitrobenzene with K_2CrO_4 (a) and $K_2Cr_2O_7$ (b) at initial pH.

indicating that there is presence of intermediates, without ever achieving complete photodegradation nitrobenzene.

Table 7 shows the results of behavior when adding sodium chromate and dichromate have the same behavior as the salts of $FeSO_4$ and $CuSO_4$. For both types of salts spectra (Figs. 6a and 6b) show a slight reduction in the degradation of nitrobenzene. Degradation is observed that the organic contaminant peak is 50%-60%, at 60 min of irradiation.

5. Conclusions

The suitable conditions for achieving an efficient degradation of nitrobenzene are those developed in acidic media (pH = 2.5).

Na_2SO_4, $MnSO_4{\cdot}H_2O$ and $MgSO_4{\cdot}7H_2O$ salts, do not show any negative influence on the photodegradation process, if they are in acidic media. Na_2SO_4, $MnSO_4{\cdot}H_2O$ and $MgSO_4{\cdot}7H_2O$ are limiting factors in the process is different pH to 2.5.

Usually chlorine salts either in acidic or in initial conditions of pH do not interfere if they are present in low concentrations.

The oxidative photodegradation process is negatively influenced by the presence of salts of heavy metals ($CuCl_2·2H_2O$ and $CuSO_4·5H_2O$) at high concentrations due to the formation of intermediates during the photooxidative process. A relatively low concentration of those salts has no influence on the photodegradation process.

In the case of potassium chromate and potassium dichromate, the process results unsatisfactory due the formation of intermediates or because the coloring of the solutions which acts like a radiation or absorbing filter.

Into some experimental results ($FeSO_4$ and $K_2Cr_2O_7$) suspended particles were observed in the solution, the presence of these particles interfere whit photodegradation because no absorption of ultraviolet light (the light is reflected and there is not transparency) is developed, also causing problems for the spectroscopic determination of treatment samples.

In the presence of sodium phosphate, photodegradation is efficient in acidic conditions, obtaining results even to 100% degradation of nitrobenzene. However, in other pH values, the nitrobenzene degradation process is interfered.

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