Chapter 7: Results and discussion

Results will be given following the order of the general work plan outlined in section 6.1

7.1 Hydraulic excel worksheet

Powered by the equations 4-1, 4-2, 4-3 and 4-4 with the parameters mentioned in chapter 4, the Excel worksheet calculated the theoretical power a pump would require to drive the system. There are two parts of the program, the "User" data collection sheet, and a second "Calculation" sheet. On the user sheet, information about the system is to be provided. The information is divided into five blocks: pump data, fluid data, piping system data, accessories data and flow data. Next to it, a final answer block gives results on pump power, net positive suction head, flow regime and residence time. The user sheet is presented in figure 7-1.
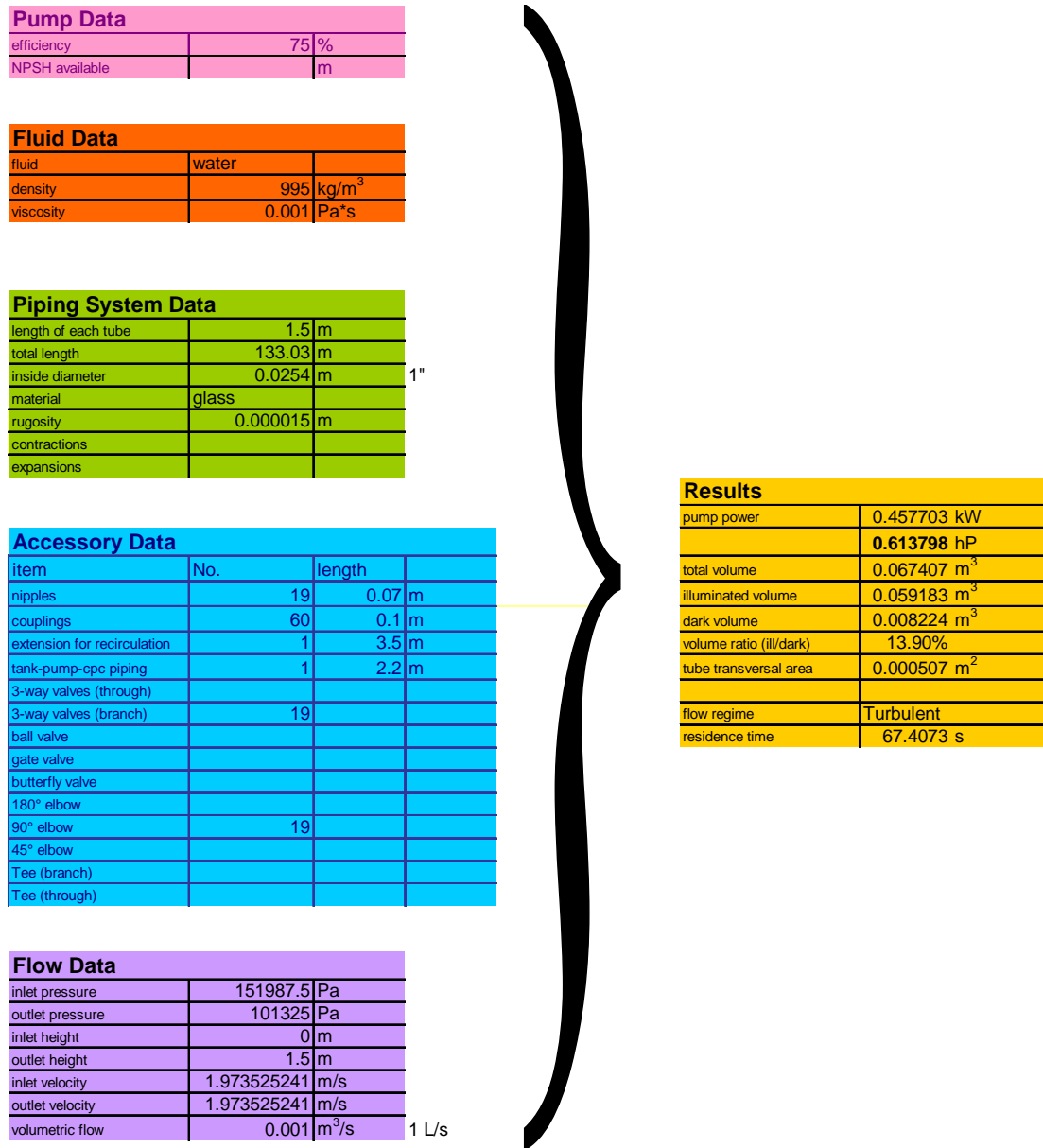
Pump Data		
efficiency	75	%
NPSH available		m

Fluid Data		
fluid	water	
density	995	kg/m^3
viscosity	0.001	Pa*s

Piping System Data		
length of each tube	1.5	m
total length	133.03	m
inside diameter	0.0254	m	1"
material	glass	
rugosity	0.000015	m
contractions		
expansions		

Accessory Data		
item	No.	length
nipples	19	0.07 m
couplings	60	0.1 m
extension for recirculation	1	3.5 m
tank-pump-cpc piping	1	2.2 m
3-way valves (through)		
3-way valves (branch)	19	
ball valve		
gate valve		
butterfly valve		
180° elbow		
90° elbow	19	
45° elbow		
Tee (branch)		
Tee (through)		

Flow Data		
inlet pressure	151987.5	Pa
outlet pressure	101325	Pa
inlet height	0	m
outlet height	1.5	m
inlet velocity	1.973525241	m/s
outlet velocity	1.973525241	m/s
volumetric flow	0.001	m^3/s	1 L/s

Results		
pump power	0.457703	kW
	0.613798	hP
total volume	0.067407	m^3
illuminated volume	0.059183	m^3
dark volume	0.008224	m^3
volume ratio (ill/dark)	13.90%	
tube transversal area	0.000507	m^2
flow regime	Turbulent	
residence time	67.4073	s

Figure 7-1. Hydraulic excel sheet, "user" interface

Due to the modular nature of the interface, it is easy to use and interact with. The user can instantly see the effect that changing any condition will have on the energy required to pump the system and the variables that are most affected. This enables

the user to easily alter the conditions (mainly of inlet pressure, type and number of accessories and volumetric flow rate) and to choose the most energy efficient configuration. Once the conditions are chosen and set, the residence time will determine how long the system has to work in order to achieve the desired degradation based on laboratory level research.

7.2 Available area and selected system configuration

The area for the pilot plant is a rectangle measuring 7.03 m long and 3.50 m wide. The studied configurations are shown on figures 7-2, 7-3, 7-4 and 7-5. Table 7-1 summarizes the amount of accessories needed for each configuration and a total estimated cost.

Table 7-1. Summary of number of accesories needed for each configuration and estimated cost (MXN)

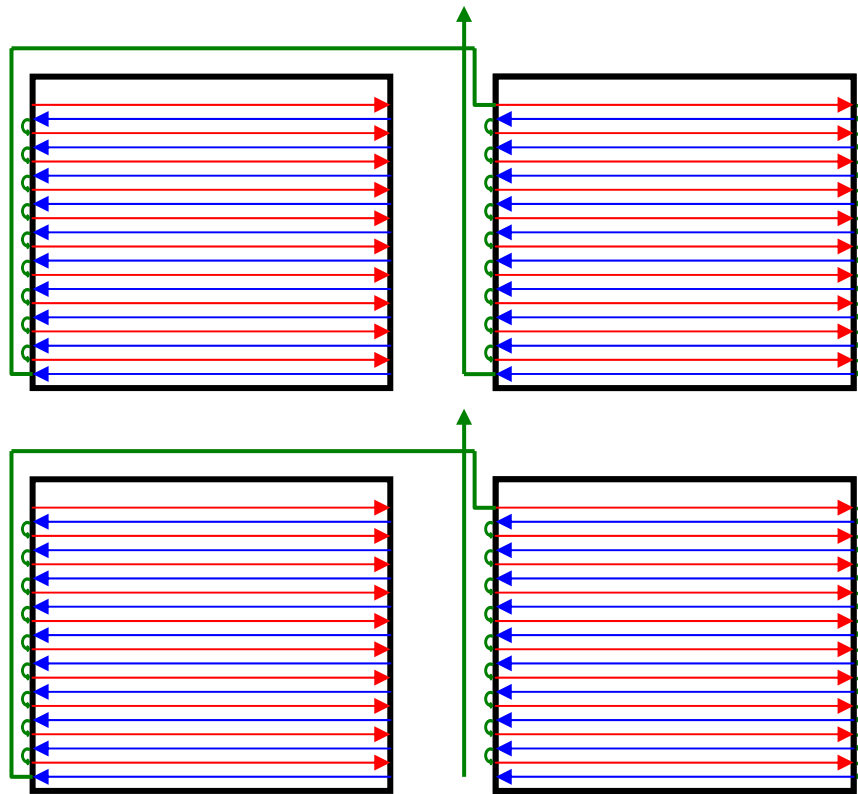| Item	Figure 7-2	Figure 7-3	Figure 7-4	Figure 7-5
m^2 of compound parabollic collector	4	4	4	4
CPVC 3-way valve	0	38	0	19
PVC coupling	0	40	0	60
PVC 90° elbow	76	45	152	22
PVC Sampling valve	4	40	4	19
O-Ring	152	250	304	281
Rotomex tank (450 L)	1	1	1	1
PVC ball valve for the exit of the tank	1	1	1	1
HPDE hose	4	2	4	1
PVC tubing	1	1	1	1
Centrifuge pump (0.5 hp)	1	1	1	1
Tee	4	0	4	0
Total estimated cost	**$53,379.38**	**$106,017.13**	**$54,063.38**	**$79,714.76**

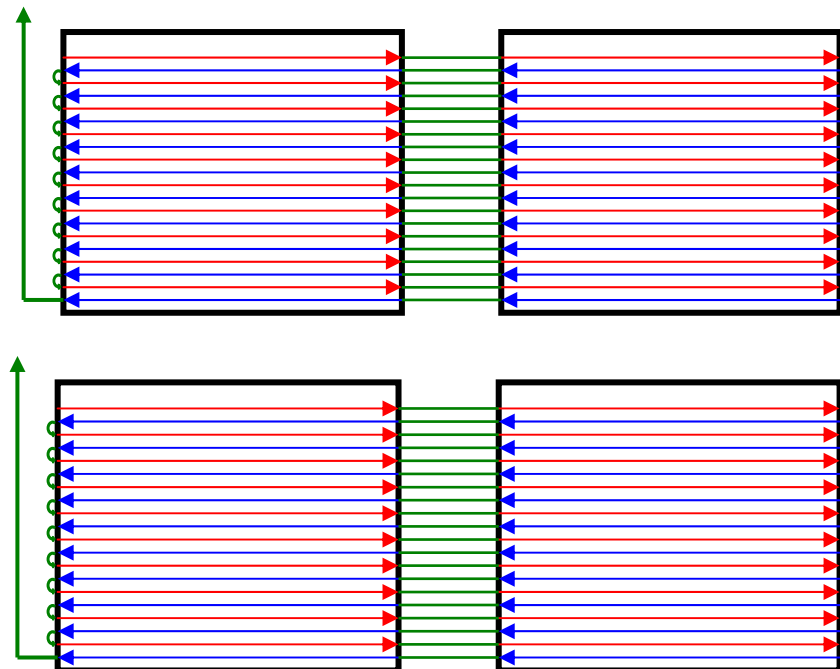**Figure 7-2.** Individual CPCs in parallel

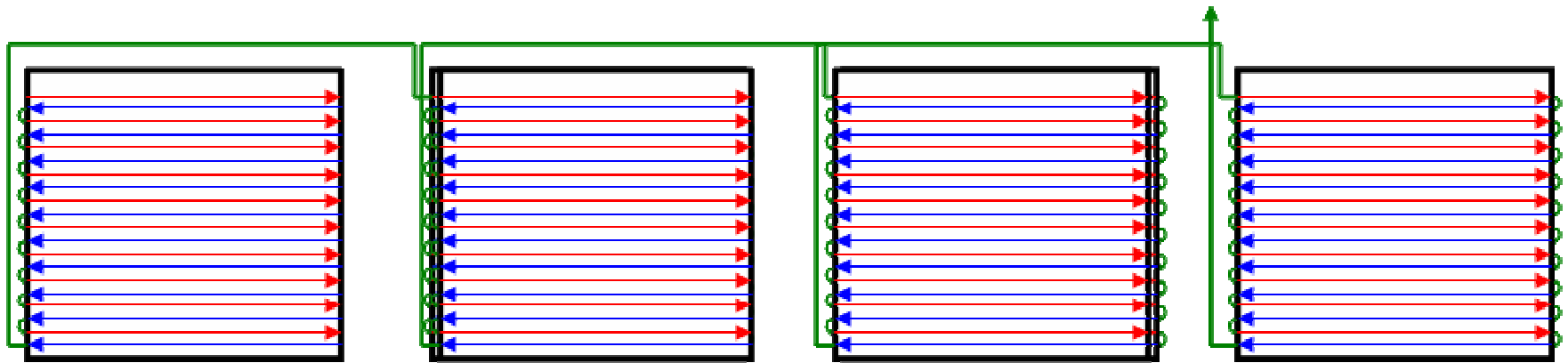
Figure 7-3. Flow-through 2 CPCs in parallel

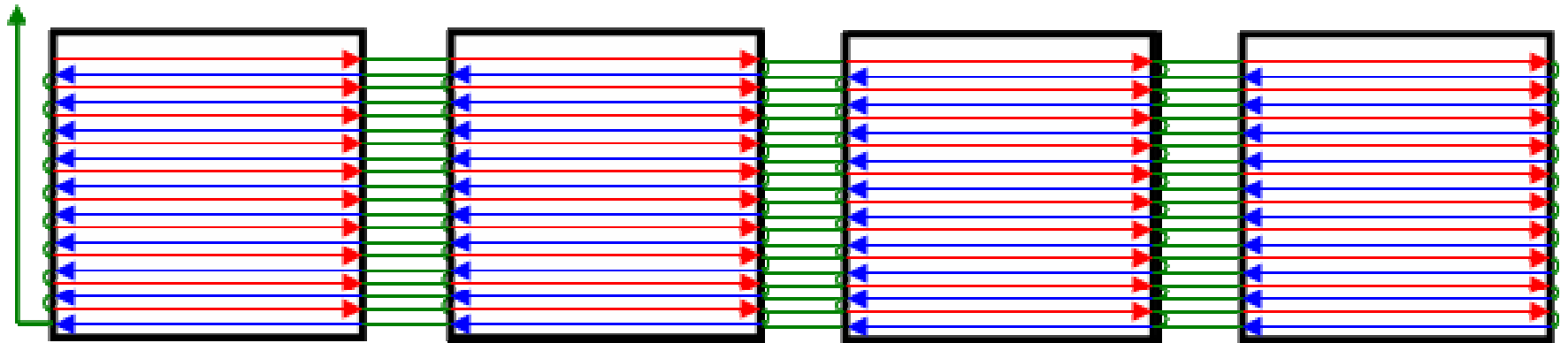**Figure 7-4**. Single panel with 4 CPCs in series

Figure 7-5. Flow-through 4 CPCs in series

The chosen design is depicted in Figure 7-5. It was selected for its versatility in using any number of lines required, lower energy need and minimization of recirculation lines. Twenty lines are available, that can hold a volume of 67.5 L. Total volume of 350 L will take into account the recirculation tank, which at any given time after startup will hold 292.5 L.

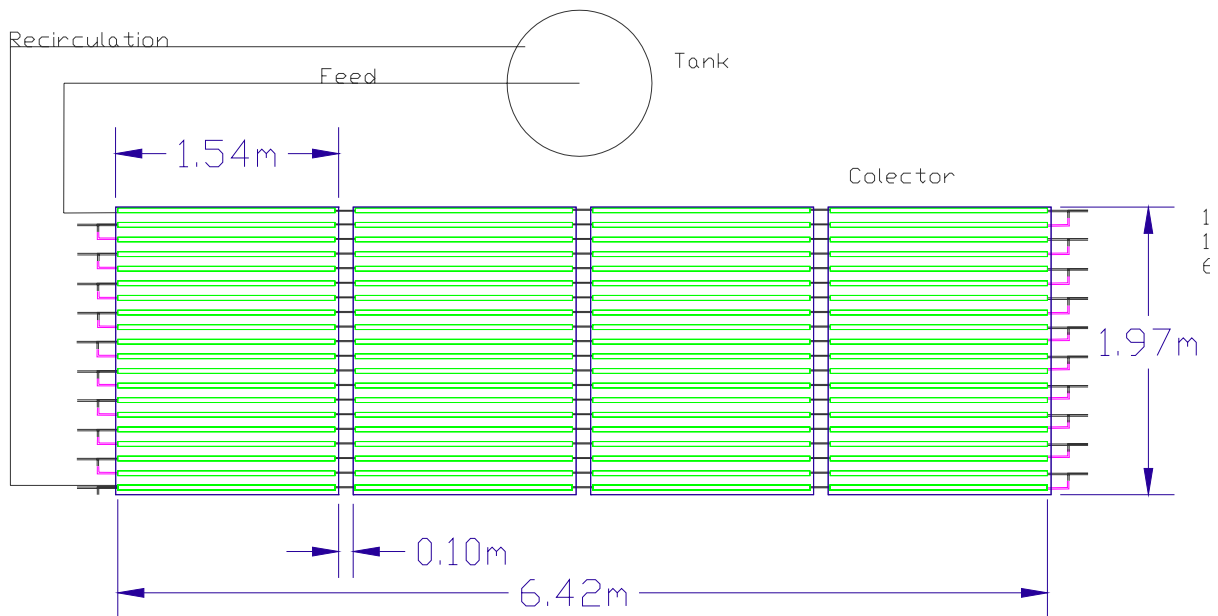A simple scheme of the plant is shown in Fig 7-6. In it, the four CPCs, the tank and main accessories are shown.

Figure 7-6. Basic arrangement of the solar photocatalytic pilot plant

The proposed measurements of the pilot plant are only an estimate of the real dimensions. The reason for this is that the supplier of CPCs gave inaccurate information regarding the size of the collectors and did not specify if the glass tubes would be emerging from the frame or not. The proposed 10 cm gap between each collector is a safety margin to account for these uncertainties.

More detailed illustrations are shown next. Fittings and valves are exposed in further detail. Dimensions (not shown) are the same as in Figure 7-6.
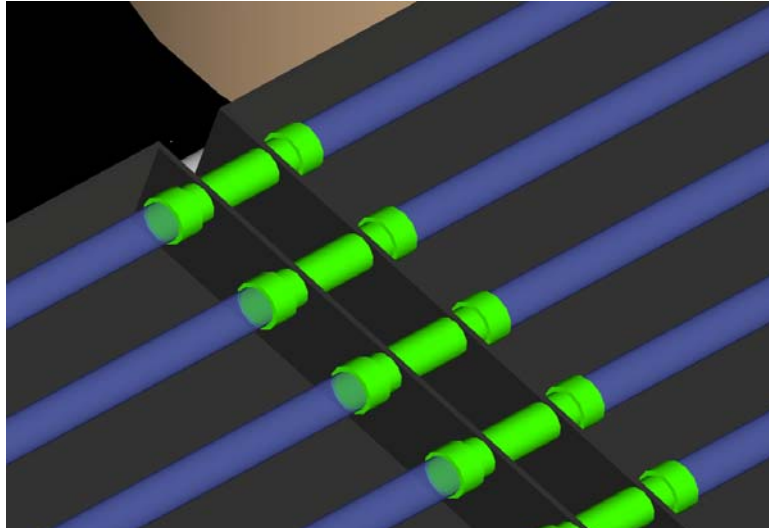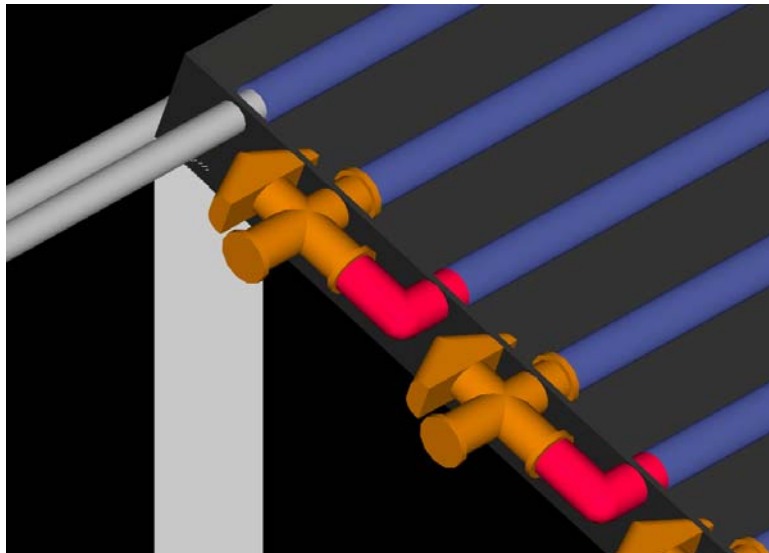

Figure 7-7. Detail of couplings

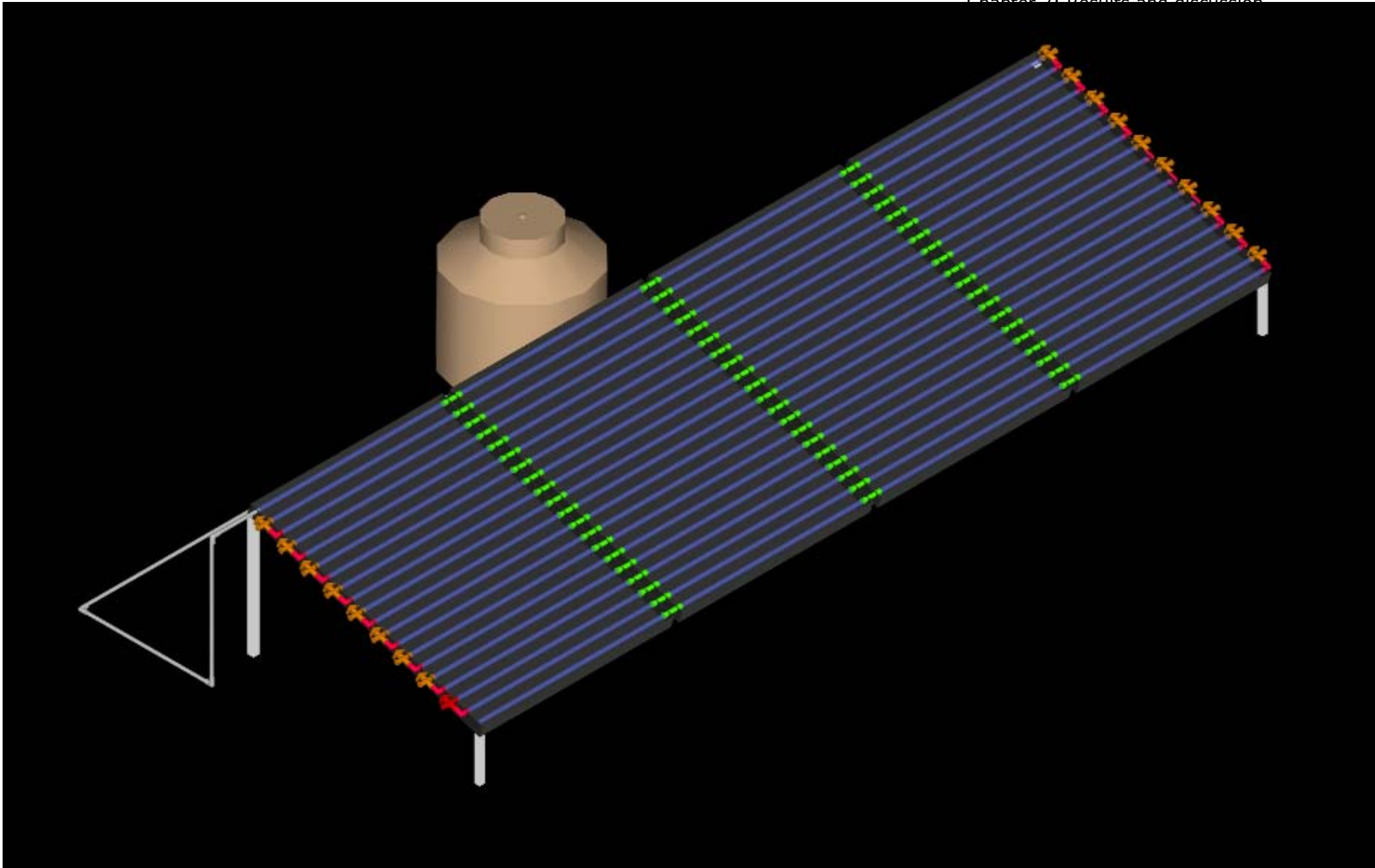**Figure 7-8**. Detail of end connections

Figure 7-9. 3-D view of the pilot plant

7.3 Selection of accessory type and materials

Accessory materials were chosen for their smoothness, capacity to be adapted to glass tubes and chemical resistance.

To begin with, plastic was chosen over metal due to less frictional loss in the system and light weight (so the glass tubes could support them). Three plastics were considered for the joints and valves: polyvinylchloride (PVC), chlorinated polyvinylchloride (CPVC) and high density polyethylene (HDPE). According to Robert Zona and Sonja Solar, arising sub-products of 2,4-D photolytic degradation include phenoxyl radicals and 2,4-dichlorophenol which are potent oxidizers [Zona and Solar, 2002]. *Empresa Mexicana de Manufacturas S.A.*, when contacted as a supplier for valves, sent a chemical resistance table by Hayward (Annex C). The table reports PVC unsuitable for phenols, but CPVC shows excellent resistance to them. Therefore CPVC was chosen as the material for the most specialized accessories, the three-way and sampling valves. CPVC is more expensive, but durability had a higher priority. HDPE was considered because in Almería, Spain, a photocatalysis plant was built using this material to connect the glass tubing [Blanco and Malato, 2000].

Specification sheets are in appendix D.

7.4 Suppliers, cost and units needed

Suppliers for most accessories are local hardware stores. PVC material (ball valves, couplings and tubing) are common, and thus may be purchased locally. Due to the size and type of pump, it will also be purchased at a local hardware store.

Table 7-2 shows the list of suppliers for the parts needed.

Table 7-2. List of suppliers for accessories chosen

Item	Supplier	Name of Contact	Telephone
3 way valve	EMMSA	Ing. Leon F. Valdes	55 91717000-13, 5591717001
PVC coupling	Local hardware stores		
PVC 90° elbow	Local hardware stores		
CPVC Sampling valve			
Viton O-Rings	Refaccionaria Industrial Casa Salinas		3206996, 3201746, 3201747
Rotoplas tank (450 L)	Local hardware stores		
Rotomex tank (450 L)	Local hardware stores		
PVC globe valve for the exit of the tank	Local hardware stores		
HPDE hose	Local hardware stores		
PVC tubing	Local hardware stores		
Centrifuge pump (0.5 hp)	Local hardware stores		

Unit cost of the items is presented in Table 7-3. Three-way valve's cost is updated to Oct 13 2005, prices may be subject to variation. The cost for the CPVC sampling valves had not been obtained at the time of writing, and is not considered. All prices date from Oct-Dec 2005 quotations.

Tabla 7-3. Estimated cost of the accessories needed to setup the plant (Oct-Dec 2005, MXN)

No.	Item	Unit price (MXN)	Subtotal
4	m^2 of compound parabollic collector	$12,682.42	$50,729.68
19	CPVC 3-way valve	$1,383.13	$26,279.38
60	PVC coupling	$3.60	$216.00
22	PVC 90° elbow	$5.00	$110.00
19	CPVC Sampling valve		$0.00
240	O-Ring	$2.00	$480.00
0	Rotoplas tank (450 L)	$860.00	$0.00
1	Rotomex tank (450 L)	$570.00	$570.00
1	PVC ball valve for the exit of the tank	$35.70	$35.70
1	HPDE hose	$42.00	$42.00
2	PVC tubing	$30.00	$60.00
1	Centrifuge pump (0.5 hp)	$850.00	$850.00

	TOTAL (MXN)	$79,372.76

In addition, cost of reagents must be considered. Table 7-4 has the approximate costs of reagents, but update of costs is recommended. Source is Sigma-Aldrich's 2002-2003 Reagent Catalogue.

Table 7-4. Reagent approximate costs

Code	Name	Molecular formula	Amount (kg)	Price (USD)
For Fenton				
F2387	Ferrous sulfate heptadydrate minimum 99.0%, ACS	$FeSO_4.7H_2O$	0.25	25
	Hydrogen Peroxide (Industrial)	H_2O_2	1	0.74
For Co-PMS				
22,803-6	Oxone, monoulfate compound (Potassium peroxymonosulfate)	$KHSO_5$	0.1	25.7
40,302-4	Cobalt(II) acetate tetrahydrate 98-102% ACS	$(CH_3COO)_2Co.4H_2O$	0.025	20

7.5 Detailed assembly process

The process of setting up the solar photocatalysis pilot plant will be described by steps. This process will be described in detail from the early stages of the setup through its complete assembly.

Preliminary steps

1) **Construct the supporting structure**. Supporting structure made of cast iron. It consists of an elevated bed with a general structure shown in Figure 7-10.
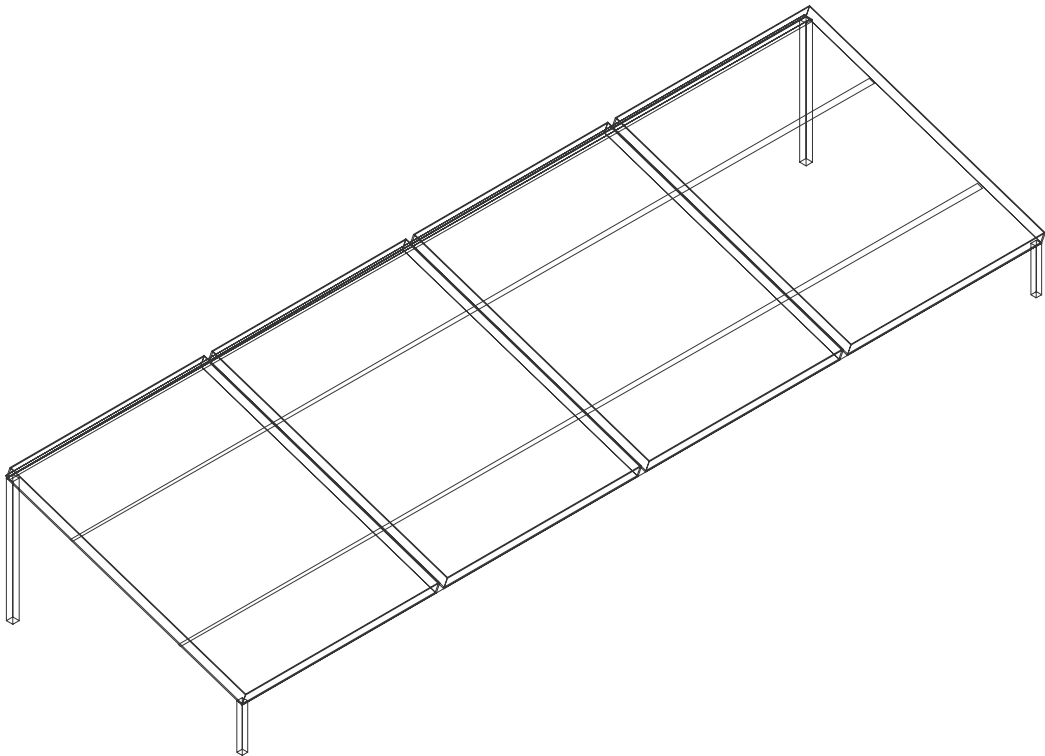

Figure 7-10. Cast iron base to mount CPCs

The flanges to support the CPC are 3 cm wide and run through the whole bed. Height was determined by equaling the top of the tank to the top of the CPC (considering that they are tilted to the local latitude, 18.5°). The difference between the top of the CPC to the bottom is of 0.64 m. Total height should be 1 m, so the difference of 1-0.64=0.36 m. 0.36 m is the height of the structure.

2) **Purchase few units of the joining accessories**. A few pieces of the following types should be bought to conduct joining tests:

PVC couplings

O-rings

Three-way valves

PVC 90° elbows

The couplings shall be carved to fit the O-rings. 90°elbows can be cemented to the three way valves. Testing of leaks and firmness should be conducted for all connections.

3) **Verify with the CPC that the accessories fit**. With the compound parabolic concentrator verify that the accessories chosen fit the CPC. If they do, buy all the pieces needed for full assemblage of the pilot plant. If they do not fit, look for alternative connecting devices.

Pilot plant assembly

4) **Make sure there are enough and prepared pieces**. PVC couplings should be engraved with two canals on each side to fit the O-rings. There should be

20   3 way valve

60   PVC coupling

22   PVC 90° elbow

19   PVC Sampling valve

240   O-Ring

1   Rotomex tank (450 L)

1   PVC ball valve for the exit of the tank

1   HPDE hose

2   PVC tubing

1   Centrifuge pump (0.5 hp)

5) **Mount the CPCs in the base and arrange the accessories.** Lay the CPC's on the base and connect them using the couplings fitted with double O-rings. The base should be tilted at local latitude angle (Cuernavaca, 18.5°). Make sure the tubes are inserted all the way and ensure the CPCs at their ends with metal railing (welded at the moment). At the ends of the tubes where a 3-way valve corresponds, the order of assembly is: glass tube end, sampling valve, 3 way valve. Refer to Figure 7-8 noting the inclusion of the sampling valve. Cementing or screwing can be used between valves and the elbow.

6) **Measure the feeding and recirculation lines and cut tubes as needed.** PVC tubing must be cut into two segments: 1) from the bottom of the tank to the inlet of the pump and 2) from the outlet of the pump to the entrance of the first glass tube. PVC-glass transition will be made with the double O-ring technique.

7) **Install the centrifugal pump.** Install the centrifugal pump according to manufacturer's instructions.

8) **Connect the PVC tubing to and from the pump.** Connect the tubing from the tank to the pump and from the pump to the inlet of the first CPC. A flow controller valve (ball valve) is placed

between the outlet of the pump and the CPC. This valve serves as a safeguard and flow reducer when needed.

Performance tests

9) **Run a leakage test**. Start the system at full flow to check for any leaks, loose connections and other malfunctions. Correct them as needed.

10) **Run a valve test**. With water flowing, open and close all valves one by one to ensure there are no obstructions and are firmly placed.

7.6 Selection and evaluation of a figure-of-merit

Based on the Bolton *et al.*'s proposal, the figure-of-merit chosen was collector area per order (A_{CO}). A_{CO} was selected because the plant is driven by solar energy, the concentrations tested will be of 100 mg/L or less and it has been observed to follow a first order reaction rate. Remembering equations 5-24 and 5-25, where A_{CO} is described as:

$$A_{CO} = \frac{A\overline{E}_s t}{V \log\left(\dfrac{c_i}{c_f}\right)}$$

Eq. 5-24. Batch operation

$$A_{CO} = \frac{A\overline{E}_s}{F \log\left(\dfrac{c_i}{c_f}\right)}$$

Eq. 5-25. Flow through operation

A_{CO} for batch operation was chosen because the system starts with an initial concentration which decreases through time until the desired concentration is achieved and the water can be removed. A_{CO} was calculated using known parameters of the system, such as collector area (4 m^2) and volume (350 L). For unknown parameters (c_i, c_f, E_s, t) preliminary laboratory experimentation data was taken. The resulting A_{CO} was a combination of laboratory results and actual pilot plant size. Values for the variables are:

t = 2 (h) c_i= 100 mg/L

E_s= 242.95 (W/m2) c_f= 2.5 mg/L

V= 350 (L)   **A**= 4 (m2)

E_s was obtained from solar irradiation data taken during summer (June-July). Fenton and Fenton-like processes use only approximately 30% of the wavelengths of the solar spectrum to react. 30% of nine measures were taken and averaged, resulting in the above number. On experimental runs of 2,4-D mineralization using Fenton reagent, in two hours, concentration dropped from 100mg/L to 2.5 mg/L. The resulting A_{CO} was 3466.39 m^2/m^3-order. This result means that approximately   3500 m^2 would be needed to decrease the concentration from 100 mg/L to 2.5 mg/L in one pass (i.e. without recirculation).   Since areas of that magnitude are unpractical, and systems fill their area needs with multiple passes through a recirculation system, the A_{CO} result had to be modified to give an equivalent plant operation time. With a simple equivalence factor (4 m^2 = 1 pass), the number of passes was calculated and resulted in 866.6. With data obtained from the hydraulic Excel sheet, each pass lasts 1.12 min; therefore the pilot plant operating time came to be of 16.2 h.

Several absurds were found using the A_{CO} figure-of-merit. The term arrangement on the equation says that with larger A and E_s, the needed area per m^3-order will increase. This means that having

larger collection areas available or having more radiation energy results in *needing* larger areas to degrade contaminant C. The equation's form has in the denominator the logarithm of the initial concentration divided by the final one. This implies that as the difference between initial and final concentrations increase, the area per m^3-order will decrease (i.e. solar collection area needed is less to bring about a change from 100 mg/L to 2.5 mg/L than a change from 100 mg/L to 10 or 50 mg/L).

For these reasons, A_{CO}'s inherent parameters were examined. In a first order reaction the reaction rate (k) can be determined by:

$$k = \frac{\ln \dfrac{c_i}{c_f}}{t} \qquad \text{(Eq. 7-1)}$$

In a plot of logarithm of concentrations versus reaction time, the slope of the line is k (Fig 7-11). Then, this value is indicative of the velocity of the reaction, which depends in the species involved, and in the case of a solar driven AOP, in the amount of energy given to the system.
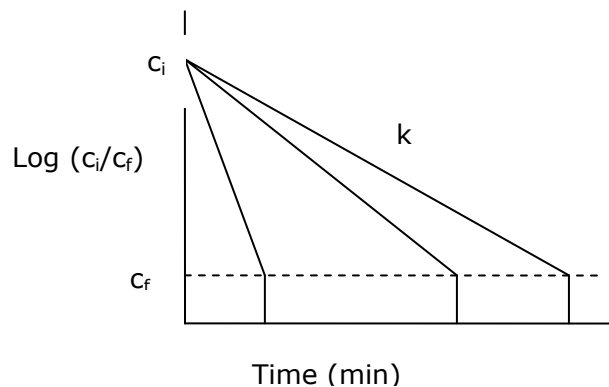

Figure 7-11. First order reaction kinetics. K is the slope

As k tends to infinite, the time required to achieve c_f decreases. Therefore, if k could be inserted into the equation, which is done by rearrangement of terms, a clearer understanding of the influence of reaction kinetics in the area needed could be achieved. Presumably, the more intense the solar irradiation, the more energy would be available for ·OH production and k would increase. Also, different compounds would exhibit different values for k, and it is a more convenient parameter if laboratory work is to precede scale up. A_{CO} can also be expressed as:

$$A_{CO} = \frac{A\overline{E}_s}{Vk}$$
(Eq. 7-2)

A k (min^{-1}) value obtained from the 2,4-D photo Fenton degradation data that was the source for E_s. This time, $A_{CO} = 6310.65$ m^2/m^3-order, or 29.4 h of pilot plant operation. This is approximately double the value obtained by the original A_{CO}.

It was noticed with this new equation that energy proportioned by solar irradiation was taken into account for A_{CO}, but it did not affect the value for k. This means that the velocity of degradation of a compound is independent of solar conditions; a sunny day would be the same as a cloudy day and midday would be the same as dusk. It is not within the scope of this work to relate the influence of irradiation on the value of k, and further research should be conducted to validate the hypothesis that increased incident irradiation increases k value.

A second Excel sheet (A_{CO} Excel sheet) was built to automate the calculation of pilot plant working time (Fig 7-12). Again, the sheet is divided in the "User" and the "Calculation" workbooks. The "user" interface is modular and offers the user the calculation of operating time by either Eq 5-24 or Eq 7-2.

Data when k is known		
collection area	4	m^2
average solar irradiance	242.96	W/m^2
treated volume	0.35	m^3
rate constant	0.44	t^{-1}
residence time	1.12	min

Results	
Collection area per order	6310.65 m^2/m^3-order
Operating time	29.4 h
	1767.0 min

Data when k is not known		
collection area	4	m^2
average solar irradiance	242.96	W/m^2
treated volume	0.35	m^3
elapsed time	2	h
initial concentration	100	mg/L or M
final concentration	2.5	mg/L or M
residence time	1.12	min

Results	
Collection area per order	3466.39 m^2/m^3-order
Operating time	16.2 h
	970.6 min

Figure 7-12. A_{CO} excel sheet, "user" interface

7.7 Operation times for the degradation of selected pesticides using Fenton reagent and Co-PMS

Originally, kinetic parameters on the degradation of 2,4-D and atrazine using photo Fenton and photo Cobalt-peroxymonosulfate (Co-PMS) were to be obtained from laboratory research at IMTA. However, full studies were not completed at the time of writing, and scientific documentation sources were used.   There are four combinations of treatment, shown on Table 7-5.

Table 7-5. Processes to be assayed by the solar photocatalytic plant.

	Fenton reagent	Co-PMS
2,4-D	A	B
Atrazine	C	D

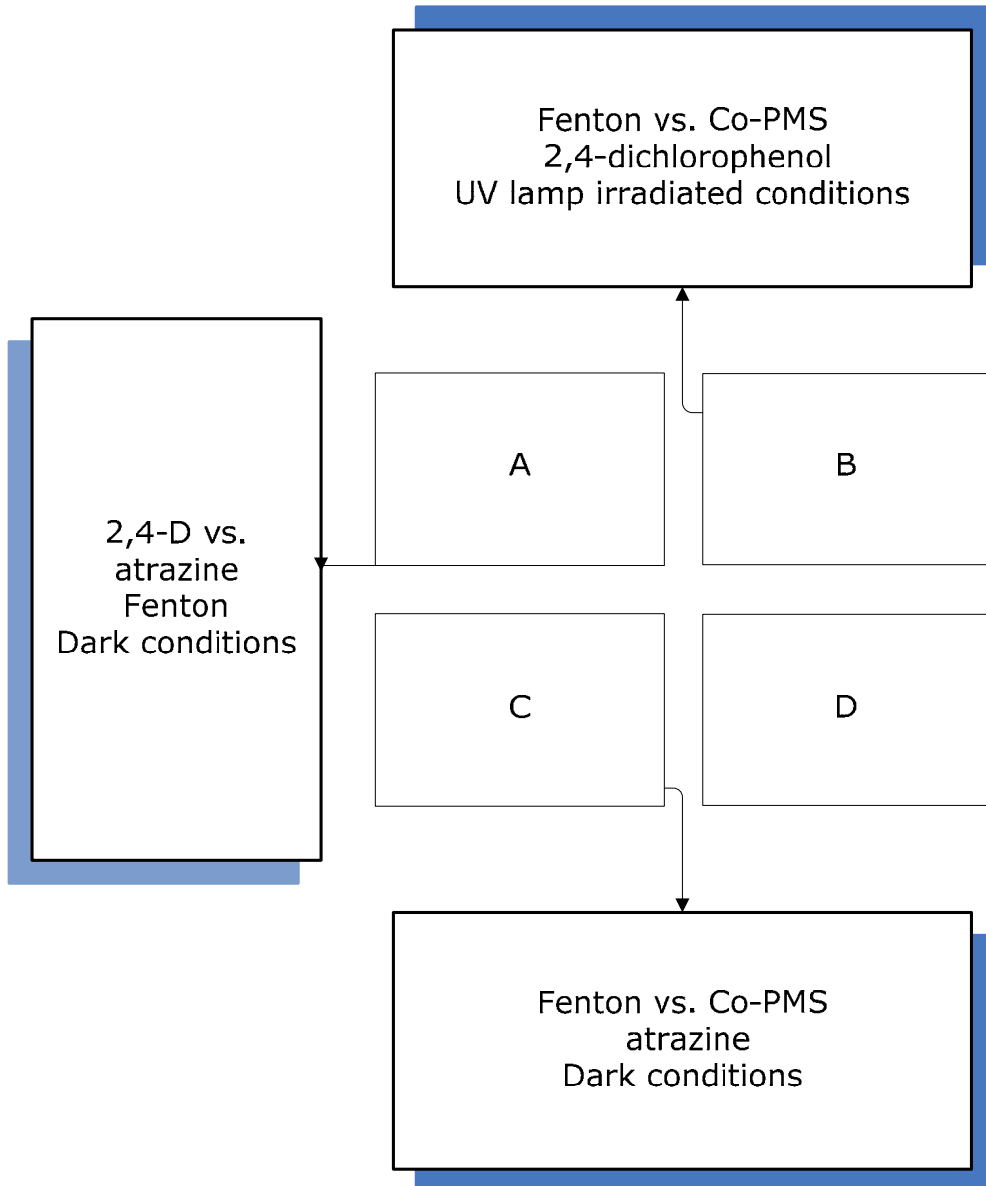From the literature, data was found that enabled comparison in three ways:

Figure 7-13. Catalyst and pesticide comparisons

1. Fenton reagent *vs.* Co-PMS for 2,4-dichlorophenol (the first degradation intermediary of 2,4-D).

2. Fenton reagent *vs.* Co-PMS for atrazine under dark conditions.

3. 2,4-D *vs.* atrazine degradation using Fenton reagent under dark conditions.

Data was not found of the degradation using Co-PMS of 2,4-D. It was chosen not to use data of 2,4-dichlorophenol with Co-PMS because at the end, no accurate inferences could be made on weather photo Fenton or Co-PMS would be more efficient for both atrazine and 2,4-D.

All experiments found in literature used UV lamps as a source of radiation instead of the sun. Furthermore, some of the information was generated under dark conditions. It can be presumed that solar radiation produces faster degradation rates according to information given in Chapter 4.

A_{CO} in its original form was used to compare the systems above. In spite of the problems outlined in the previous section, it is not within this work to propose a new figure-of-merit. Care should then be exercised on the interpretation and accuracy of the results. Data for A, E_s and V is the same as given in section 7.6 for the proposed system. Literature provided with values for c_i, c_f and t.

It is worth noting that the effect of pH is not considered here. Fenton requires a pH < 3, while Co-PMS can work at neutral conditions. The fact that using Fenton requires pre-acidification of the samples and neutralization at the end (to be in accordance to water release needs for further treatment or incorporation to water bodies) must be considered. Anipsitakis and Dionysiou (2003, 2004) show that at higher pHs, Co-PMS outperforms Fenton in degradation rates. All data shown here was taken under Fenton-favorable conditions, at a pH≈3.

7.7.1 Fenton reagent *vs.* Co-PMS for 2,4-dichlorophenol.

Data was taken from Anipsitakis and Dionysiou (2004).

As a radiation source, four germicidal 15 W UV lamps were used emitting almost monochromatic radiation at 253.7 nm. Data is shown in Table 7-6.

Table 7-6. Data used for the comparison of Fenton and Co-PMS in degrading 2,4-dichlorophenol [Anipsitakis and Dionysiou, 2004].

	Fenton	Co-PMS
Compound	2,4-diclorophenol	
c_i (mg/L)	20	20
c_f (mg/L)	0	0
t (h)	0.5	1
V (L)	350	350
E_s (W/m^2)	242.95	242.95
A (m^2)	4	4
A_{co} (m^2/m^3-order)	220.34	440.67
Operation time (h)	**1**	**2.1**

Using Fenton reagent to degrade 2,4-dichlorophenol results in a lower plant operation time. This is in accordance with literature from the same article. Results shown here are probably over specified since the sun has a more ample λ spectrum that can be used by reactants. Also, at times irradiation on the reaction vessels will have more energy. However, it has to be taken into consideration that these experiments are made under stable and predictable irradiation, whereas in a solar-driven plant, these factors can't be assured.

7.7.2 Fenton reagent *vs.* Co-PMS for atrazine under dark conditions.

Data was taken from Anipsitakis and Dionysiou (2003).

Table 7-7. Data used for the comparison of Fenton and Co-PMS when degrading atrazine [Anipsitakis and Dionysiou, 2003].

	Fenton	**Co-PMS**
Compound	Atrazine	
c_i (mg/L)	8	8
c_f (mg/L)	0.8	0
t (h)	0.33	2
V (L)	350	350
E_s (W/m^2)	242.95	242.95
A (m^2)	4	4
A_{CO} (m^2/m^3-order)	924.64	940.76
Operation time (h)	**4.3**	**4.4**

In this case, Fenton is again, a faster decomposition agent than Co-PMS. Nevertheless, complete disappearance of atrazine could not be achieved with Fenton, and even if time was extended, still the final concentration was of about 10% of the initial one [Anipsitakis and Dionysiou, 2003]. Co-PMS, although somehow slower, shows complete atrazine decay. Literature assays from which data was taken, were performed under dark conditions and it should be noted that several sources support the fact that irradiation greatly decreases degradation time. Results shown above are then greater than what would be expected with the actual running of the pilot plant.

7.7.3 2,4-D vs atrazine degradation using Fenton reagent under dark conditions.

Data for 2,4-D was taken from Kwan and Chu (2003). For atrazine the source is Tang (2003).

Table 7-8. Data used for the comparison of 2,4-D and atrazine when using Fenton [Kwand and Chu, 2003; Tang, 2003].

	2,4-D	**Atrazine**
Catalyst	Fenton	
c_i (mM)	1	.132
c_f (mM)	0.8	.00132
t (h)	1	24
V (L)	350	350
E_s (W/m^2)	242.95	242.95
A (m^2)	4	4
A_{co} (m^2/m^3-order)	28652.21	33320.23
Operation time (h)	**133.7**	**155.5**

The pesticide 2,4-D degrades faster with Fenton than atrazine. The results are in agreement with literature citing atrazine as less susceptible to degradation. Also, recalling information in Chapter 4, atrazine's last known degradation compound is cyanuric acid, therefore information shown here is of atrazine's disappearance, but not complete mineralization. Again, and as is the case for comparison number 2, under irradiated conditions, it can be expected that plant A_{CO} and plant operation time decrease from results presented. Operation times shown here refer to irradiated hours, and are unacceptable for a pilot plant that depends on the sun, because at best, every day has 15 hours (at selected latitude) of solar irradiation. Laboratory experiments that are based on the conditions of operation (irradiation by the sun) are strongly recommended to accurately evaluate the difference in the breaking down of the two pesticides.