

# Effect of Type of Substrate, Ions and Aeration on Photo-catalytic Oxidation of Phenol

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**ABSTRACT:** The effect of different parameters on photo-catalytic oxidation of phenol was studied. Photo-catalytic oxidation of phenol in various substrates - groundwater, milliq water & evian water was studied. Rate of the reaction in various experimented substrate was found to be in the following order: Milliq > Evian Water > Groundwater, presence of ions in the substrate decided the rate of the reaction. Effect of various ions - calcium, magnesium, carbonate, chloride and bi-carbonate, which were abundantly found in water, was studied. Cations - magnesium and calcium had no effect on the rate of reaction, whereas anions had detrimental effect on the rate of reaction. Aeration of solution had positive effect on the rate of reaction.

**KEYWORDS:** Photo-catalytic oxidation, Phenol, Ions, Aeration, Milliq water (de-ionised water), Groundwater, Rate Constant.

## I. INTRODUCTION

Phenol compounds have turned out to be a major pollutant in water bodies because of their extensive usage in daily life and industries. Phenol is stable hence remain in environment for longer period of time [1]. Moreover, high toxic nature of phenol makes them dangerous causing various health problems. Hence there is an alarming need for an economic method for the removal of phenol from water [2]. Lot of research is being carried out on photo-catalytic treatment of phenol in waste water, as it has shown some promising results ([3]; [4]; [5]).

A photo-catalyst is a substance capable of accelerating reaction, wherein it is being activated by adsorbing photon. Photo-catalysts are mainly semiconductors which has enormous potential to treat organic contaminants. This process is known as advanced oxidation process (AOP) [6]. Photo-catalytic degradation is an AOP which involves generation of oxidising species like hydroxyl radicals that takes part in reaction accelerated by the presence of catalyst.

Various semiconductors can act as photo-catalyst but  $\text{TiO}_2$  was found to be the most effective one which can carry out complete mineralization of phenol in water ([6]; [7]; [8]; [9]). Salient features of  $\text{TiO}_2$  which makes it a widely chosen photo-catalyst is its non-toxicity, insolubility in water and inexpensive ([10], [11]). Though  $\text{TiO}_2$  is an effective photo-catalyst but its fast charge carrier recombination and recycling difficulties is a major concern. Hence, usage of supporting materials like carbon, clay and zeolite is a cogent solution. Of these supporting materials, Zeolite is the best because of its standalone properties such as high surface area, good thermal stability and high absorption towards organic compounds [12]. Hence, for this study  $\text{TiO}_2$ / Zeolite was used as a catalyst.

## II. EXPERIMENTAL

### A. Materials:

Laboratory grade phenol, commercially available AEROXIDE P25 (Antase) along with Zeolite as photo-catalyst, MilliQ deionised water from a Merck Millipore Unit, groundwater from JN Tata, IISc, laboratory grade chemicals: Sodium Chloride, Magnesium Nitrate, Calcium Nitrate, Sodium Carbonate, Sodium Bi-carbonate.

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## B. Instruments:

Max 303 (ASAHI SPECTRA) Compact Xe Light Source with UV radiation of wavelength 350nm with an intensity of 1 mW/cm<sup>2</sup>, HPLC Unit 1220 Infinity LC (Agilent Technologies), Stirrer -IKA RO 10 magnetic stirrer RO10 magnetic stirrer.

## C. Degradation Experiment:

The photo-catalytic experiments were carried out on 1ppm phenol solution prepared in separate 100ml solution. In all experiments conducted, 0.1g of catalyst (0.025g of TiO<sub>2</sub> and 0.075g of Zeolite) was added to the bottle containing phenol solution. This was followed by sonication for about 5min in a sonicator and then a subsequent stirring on a magnetic stirrer for about 2hr. 2ml of the sample was filtered and collected at the 0min sample. 5ml of the sample was transferred to a 5ml PFA vessel and subjected to UV light for a time period of 1min. After exposure to radiation for the stipulated time, 2ml of sample was pipetted from the 5ml vessel, filtered and collected separately. The same procedure was followed for the time period of 2, 4, 6, 8, 10 and 12 min. The samples were then analysed using HPLC equipment. A set of experiments were carried out with MilliQ, groundwater and evian water. The degradation rate of phenol in each of these solutions was compared with each other. With an objective to analyse the individual effect of different ions on the rate of degradation of phenol experienced in J.N Tata groundwater, different solutions were prepared with the concentration of various ions ( Ca, Mg, Cl, CO<sub>3</sub>, HCO<sub>3</sub>) equivalent to that found in groundwater and finally an artificial groundwater was prepared and the degradation experiments were executed. Chemicals used to get the concentration of a particular ion for the study was chosen such that the neighbouring ion of the corresponding chemical has least effect on the rate of reaction [10]. Given below in Table 1 is the list of chemicals used for the preparation of corresponding ion concentration.

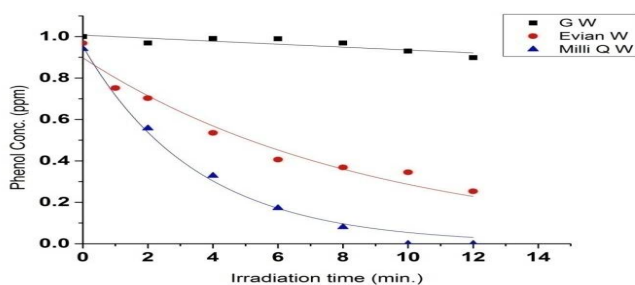
**Table 1. Chemicals used for preparation of solution of corresponding ions**

Sl. No	Ion	Chemical Used
1	Calcium	Calcium Nitrate
2	Magnesium	Magnesium Nitrate
3	Chloride	Sodium Chloride
4	Carbonate	Sodium Carbonate
5	Bicarbonate	Sodium Bi-carbonate

With an objective to understand the effect of aeration on rate of reaction, groundwater and milliQ water were aerated for two hours before carrying out the degradation experiments.

## III. RESULT AND DISCUSSION

### A. Effect of Substrate



**Figure 1. Degradation of phenol in (a) milliQ water (b) Groundwater (c) Evian water**

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Figure 1, which is the plot of concentration of phenol against time, shows that the rate of reaction in different substrates is in the following order: milliQ water >evian water > groundwater. That is, the rate of photo-catalytic oxidation of phenol is highest in milliQ water and least in groundwater.

**Table 2. Rate Constant for photo-catalytic oxidation of phenol in different substrate**

Type of Substrate	Rate Constant (min <sup>-1</sup> )
Milliq Water	0.310
Groundwater	0.009
Evian Water	0.114

The rate constant (slope of the curve for following reactions) for the reactions in various substrates are given in Table 2 which are in the following order: milliQ water >evian water > groundwater.

Presence of ions in the substrate is the decisive factor affecting the rate of reaction. Groundwater comparatively has lot of ions, whereas milliQ is de-ionized water ([13]; [14]). Lot of studies have been carried out with an objective to find the effect of inorganic ions on the photo-catalytic degradation of organic contaminants ([15]; [16]; [17]; [18]; [19]; [13]; [20]). Various mechanisms for the fouling of catalyst by inorganic ions have been proposed. According to one of the mechanism displacement of hydroxide ions from the surface of TiO<sub>2</sub> by inorganic anions thereby further reducing the generation of radicals results in decrease of rate of reaction ([10]; [21]).Hence, rate of photo-catalytic oxidation of phenol is least in groundwater and maximum in milliQ water.

### B. Effect of Ions

As discussed earlier, the reason for low rate of degradation of phenol in groundwater is the presence of inorganic ions. With an objective to determine the individual effect of each ion on the final rate of degradation of phenol in groundwater, different solutions were prepared with the concentration of various ions equivalent to that found in groundwater.

**Table 3. Concentration of different ions in groundwater.**

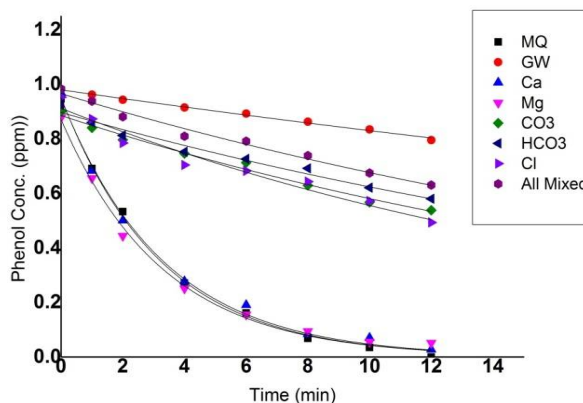
Ion	Concentration (ppm)
Calcium	73
Magnesium	32
Chloride	153
Carbonate	340
Bicarbonate	235

Concentration of different ions in groundwater was found out of which concentration of carbonate, chloride, bi-carbonate, calcium and magnesium were dominant. Abundantly found ions were considered for analysis and the concentration of these ions in groundwater is given in Table 3.

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**Figure 2. Degradation of phenol in (a) milliQ water (b) groundwater (c) in presence of only calcium (d) in presence of only magnesium (e) in presence of only carbonate (6) in presence of only bicarbonate (f) in presence of only chloride (g) artificial groundwater (all mixed).**

Figure 2, which is the plot of concentration of phenol against time, shows the degradation of phenol in solution containing different ions whose concentration is equivalent to that of ion concentration found in groundwater.

It can be inferred from Figure 2 that the effect of cations (calcium and magnesium) on the rate of degradation is almost negligible as the slope of the curve for the degradation reaction whose substrate contains calcium and magnesium is almost equal to that of MilliQ water. Cations that are Calcium and magnesium had no effect on the rate of reaction because they are at their maximum oxidation states resulting in their inability to inhibit the photo-catalysis reaction. Moreover, it can be seen that anions- chloride, carbonate and bi-carbonate have detrimental effect on the rate of photo-catalytic oxidation of phenol as the slope of curve for the degradation reaction whose substrate contains these anions is lower compared to that of MilliQ water. Scavenging effect of various ions in the groundwater is in the following order: Bicarbonate > Carbonate > Chloride.

The rate of photo-catalytic oxidation of phenol in artificial groundwater ('All Mixed' in the plot), containing all the abundantly found ions, was compared against natural groundwater. It is found that the rate of degradation is better in artificial groundwater than that in natural groundwater. The reason could be the absence of some of the scarcely found ions in artificial groundwater ions which could have had a notable aggregate effect on the rate of reaction in natural groundwater.

**Table 3. Rate Constant for photo-catalytic oxidation of phenol in different solutions.**

Type of Water	Rate Constant (min <sup>-1</sup> )
MilliQ Water	0.310
Groundwater	0.009
Calcium	0.308
Magnesium	0.301
Chloride	0.050
Carbonate	0.042
Bicarbonate	0.036
Artificial Groundwater	0.028

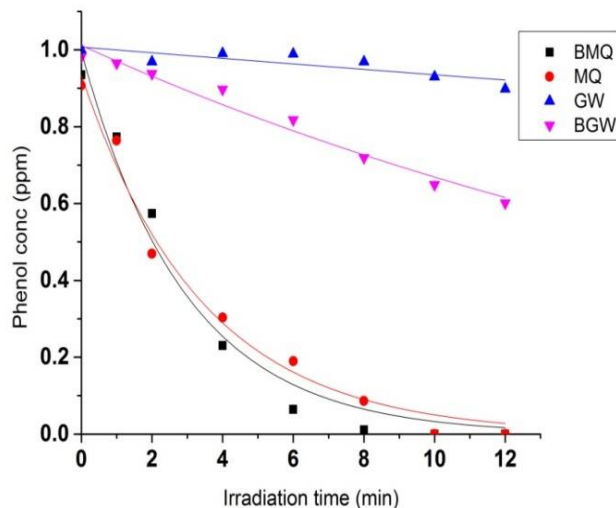
Rate constants (slope of the curve for following reactions) for the reactions shown in Figure 2 has been given in Table.3 which supports the explanation given for the Figure 2.

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### C. Effect of Aeration



**Figure 3. (a) Aerated groundwater (BGW) against normal groundwater (GW) (b) Aerated milliQ (BMQ) water against normal milliQ (MQ)**

Figure 3, which is the plot of concentration of phenol against time, shows the photo-catalytic oxidation of phenol in groundwater and milliQ water in comparison to that of aerated groundwater water and milliQ water.

The slope of the curve for the degradation reaction in bubbled groundwater is higher compared to that of normal groundwater which shows that DO has significant effect on the rate of reaction. Dissolved oxygen (DO) plays an important role in  $TiO_2$  photo-catalysis reaction to assure sufficient oxygen is present to trap the excited conduction-band electron. Moreover, with the increase in DO the concentration of oxidants like super-oxides increases thereby increasing the rate of degradation [22].

Herein, the presence of ions in normal groundwater had affected the rate of degradation by scavenging the oxidants. So when the groundwater is aerated, the extra oxygen provided reacts with the excited  $TiO_2$  electrons thereby preventing recombination of electrons, at the same-time overcoming oxidant deficit issue. Hence, the rate of degradation in aerated groundwater showed far better result.

Unlike groundwater, degradation in aerated and normal milliQ water remained almost same that is slope of the curves for the degradation reaction in aerated MilliQ water and normal MilliQ water almost equal. This is mainly because milliQ has no ion contamination for scavenging of oxidants to take place. Hence, there is not much difference in the results.

**Table 4. Rate Constants for photo-catalytic oxidation of phenol in different solutions.**

Type of Water	Rate Constant ( $\text{min}^{-1}$ )
MilliQ Water (MQ)	0.310
Aerated MilliQ Water (BMQ)	0.313
Groundwater (GW)	0.009
Aerated Groundwater (BGW)	0.040

Rate constants (slope of the curve for following reactions) for the reactions shown in Figure 3 has been given in Table.4 which supports the explanation given for Figure 3.

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## IV. CONCLUSION

Rate of degradation of phenol depends on the type of substrate, as the ions present in them is a deciding factor. Rate of degradation of phenol was found to be in following order for different substrate: MilliQ > Evian Water > Groundwater, i.e substrate with least ions showed better result. Effect of individual ions (abundantly found) on the rate of degradation of phenol in groundwater was determined. Cations : Magnesium, calcium had almost no effect whereas anions: chloride, carbonate and bi-carbonate had detrimental effect on the rate of degradation. Furthermore, experiments determining the effect of aeration on the rate of degradation of phenol showed that aeration improved rate of degradation.

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