Photocatalytic Removal of Cyanides From Polluted Waters

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Abstract

Cyanide compounds are considered one of the most dangerous hazardous wastes that may be found in industrial wastes. Recent research works [1,2,3,4], as well as this work proved that cyanide compounds could be removed from water by the oxidation of these compounds and transferring them into simple compounds such as CO_2, N_2, ...etc. This process is done on the surface of some materials suspended in water which are used as photocatalyst. The suggested photocatalyst is Anatase (TiO_2). Photocatalysis is achieved by direct exposure of polluted water having Anatase in suspension to the sun's radiation or UV of wave length of 300-400 nanometer.

The technology used to produce the photocatalyst was the advanced Sol-Gel technology. In this technology the gel is produced in the form of granules of Titania-Silica (TiO2-SiO_2 Aerogel) with size of 3 mm. The Aerogel proved to be a good catalyst for the treatment of cyanide polluted water, besides may be used for several times without a considerable weight loss.

1. Introduction

Discharging industrial wastes may cause different problems to streams. Most industrial wastes may be poisonous to fish and other fauna in water. It is well known that the presence of harmful substances will complicate the process of biological treatment of waste water specially in case of the need of reusing it.

Cyanide compounds are one of the most dangerous pollutants that may be found in industrial wastes. These compounds usually come from chemical, petro-chemical metallurgical, gold and silver extraction industries. At a pH usually less than 8, the poisonous hydrogen cyanide gas (HCN) is produced from water polluted with cyanide compounds, which by its turn will pollute the air around the area. Industrial water wastes that contain cyanide compounds are usually treated separate from other industrial water wastes. Some of the methods used for treating such water are:

- Alkaline chlorination
- Electrolytic oxidation
- Ozonation
- Wet air oxidation
- Ion exchange

The Alkaline chlorination is one of the best and cheapest method used now, nevertheless it has some disadvantages:

a. It treats only simple cyanides, but the complex cyanides will precipitate in a poisonous form, which will need special method of disposal.

b. Cyanogen chloride which is poisonous will be formed during the process.

c. The chlorine gas which is used in the process may combine with some organics present in water such as phenols producing very dangerous compounds. These compounds are hard to be removed.

Recent researches [1,2,3,4] proved that cyanide compounds and most organics too, could be removed from water by oxidation and converting them into simple compounds such as CO_2 , N_2 , H_2O , ...etc., which are not harmful to the environment. The oxidation process is done on the surface of fine grains, suspended in water, of semi-conductors such as Titanium Oxide (TiO_2 anatase). This process uses photocatalysis to the sun's radiation or an artificial UV radiation of 300-400 nanometer. Some research work [5,6,7] has been done to reach an economic and efficient production of the photocatalyst Titinium Oxide (TiO_2 anatase).

2. Theory

2.1 Photocatalysis to the surface of Semi-conductors Suspended in Water

When the surface of some semi-conductors as (TiO_2 anatase) is exposed to UV radiation of a wave length of 300-400 nanometer or sun's radiation, an excitation will occur to the electrons. Then the electrons will move to the level of conduction band, leaving behind it positive centers in the valence level. These positive centers and the electrons will move to the surface of the catalyst and hence the electrons will reduce the oxygen molecules in water. The cyanide ions (CN^-) will be oxidized on the positive centers. Figure 1 shows these reactions.

Because these reactions occur on the surface of the photocatalyst particles (TiO_2 anatase), so the rate of oxidation will increase as the surface area of the photocatalyst increases, i.e. the volume of the particles decreases. But the disadvantage of using fine photocatalyst (fine powder) is the difficulty of recovering it completely after the treatment process.

2.2 The Suggested Form of the Photocatalyst

A new technique was developed [8] to produce a solid, porous, and transparent photocatalyst. This new technique is The Advanced Sol-Gel Technology that allows us to produce the photocatalyst (TiO_2 anatase) in a new shape that can be used in the treatment of polluted water in a continuous way with a high efficiency and minimum loss of the photocatalyst. Since it is difficult to produce the photocatalyst (TiO_2 anatase) alone as particles, so it is produced in the form of Titania-Silica aerogel form (TiO_2-SiO_2), so that the required transparency, porosity, and large surface area could be reached. The best size for the particles was found to be 3 mm with a silica content of 75 %.

3. Experimental Work

The factors which were taken into consideration for studying the treatment of water polluted with cyanides using the process of Photocatalysis were:

a. Amount of Aerogel particles added to each liter of polluted water.

b. The treatment time.

c. The number of times the Aerogel has been recycled.

In order to study the above factors affecting the treatment process, two bench scale units were designed to study these factors. The first unit with a capacity of 150 cm^3 for the treatment of Cyanide Potassium solution prepared in the lab, 300-400 nanometer UV radiation was used for the photocatalysis of the Aerogel.

The second unit is a one liter container to treat an industrial waste contains cyanide. In this case the direct sun's radiation (for the photocatalysis of the Aerogel) was used. Figure 2 shows a flow diagram for these 2 units

3.1 Treatment of Potassium Cyanide Solution

a. A Suitable amount of 65 ppm potassium cyanide solution was prepared. This solution is more than a hundred times of the permissible limit of cyanide in the water discharged to streams according to the number four law of 1994, this concentration is also higher than the cyanide content that may be present in some industrial wastes.

b. The pH of the Potassium Cyanide solution was raised to a pH higher than 8 by adding sodium hydroxide in order to avoid the formation of hydrogen cyanide gas (HCN) during the treatment process.

c. A 150 cm^3 of the above Potassium Cyanide solution was put in a container exposed to U V radiation. A known amount of Aerogel particles was added to the solution. Air bubbles were pumped to the solution to keep the Aerogel particles in suspension and accomplish a complete mixing; the air-bubbles also supply the necessary oxygen for the oxidation of the cyanide ions.

d. Samples were taken at different times from the solution to measure the concentration of cyanide remained. The measurements were done according to the Standard Methods [9], and using the volumetric analysis procedure.

3.2 Treatment of an Industrial Waste Containing Cyanide

a. An industrial waste containing a 23 ppm cyanide was used in a 1-liter container. The pH of the solution was raised to a pH higher than 8 to avoid the formation of hydrogen cyanide gas.

b. The container was exposed to direct sun's radiation. A known amount of Aerogel particles were added.

c. Samples were taken at different times from the solution to measure the concentration of cyanide remained (as in 3.1)

3.3 Aerogel amount used during the study

1.5, 3, 6, 9 gm/ L were used to study the effect of the amount of aerogel on the treatment of cyanides. Samples were taken at different times (up to 6 hours) for each of Aerogel dose for the study of the effect of exposure time on the treatment.

3.4 Study of the Number of Aerogel Recycles

Unit one was used to study this factor. The aerogel particles were recycled five times. For each cycle the illumination time was six continuous hours. At the end of each cycle the air pumping was terminated to allow the settlement of the Aerogel particles. The treated solution then was emptied from the container and the Aerogel particles were retained on a filter paper.

The second cycle started with a new untreated solution using the same Aerogel particles retained from the first cycle. This procedure was repeated for five cycles. Cyanide concentrations were measured for each cycle (as in 3.1).

At the end of the fifth cycle the Aerogel particles were separated from the solution on a filter paper, washed with distilled water, dried and then weighed to determine the lose percentage after its use.

4. Experimental Results

The determination of the loss percentage of Aerogel particles can be expressed as follows:

a) Weight of the fresh particles used for the treatment = 0.5 gm.
b) Weight of the particles after five recycles = 0.452 gm.
c) The volume of polluted water treated during the five cycles = 150 x 5 = 0.75 L
d) Amount of lost particles = 0.5 - 0.452
 = 0.064 gm/L

Figures 3 and 4 represent the effect of Aerogel dose and the illumination time on the removal of cyanide.

Table 1 shows the efficiency of cyanide removal when recycling the Aerogel particles. The percentage of the cyanide removal was in the range of 93 -96.

5. Conclusions and Recommendations

a. As shown in Figures 3 and 4, the increase of the Aerogel dose will decrease the illumination time required for the removal of cyanide.

b. Using the Aerogel particles as a photocatalyst prove to give a high efficiency for the removal of cyanides in industrial wastes. The method is environmentally safe since it converts the cyanides to simple harmless compounds such as N_2, CO_2, ...etc.

c. Reusing the Aerogel results a very low loss percent.

d. It is recommended to use the photocatalytic method for the removal of other hazardous materials other than cyanides.

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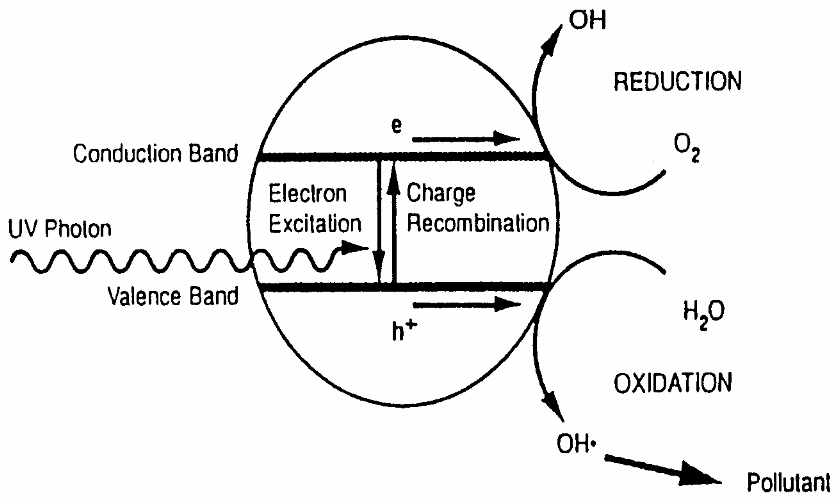

Fig. 1. Oxidation Reduction Reactions Occurs on the surface of Aerogel due to photocatalysis.

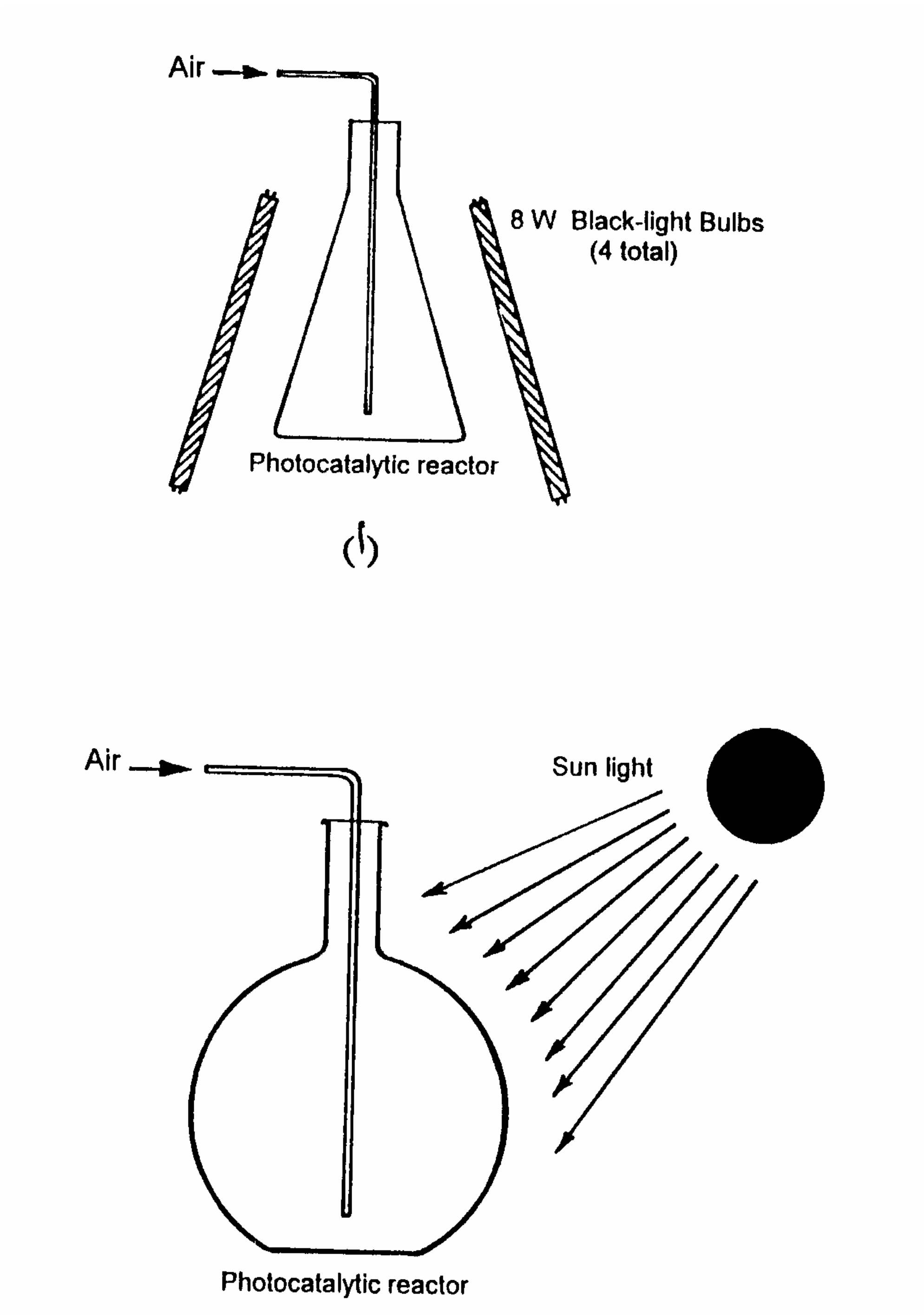

Fig. 2. Diagram of the two units used to study the effect of different factors affecting the treatment of Cyanide – polluted- water, using the photocatalysis for the Aerogel.

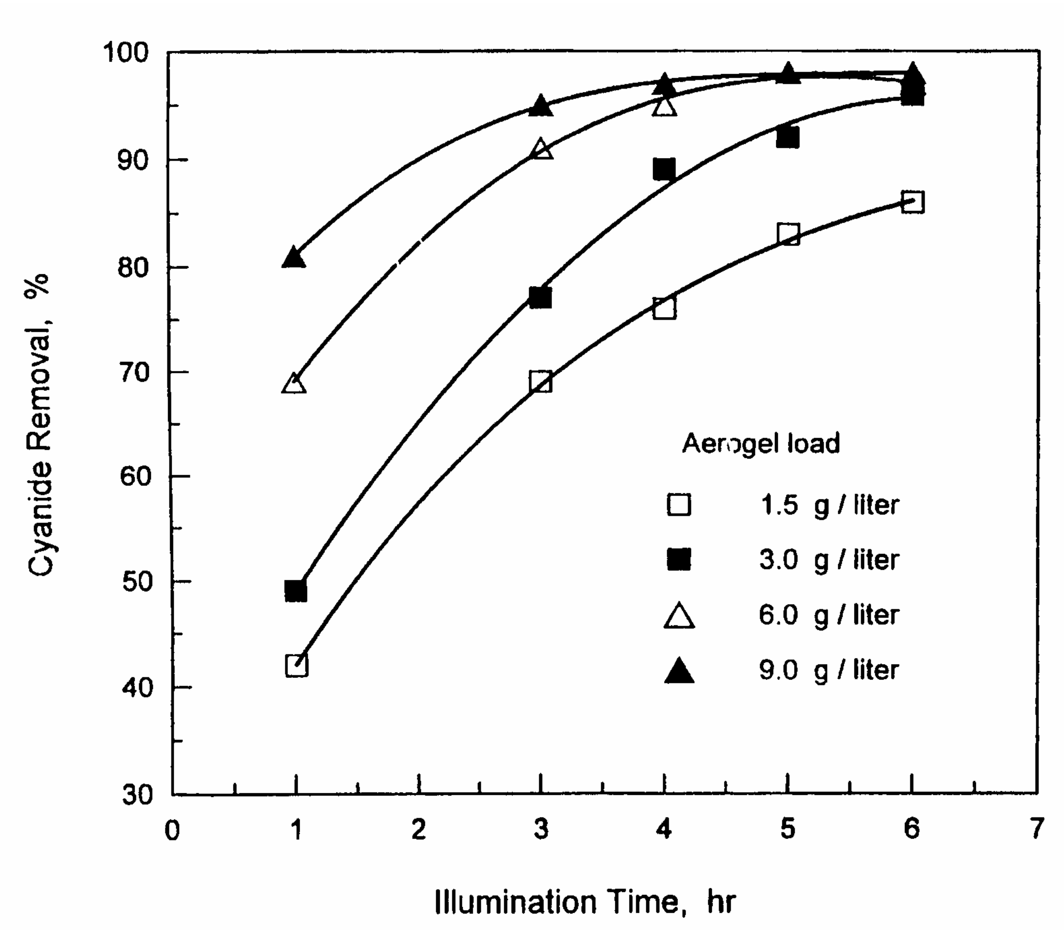

Fig. 3. Effect of the Aerogel dose and Illumination Time on the Removal of cyanide from a. 001 M KCN Solution.

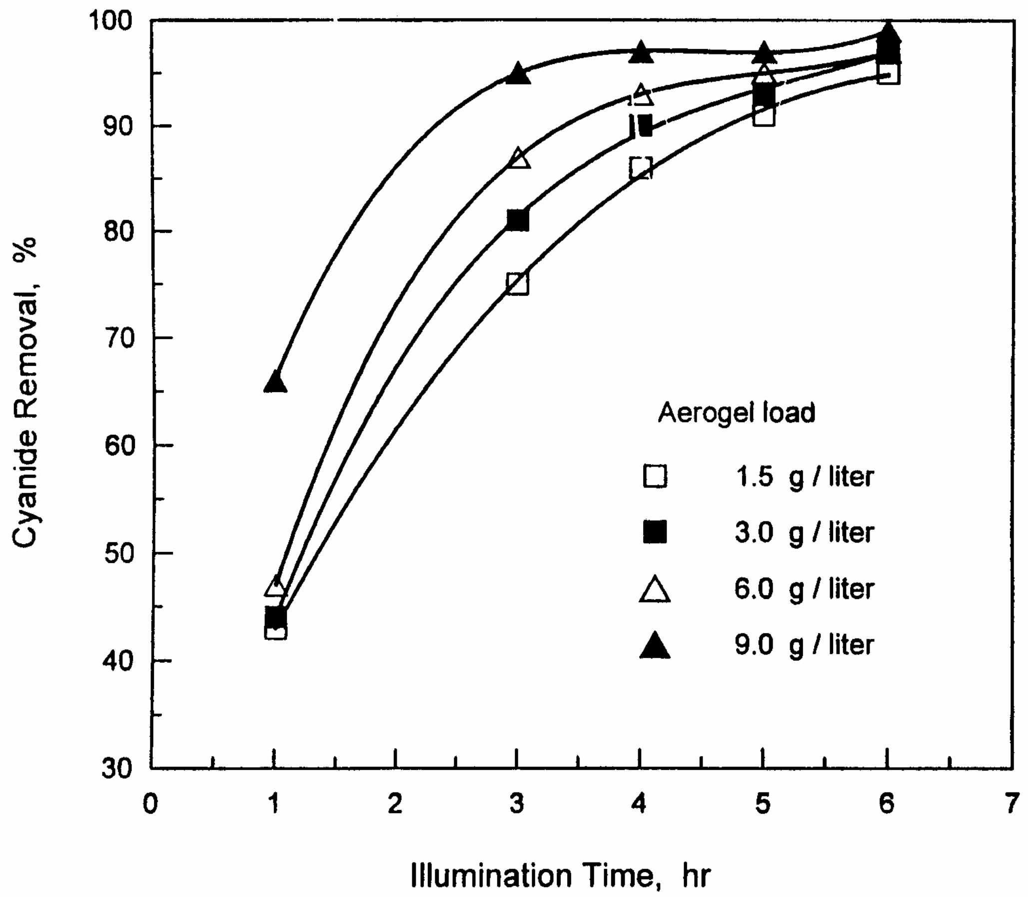

Fig. 4. Effect of Aerogel dose and Illumination Time on the Removal of Cyanide from an Industrial waste (CN^{-} = 23 ppm)

Table 1: Effect of Reusing the Aerogel on the Removal of Cyanide from a potassium cyanide (KCN) of .001M

No. of Cycles	1	2	3	4	5
Cyanide removal, %	96	94	94	93	95