



DECONTAMINATION OF DRINKING WATER BY A COMBINED PHOTOCATALYSIS-SORPTION SYSTEM AT LOW ENERGY

S.P. Paredes¹, M. A. Valenzuela¹, M. L. Hernández-Pichardo¹, Rodríguez-Clavel I. S¹.

¹Instituto Politécnico Nacional, ESIQIE, Laboratorio de Catálisis y Materiales, Av. IPN S/N Zacatenco, 07738 México, México.

* contact email: silviappcar@gmail.com

ABSTRACT

A photocatalysis-sorption coupled system was studied to degrade and reduce organic and inorganic contaminants from drinking water. The pollutants contained in water of Mexico City was identified, quantified and classified. A photocatalytic annular reactor was designed, built and tested. It was found that the photo-reactor was able to degrade up to 200 ppm of organic contaminants, using TiO₂ supported on glass beads as catalyst. The remnants of degradation were treated by sorption. The sorption procedure developed was capable to remove organic pollutants and reduce the concentration of metal cations and anions. The calcined hydrotalcite with nitrate as interlaminal component and synthesized by ultrasonic irradiation is the best option to remove anionic species. In the case of cationic species the activated carbon, in all cases, was a better material than bentonite or natural zeolite. Finally, both systems were coupled into a photocatalytic-sorption assembly.

Key words: sorption; photocatalysis; hydrotalcite; ultrasound irradiation and sorption.



1. INTRODUCTION

Increasing water contamination caused by toxic compounds is a matter of great concern. Particularly, the reduction of drinking water quality due to the contamination of soils and groundwater by volatile organic petroleum hydrocarbons and some other contaminants has been extensively documented [1-2]. This pollution is in part originated during the stages of extraction and distribution, as well as result of continuous leaking of fuels from underground storage tanks in gas stations [3]. Recent studies [4] have shown that in the particular case of Mexico City some of the main contaminants founded in drinking water are: benzene, toluene, ethylbenzene and xylenes (BTEX in low concentration) as well as some traces of Cr(VI), among others. These pollutants are considered hazardous substances because of their high toxicity, confirmed carcinogenicity, and environmental persistence [5]. Then, the development of an efficient technology to remove these substances from drinking water is absolutely necessarily.

Photocatalysis and advanced oxidation processes (AOPs) based on the photocatalytic destruction of organic pollutants and the removal of some toxic ions, in combination with basic procedures of filtration are novel proposal for the decontamination and/or final disinfection of drinking water. However, these processes must be complemented by technical high removal of pollutants such as sorption methodologies with new materials, which have not been exploited in such applications.

Sorption studies of chemical species with cationic clays (bentonite and zeolite), silico aluminates and activated carbon are successful on the sorption of cationic compounds [6]. However these compounds are unable to efficiently remove anionic species of Cr(VI), such as chromates for example. These materials also exhibit low performance in the sorption of organic compounds such as phenol, hexane, benzene, toluene, ethylbenzene, xylenes etc. Then, a study of different integral sorbents systems is lacking.

Some of the new materials with adsorbent features are the hydrotalcites-like compounds (HTC). However, previous studies have failed to increase yields in the capture of these pollutants using HTC with interlayer carbonate component conventionally prepared (hydrothermal methods) [7,8]. Then, in this work nitrated hydrotalcite-like compounds were synthesized by ultrasound-



assisted coprecipitation in aqueous solution in order to obtain an adsorbent with improved features for the removal of Cr(VI). Moreover, the study of different sorbents for BTEX uptake was also carried out. Thus, a comparative study of the sorption properties of different anionic and cationic solids was performed in order to obtain a sorption system for an integral treatment of contaminated waters by a combined photocatalytic–sorption system.

With respect to the photocatalytic system, commercial titanium oxides (Degussa P-25, Titania Aldrich y Titania Hombikat) were studied [9]; the most active titanium oxide in the photodegradation was supported on materials of different geometry (spheres, plates, rings, or fibers), thus avoiding the separation process of the $\text{TiO}_2\text{-H}_2\text{O}$ mixture. The photocatalytic process was optimized considering mass ratio of catalyst-pollutant, from this way the photocatalytic annular reactor was designed and constructed. Finally the sorption and the photocatalytic processes were combined.

2. MATERIALS AND METHODS

2.1 Sampling

It was structured a sampling plan that covered the entire urban area of D.F. Analysis was performed for cations: arsenic, copper, chromium, cadmium, mercury, manganese, lead, sodium, barium, iron, aluminum and zinc accordance with the NMX-AA-051-SCFI-2001. In addition, analysis was performed to determine organic contaminants (VOCs) according to EPA method 524.2. These pollutants were classified according to their concentrations and toxicity found.

2.2 Photocatalytic system

The annular photocatalytic reactor was designed and built with the following specifications: PVC outer tube with an external diameter of 40.22 mm and thickness of 1.975 mm, inner glass tube with an external diameter of 16.30 mm average; the annular space created by these two tubes was packed with uniform spherical glass beads coated with TiO_2 (diameter= 3 mm) and methyl orange was used as a model for the evaluation of the system.



2.3 Sorbent materials

The sorption process was evaluated for both anionic and cationic solids, and then three kind of sorbent materials were evaluated: a) activated carbon, b) cationic clays (bentonite and natural zeolite) and c) anionic clays (hydrotalcites Al-Mg/Nitrate). The activated carbon and natural zeolites were commercial samples provided by Aldrich (99.2 %), while hydrotalcite-like compounds were synthesized by an ultrasound-assisted method described below.

2.3.1 Synthesis of hydrotalcite-like compounds (HTC) by ultrasound-assisted coprecipitation.

Nitrated hydrotalcite-like compounds with an Al/ (Mg+Al) molar ratio of 0.25 were synthesized by ultrasound-assisted coprecipitation. A 1.86 N aqueous solution of NaOH was added to a 2.5 M aqueous solution containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99 %) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98 %) to reach a pH value of 10.5 under a nitrogen inert atmosphere. The obtained gel was treated at 80 °C with ultrasound irradiation at 42 kHz and an ultrasound power of 4.34 kW using different irradiation times (10, 20 and 30 min). The obtained samples were washed with deionized water, dried at 70 °C and calcined in air atmosphere at 500 °C for 18 h. These samples were labeled as HT-x, where x represent the irradiation time used in the synthesis.

2.3.2 Characterization of sorbents

All the adsorbents were characterized by X-ray diffraction (XRD) and nitrogen physisorption at 74 K. X-ray diffraction patterns were obtained in a Siemens D-500 diffractometer coupled to a copper anode X-ray tube. A diffracted beam monochromator selected the K_α radiation. The BET surface areas, pore volume and mean pore diameter were determined by standard multipoint techniques using a Micromeritics ASAP 2010 instrument.

2.3.3 Analytical sorption methods

2.3.3.1 Sorption of Cr (VI) using hydrotalcites

The sorption of the anionic component Cr (VI) was carried out using nitrated hydrotalcite-like compounds. The evaluation of the sorption process was performed by UV–Vis spectroscopy using a GBC Cintra 20 equipment. A series of aqueous Cr (VI) solutions at different concentrations (50, 100, 200 y 300 ppm) were prepared using potassium dichromate (Aldrich, 98



%), and concentration was measured by UV-VIS spectrophotometry in order to obtain the calibration curve.

2.3.3.2 Sorption of BTEX using cationic clays

The sorption of cationic components: benzene, toluene, ethylbenzene and xylenes (BTEX) was carried out using activated carbon and cationic clays (bentonite and natural zeolite). The evaluation of the sorption process was also performed by UV-Vis spectroscopy. A series of aqueous solutions of an equimolar mixture of BTEX at different concentrations (50, 100, 200 y 300 ppm) were prepared using reagents (Aldrich, 98 %); the sample concentrations were measured by UV-VIS (GBC Cintra 20 UV-Vis spectrophotometer) spectrophotometry in order to obtain the calibration curve.

For both cases the sorption process was conducted in a glass vial (10 ml), in which 0.1 g of sorbent was weighed. Then, 10 ml of the polluted solution was added, the vial was stirred and it let to stand for periods of 0.25, 0.5, 0.75, 1.0, 1.5 and 2 hours. Later, the vials were centrifuged for 5 min to separate the sorbent of the purified solution. After that, the solutions were analyzed spectrophotometrically at λ_{max} 265 nm for Cr(VI) and λ_{max} 270 nm for BTEX in order to determine their concentrations; finally the amount of both, Cr(VI) and BTEX sorbed ions was determined by comparison with the blank.

3. RESULTS AND DISCUSSION

3.1 Sampling

The information of each pollutant was concentrated on different maps of the city; a color scale was used to identify the levels of concentration in each case. Figure 1 shows the amounts (ppm) of Cr (VI) contained in the sampled water. It is observed that the highest concentration of this pollutant is located on the north and the city center.



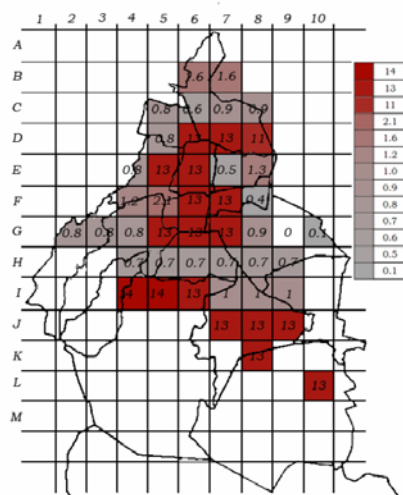


Figure 2. Concentration of Cr (VI) (PPM) in drinking water in Mexico City.

In addition to this pollutant: benzene, toluene, ethyl benzene, xylene (BTEX), trihalomethanes, arsenic, cadmium, manganese, lead, barium, aluminum, barium, iron, sodium and zinc were detected at concentrations lower than the Mexican standard (NMX-AA-051-SCFI-2001) (except chrome); however, the recommendations of values recommended by international organizations (U.S. EPA) agencies provide lower values. Table 1 summarizes these values and shows the characterization of water samples considering an average consumption of 2 L of water per day and an average weight of 65 Kg people, considering the ethnic population of the metropolitan area [4].

Table 1. Characterization of drinking water in Mexico City.

Pollutant	Maximum allowed limits		
	NMX-127-SSA1-2000 (mg/L)	U.S. EPA	Consumed daily value
arsenic	0.025	0.005 µg/Kg./día	0.025 µg/Kg./día
aluminum	0.200	0.0015 mg/Kg./día	0.003 mg/Kg./día
barium	0.700	0.0615 µg/Kg./día	0.003 mg/Kg./día
zinc	5	0.1540 mg/Kg./día	0.0043 mg/Kg./día
copper	2	0.0310 mg/Kg./día	0.185 mg/Kg./día
Cr (VI)	0.050	0.0050 mg/Kg./día	0.006 mg/Kg./día
cadmium	0.005	0.0020 mg/Kg./día	0.0012 mg/Kg./día
iron	0.300	-----	-----
mercury	0.001	0.00003 mg/Kg./día	0.000015 mg/Kg./día
manganese	0.150	0.0015 mg/Kg./día	0.0043 mg/Kg./día
lead	0.010	0.0003 mg/Kg./día	0.00077 mg/Kg./día
sodium	200	-----	-----
trihalomethanes	0.200	0.030 mg/Kg./día	0.0016 mg/Kg./día
benzene	0.010	0.00015 mg/Kg./día	0.0015 mg/Kg./día
toluene	0.700	0.030 mg/Kg./día	0.0015 mg/Kg./día
etilbenzene	0.300	0.021 mg/Kg./día	0.0015 mg/Kg./día
xylenes	0.500	0.300 mg/Kg./día	0.0015 mg/Kg./día

3.2 Photocatalytic System

3.3.1 Sorption of Cr (VI) using HTC and activated carbon.

The sorption of the Cr(VI) was carried out using activated carbon (AC) as well as nitrated hydrotalcite-like compounds synthesized by an ultrasonic-assisted method (HT-x). The samples were prepared by using different irradiation times, the description of the different samples as well as the BET surface areas are shown in Table 1.

Table 1. Description and BET surface areas of the samples used in the sorption of Cr (VI).

Sample	Irradiation time (min)	BET surface area (m ² /g)
HT-10	10	81
HT-20	20	79
HT-30	30	59
Activated Carbon	--	641

It is observed that in the case of the HTC compounds as the ultrasound irradiation time increases the surface area values diminish due to the melting agglomeration during particle collisions [7]; being the sample irradiated at 10 min (HT-10) the one with the higher surface area. However, this value is much lower than the area obtained for the activated carbon, which is almost 8 times greater than those values obtained for the hydrotalcites. The increase in the particle size and crystallinity of the HTC samples could be observed in the XRD patterns of samples prepared at different irradiation times (Figure 2), where it is possible to observe an increase in the intensity as well as the broadening of the diffraction signals, mainly observed in the 003 diffraction peak, which is an indicative of the rise in the particle size.

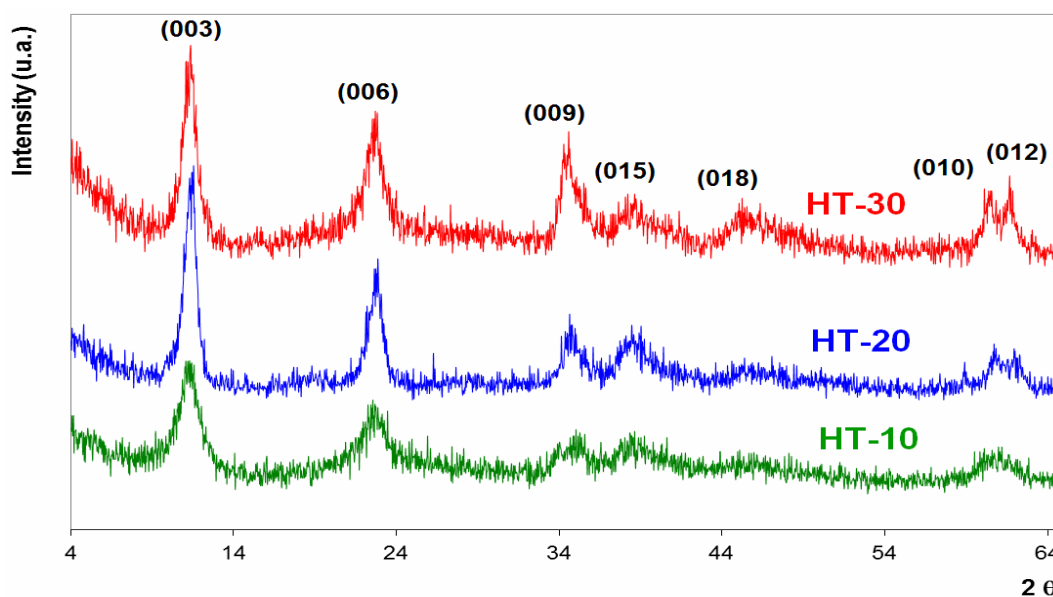


Figure 2. XRD patterns of the HTC samples synthesized at different ultrasonic irradiation times.

The sorbents uptake capacity of Cr(VI) ions was evaluated using the HTC samples as well as activated carbon in contaminated solutions with 100, 200 and 300 ppm of Cr(VI). The best results were obtained with the HT-10 sample and activated carbon; the results are shown in Figure 3. This figure shows the percentages of sorbed Cr(VI) in solutions of different concentrations. It is noted that equilibrium is reached in all cases at 2 hours of contact time, similar results were obtained by Hongxiang et al. [10] and Boumadiane et al. [11] in Adsorption of Cr(VI) on carbonated hydrotalcites. On the other hand, it is observed that within the first 15 min of contact with the solution at 100 ppm, almost 78 % of adsorption occurred for the HT-10 sample, while activated carbon adsorbed only about 13 % of chromates. As increasing chromates concentration at 200 and 300 ppm the activated carbon uptake is much lower than the hydrotalcite, due to activated carbon saturates its available surface area (641 m²/g) compared to the HT-10 sample (81 m²/g); it indicates that the hydrotalcite-like compound present a superior performance due to this material owns both, the specific surface area as well as the exchange sites in the brucite-like layer to carry out the sorption of Cr(VI). It is well known that the hydrotalcite compounds contain exchangeable ions on their surface and these materials are able to take up anions either through ion exchange or adsorption or both without affecting the structure of the hydrotalcite [7].



These results confirm that the uptake capacity depends on both, the surface area and the exchange sites available in the adsorbent.

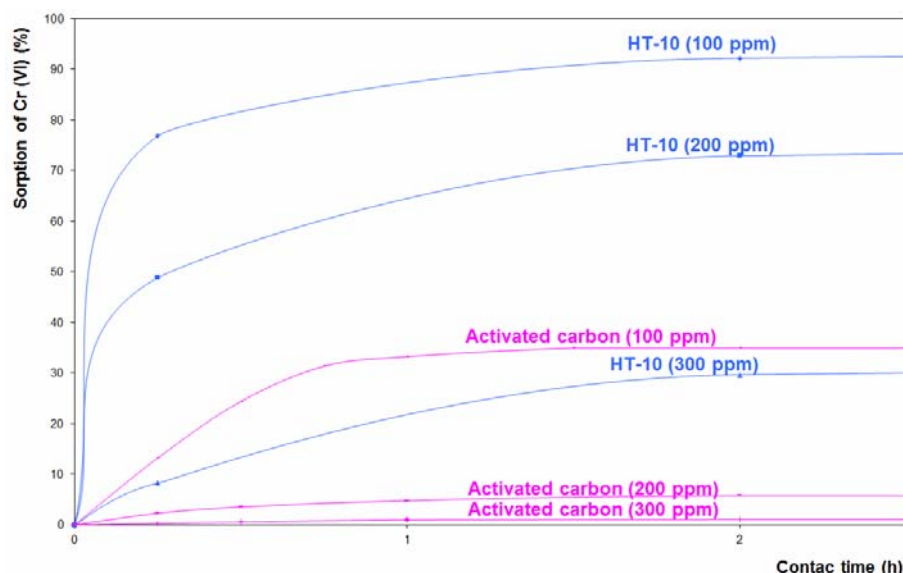


Figure. 3. Effect of the contaminated solution concentration on the uptake of Cr (VI), at different contact time.

3.3.2 Sorption of Cr(VI) using the calcined HTC

It has been reported that an increase in the amount of sorbed anions could be reached by calcining the HTC and reconstructing the material, since the HTC presents a memory effect [7], then the calcined HT-10 sample at 500°C was also evaluated in the Cr(VI) sorption process.

Figure 4 shows the effect of the calcination on the Cr(VI) uptake capacity, comparing the sorption process of the HT-10 sample with the calcined sample (HT-10C) in contaminated samples at 100, 200 y 300 ppm of chromate. It is observed that the sorption percentages are very similar in both samples at any concentration, being the HT-10 sample slightly superior. However, since the HT-10C is a calcined solid, presents the advantage that it is not going to exchange anions with the media, which is an additional benefit in the drinking water purification process.

It is likely that the number of exchange sites of the brucite-type layer and the texture obtained in the calcined sample are the most important factors in the sorption of anions. To be clear the HT-10C comes from the original sample, then, both materials have the same exchange sites, which explain the minimal difference in the sorption capacity of Cr(VI). Therefore, the calcined HT-

10C sample would be the best option for the removal of anionic contaminants traces present in drinking water.

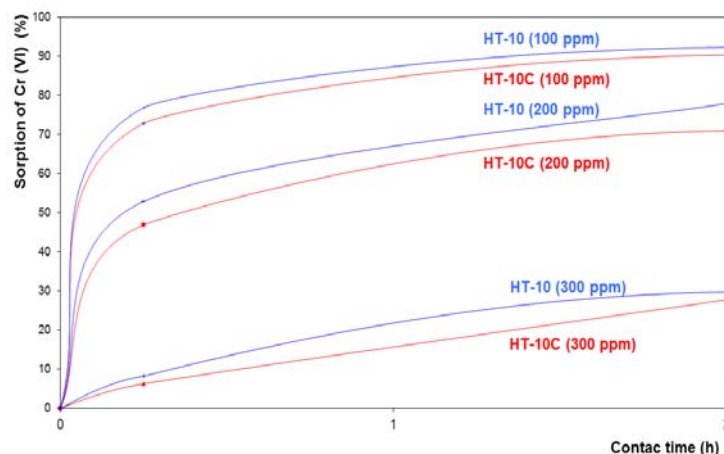


Figure 4. Effect of the calcination of the HT-10 sample at different contact time for the adsorption of Cr (VI).

3.3.3 Comparative sorption of BTEX using natural zeolite, bentonite and activated carbon

The evaluation of the cationic solids was performed in the sorption of BTEX using natural zeolite (from Tehuacan Puebla), bentonite and activated carbon using a similar experimental procedure of the anionic solids. The contaminated solutions were analyzed spectrophotometrically at λ_{\max} 270 nm for the equimolar mixtures of BTEX at 50, 100 y 200 ppm. The results are shown in Figure 5.

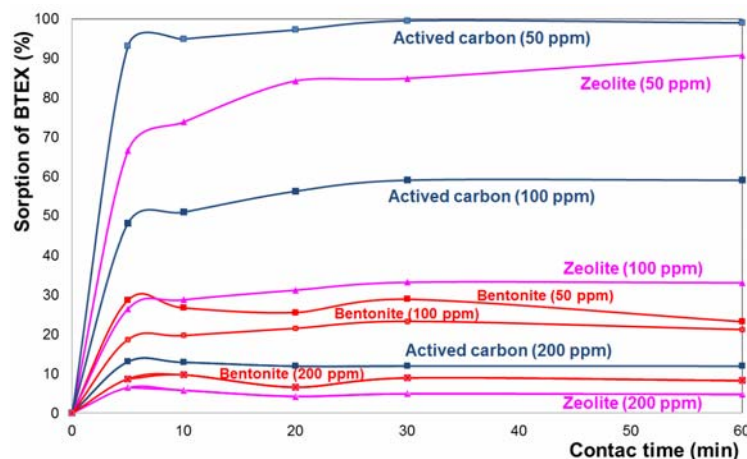


Figure 5. Percentage of sorbed BTEX in function of contact time for activated carbon, natural zeolite and bentonite at 50, 100 and 200 ppm of the BTEX mixture.



It is observed that in all cases the activated carbon presented the highest BTEX adsorption percentages, followed by natural zeolite and bentonite. From Figure 5 we can also note that bentonite is an instable sorbent since this solid presents cycles of adsorption and desorption, this is probably related to a very slow sorption process equilibrium. In all cases, as the concentration and the contact time increases, the materials saturate their available sites to entrap contaminants. These clays also contain exchangeable ions on their surface. However it is possible that the superior surface area and the low polar character of surfaces of activated carbon lead to a higher affinity to aromatic molecules, plays a more important role on the anion adsorption than the take up of BTEX anions of the clays by ionic exchange. It can be concluded that the best option is activated carbon, while bentonite is completely discarded as a possible sorbent material for this type of contaminant. On the other hand, although zeolite showed relatively good sorption capacity, the cost-benefit analysis should also be considered.

Finally, we propose using an integral system composed by a mixture of activated carbon along with calcined hydrotalcite-like compounds with nitrate interlayer component, in order to obtain an efficient system capable to perform a simultaneous decontamination in contaminated samples with Cr (VI) and BTEX. These system could be apply as an adsorption system, functioning as a supplement of photocatalytic and advanced oxidation processes to remove remaining traces of contaminants in water purification, in contaminated systems composed of both anionic and cationic species.

3.3 Photocatalytic system

We designed and built a annular photocatalytic reactor, the materials were selected according to the following criteria:

- Cost of material
- Availability
- Ease of manufacturing

Floor plans of the reactor are shown below in Figure 6.



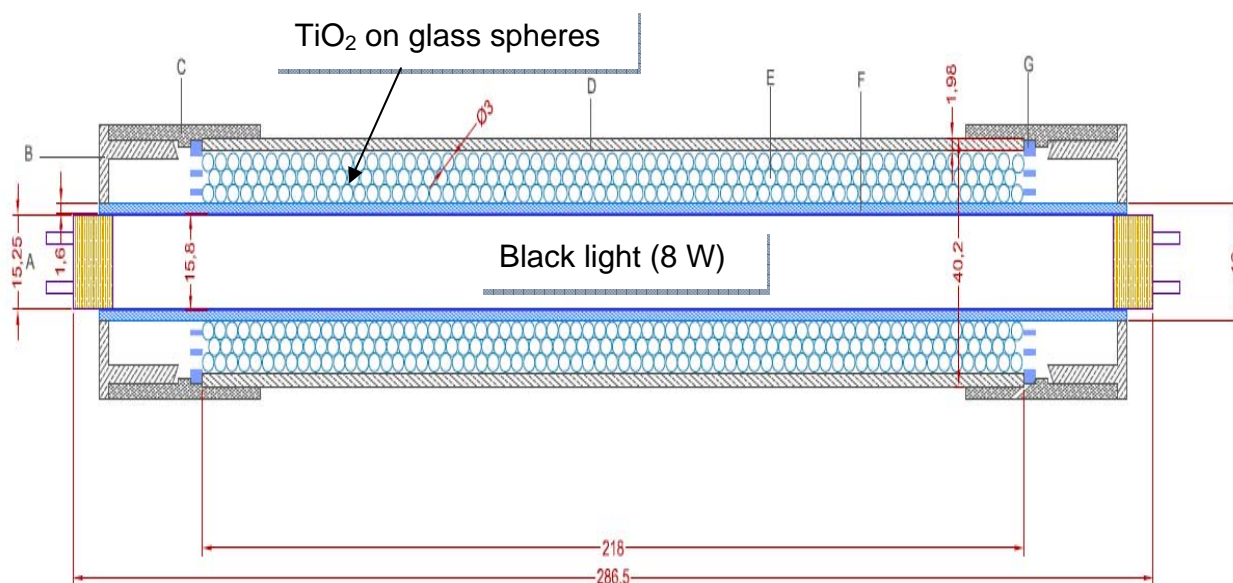


Figure 6. Floor plans of the annular photocatalytic reactor (lengths in cm).

Measurement of pressure drop

The experiment was performed to obtain pressure drop and flow rates in an annular packed bed, with a diameter ratio $D_h / d_p = 7.3$. The reactor was built with two concentric tubes, the outer tube was made of PVC with an outer diameter of 40.22 mm and a thickness of 1.975 mm. The inner glass tube had an outer diameter of 16.30 mm. The annular space created by these two tubes were packed with uniform spherical glass beads with a diameter of 3 mm and a length of 80 cm. It was explored the pressure drop for flows from 134 ml / min to 1057 ml / min along the annular packed bed. It can be observe that the pressure changes linearly with respect to the height of the catalyst bed and the equilibrium is reached with a with a length of packaging equal to 80 cm, as shown in Figure 7.



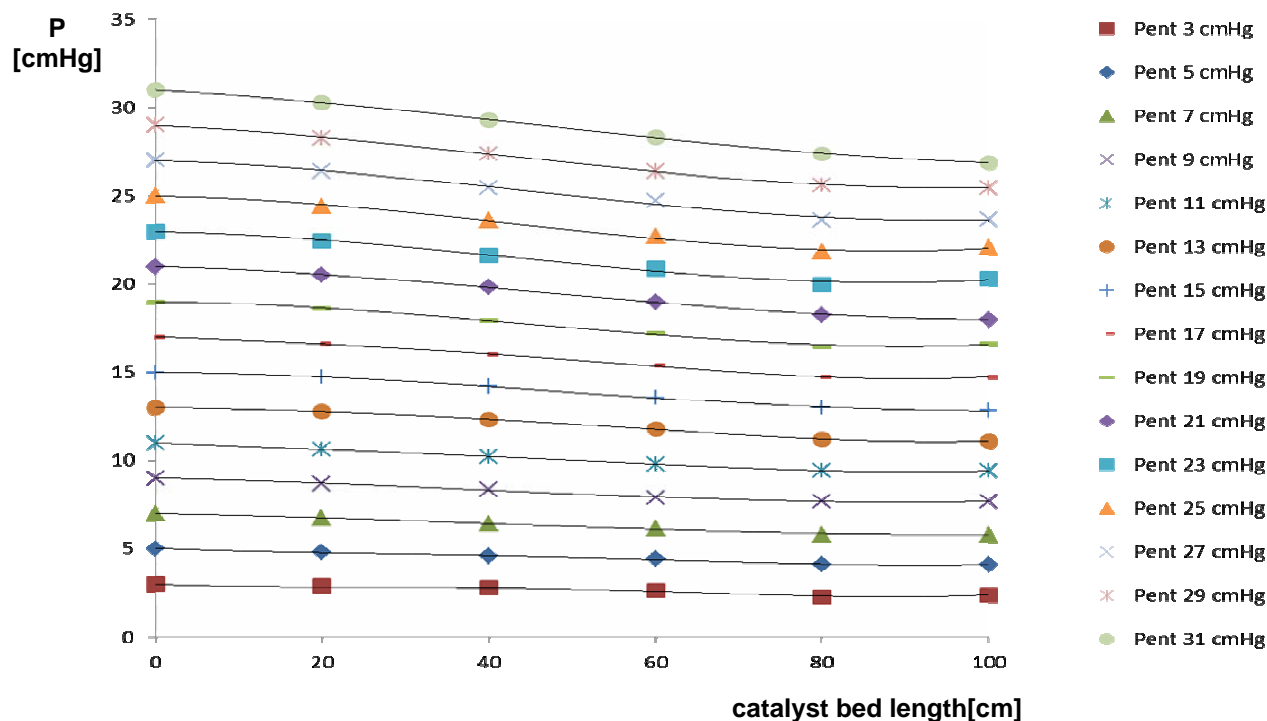


Figure 7. Profiles of pressure drop for annular photocatalytic reactor (Pent= input pressure).

Photocatalytic test

Methyl orange (100 ppm) was used as a model molecule to test the effectiveness of annular photocatalytic reactor. The reaction was performed continuously at total reflux (semibatch) with a volume flow rate of approximately 100 ml/min for 24 hours. As noted, it reaches a 50% conversion after 50 hrs (Figure 8). The system can be represented by a pseudo reaction order. In addition, It was found that annular reactor conversion was lower (20%) than by using as catalyst an aqueous solution of TiO_2 (anatase with concentration of 1g/L), although the conversion is lower, the designed reactor has the advantage that It doesn't need to separate the photocatalyst from the water.

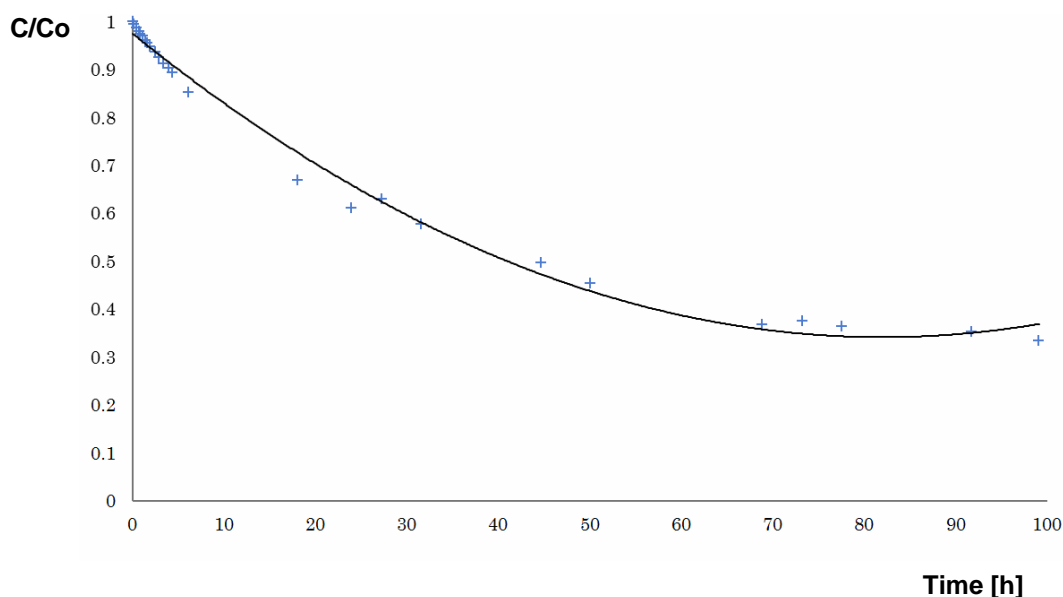


Figure 8. Degradation profile of methyl orange.

Finally and depending on the water characterization, the systems were assembled as:

sorption-photocatalysis

photocatalysis- sorption

sorption- photocatalysis- sorption

4. CONCLUSIONS

- Based on the characterization of drinking water D. F., it has low quality because of the presence of inorganic and organic species, so the water does not meet established international standards for human consumption, being the northern area of the city the most affected region.

- Hydrotalcite-like compounds (HT) with nitrate interlayer component were obtained in high purity by ultrasound-assisted coprecipitation at different irradiation times. It was found that the synthesis is favored at a frequency 25 kHz and 80% of power of the ultrasound irradiation. It was observed that the increase in the irradiation time at 30 min promotes the formation of large crystals and consequently a reduction in surface area.

- It was found that the best option for Cr (VI) removal was the calcined hydrotalcite-like compound irradiated 10 min (HT-10C), since this kind of stabilized solids are not going to exchange any kind of contaminant ion with the purified water, being also superior in terms of sorption capacity, even compared with activated carbon.



- The evaluation of the sorption process of a mixture of BTEX, it was observed that activated carbon was the sorbent material that presented the highest percentages of sorbed BTEX, followed by natural zeolite and bentonite. However, bentonite is discarded as a possible sorbent material for this type of contaminants due to this material presented a low performance in the BTEX uptake, as well as cycles of adsorption and desorption.

REFERENCES

- [1] J.A. Smith, S.L. Bartelt-Hunt, S.E. Burns, Sorption and permeability of gasoline hydrocarbons in organobentonite porous media, *J. Hazard. Mater.* **96**, 91–97 (2003).
- [2] Joint Academies Committee on the Mexico City Water Supply, Mexico's City Water Supply, National Academy Press, Washington **1995**.
- [3] C.M. Kao, J. Prosser, Evaluation of natural attenuation rate at a gasoline spill site, *J. Hazard. Mater.* **82**, 275–289 (2001).
- [4] S.O Flores, Project Technical Report “Estudio de Alternativas Tecnológicas de Bajo Costo para el Mejoramiento de la Calidad del Agua Potable en el D.F.”, recovered: <http://www.icyt.df.gob.mx/>, (2009).
- [5] M.R. Hoffmann, S.T. Martin, et al. (1995). Environmental Applications of Semiconductor Photocatalysis, **95**, 69-96 (1995).
- [6] B. Nanzai, K. Okitsu, N. Takenaka, H. Bandow, Y. Maeda, Sonochemical degradation of various monocyclic aromatic compounds. *Ultrasonics Sonochemistry*, **15**, 1235-1242 (2008).
- [7] S.P. Paredes, G. Fetter, P. Bosch, S. Bulbulian, Sol-Gel Synthesis of Hydrotralcite-Like Compounds. *J. of Mater. Sci.*, **41**, 3377-3384 (2006).
- [8] S.P. Paredes, G. Fetter, P. Bosch and S. Bulbulian; *J. Nucl. Mater.*, **155**, 359-368 (2006).
- [9] G. Mills and M. R. Hoffmann; *Environ. Sci. Technol.*, **27**, 1681 (1993).
- [10] F. Hongxiang, L. Gongxuan, L. Shuben, Adsorption and Photo-induced Reduction of Cr (VI) ion in Cr (VI)-4CP (4-Chlorophenol) Aqueous System in the Presence of TiO₂ as Photocatalyst, *J. of Photochem. A: Chem.*, **81**, 114-125 (1998).
- [11] H. Boumadiane, A. Leorgouri, A. Barroug, C. Forano and J.P. Besse, Use of the Ion-Exchange Properties of Layered Double Hydroxides for Water Purification, *Collection of Czechoslovak Chem. Com.*, **63**, 732-741 (1998).

