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Photocatalysis for Oxidation of Pulp Mill Waste Streams

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Photocatalysis for Oxidation of Components of Pulp Mill Waste Streams

SFM Network Project:
Advanced Oxidation Processes, Especially Photocatalytic

by

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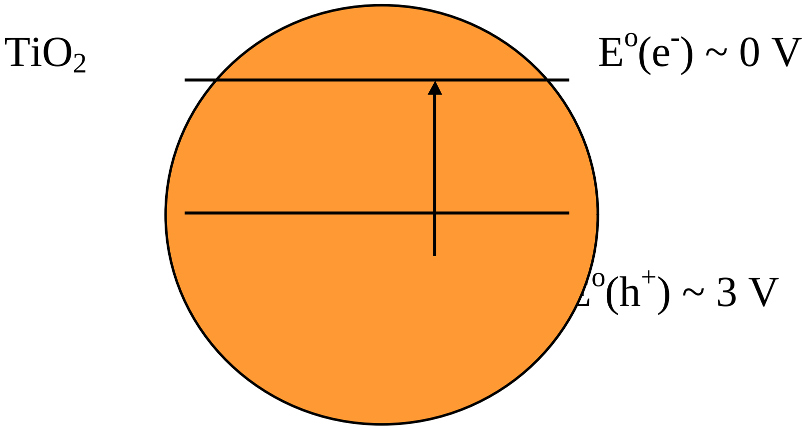
GOALS AND OVERVIEW

The form of photocatalysis that has been studied extensively for its potential as a method of advanced oxidation is reaction initiated by light absorption by a stable metal oxide. The oxide of choice is TiO_2 because it is inexpensive, non-toxic, and does not undergo photocorrosion. TiO_2 may be regarded from the point of view of semiconductor theory. From that perspective, absorption of a near uv photon (wavelength < 385 nm) can be regarded as exciting an electron from the valence band to the conduction band (see diagram). A surface trapped electron (standard potential ~ 0V on the hydrogen scale) is readily captured by molecular O_2 and the hole left in the valence band is a strong oxidizing agent (standard potential > 3 V). A surface trapped hole is a very non-selective oxidant. It can even oxidize water to give the •OH radical that attacks a very wide range of organic molecules. Thus, irradiation of TiO_2 can initiate the oxidation of most organic molecules by O_2. It is in that sense that the slight misnomer "photocatalyst" is applied. The final product of such oxidation is normally CO_2, water, and inorganic ions.



The first objective of this project was to determine whether the major components of pulp mill waste streams are efficiently photocatalytically oxidized to CO_2 and inorganic ions. With the accumulation of evidence that the desired reactions are feasible, attention focused on the identification of the most effective forms of photocatalyst and the points of application in the pulp mill stream. Experiments were directed to the acid stream, the base stream, and waters from biological treatment ponds. All three sample types can be photocatalytically treated. This result implies the consequent need to attack the problem of design of practical reactors that might be effectively implemented in pulp mills. Thus, we can identify the elements of the project under three headings.

1. Establish treatability of components of pulp mill streams.
2. Development and characterization (optimization) of photocatlaysts.
3. Design of reactors suitable for use on the streams identified.

A final, subsidiary, issue is exploration of analytical methods adaptable to monitoring performance.

It is important at the outset to note that the overall program described in the preceding paragraph is comprehensive and demanding. The level of commitment possible from the Network could not have permitted undertaking this comprehensive program if it were not for the fact that the work on pulp mill waste streams could be integrated with a more general program of research on photocatalysis which benefited from substantial support sequentially from an NSERC strategic grant and a collaborative university-industry project funded jointly by NSERC and Trojan Technologies of London, ON. Much of the basic work on photocatalysis that this program required was greatly leveraged by the effort aimed at more general application of photocatalysis. Most of the work described in this report depended on the availability of supplementary resources for parts of the effort from the other sources.

All of the major targets of the laboratory program were reached with the exception of the completion of the development of analytical methodology for monitoring which continues under NSERC undirected funding and is expected to be complete by the end of the summer of 2001. Pilot reactors that could be exploited within a mill and as an enhancement of the performance of a biological treatment pond have been constructed. We have sought the collaboration of several of the partner companies to the network but have failed to find an opportunity to carry out field trials.

The specific advantages of inclusion in the SFM network have been two. One was the early supply of samples and critical analytical support that we received in initial phases of the project from network members at the University of British Columbia that allowed demonstration of effectiveness of photocatalysts toward all major classes of components of the pulp mill streams. The other was the essential liaison with Dr. D.W. Smith’s group at the University of Alberta that led to choice and collection of “real” samples and identification of constraints on design of reactors for use in pulp mill applications. Network meetings have been a valuable channel of knowledge flow.

Among the outcomes of the project have been three conference reports directed rather specifically to pulp mill applications, journal papers dealing with more fundamental aspects of photocatalysis and reactors, and three M.Sc. theses (one still in final editing). Two of the M.Sc. students are employed in the environmental engineering industry. Two post-doctoral fellows have participated and one is now active in the water treatment industry. The senior research associate who has been a key player in this project, Dr. Alex Starosud, is now leading an effort to “spin out” a company, PERM Environmental, Inc., to commercialize photocatalytic technology developed in the course of the connected projects of which this SFM effort was one.

REACTIVITY OF PULP MILL STREAM COMPONENTS

The baseline study of photocatalysis was examination of the oxidation of the organic components of a mill white water from the Howe Sound Pulp and Paper Mill and a synthetic model white water (Vaisman et al 1999). Both are referred to here as MWW (real and synthetic respectively). The laboratories of Dr. J. Sidden of UBC supplied these samples.

Photolyses were carried out first in an exploratory fashion using a closed tube rotated with solid photocatalyst under a 40 W near uv (peak wavelength 350 NM) lamp. The changes of concentrations were monitored by HPLC. This simple arrangement is useful for semi-quantitative comparison of a number of catalyst formulations. More quantitative experiments were conducted using a reactor in which the sample flowed through a bed of photocatalyst of small diameter. The flow cell was mounted in a Rayonnet Photoreactor that ringed the cell with 16 75W fluorescent-coated uv lamps with output centred at 350 nm. Actinometry shows that light entered the reaction cell at a rate of 4×10^{-8} einsteins/s.

The course of the reactions in the flow experiments was also diagnosed by HPLC. However, simple HPLC with single wavelength uv detection cannot resolve the complexities of the real, or even the synthetic, MWW samples. In consequence, samples from selected runs were forwarded to Drs. R.P. Beatson and J.N. Saddler at UBC who arranged for inclusion of these samples in their multistep analyses that are capable of separation and determination of the major classes of compounds found in MWW. The methods exploited have been described. (See deJong et al. (1997) and references therein.) The results from the more sophisticated analyses enhanced the interpretability of the HPLC as did recording of complete uv spectra of samples.

The photocatalysts were selected from a series prepared by Dr. A. Starosud in the course of the University of Calgary collaboration with Trojan Technologies. These catalysts were composites designed to combine the capacity to adsorb target organic substrates efficiently with photoactivity. Because of the high organic loading of the MWWs, a maximal adsorption capacity was not optimal. (Coagulation could be promoted.) The catalyst of choice is the "UC210" that simply loads TiO_2 on silica gel particles of convenient engineering size.

A classic method of reducing the organic content of waters is uv irradiation after addition of H_2O_2. This was chosen as a reference method to compare to the effect of TiO_2 as a photocatalyst. As well, there have been a number of reports that H_2O_2, acting as a supplemental electron acceptor to molecular O_2, can enhance rates of oxidation of organics on the irradiated TiO_2 surface. For this reason, experiments were carried out with addition of small amounts of H_2O_2 to samples where silica gel supported TiO_2 photocatalysts were used.

In the preliminary qualitative experiments with the closed tubes, we learned that addition of H_2O_2 to photocatalysts was beneficial. However, the common explanation that it acted simply as an alternate electron acceptor could not be sustained. The rate enhancement in solutions that had received an H_2O_2 addition persisted long after all of the initial H_2O_2 was exhausted and an addition of further H_2O_2 at that time had no accelerating effect. It appears that H_2O_2 plays a role in initiation of radical chain reactions that persist after the initial dose of H_2O_2 has been consumed. This is advantageous since it indicted that the desired enhancement can be achieved with small dose. HPLC traces clearly demonstrated that the pathway of reaction and intermediates formed differ among the three cases: 1) traditional uv/H_2O_2, 2) supported TiO_2 alone and 3) supported TiO_2 with H_2O_2 added.

The overall success in treatment of MWW is illustrated in Table 1 where detailed analysis of the fate of various components of the Howe Sound MWW after 96 h. of irradiation in the flow cell is presented. (96 h in the reactor is approximately equivalent to exposure to sunlight for 4h because the irradiation volume in the reactor is a small fraction of the total volume of circulated solution.)

Table 1

Contaminant	Initial MWW composition	UC210 irradiated		1% H_2O_2		UC210 + H_2O_2	
	Mg/L	Mg/L	%	Mg/L	%	Mg/L	%
Total dissolved and colloidal organic C	2360	1120	48	340	14	160	7
Lignin	100	80	80	7.5	7.5	15	15
Ash	390	213	55	163	42	67	17
Carbohydrates	1560	670	43	n.d.	0	n.d.	0
Extractive resins and fatty acids	14	20.2•		58.3•		15.4•	
Sterols and lignans	88	34.3	39	26.6	30	16.4	19
SE & TG	16	12.3	77	11.3	71	9.9	62

• There is notable early production of resins and fatty acids from larger molecular weight components but HPLC documents significantly different pathways in the three cases.

The results in the Table illustrate the main conclusions from this phase of the project. A supported TiO_2 photocatalyst promoted with a small amount of H_2O_2 is the most effective oxidation system. A remarkable result is that the process is effective for both dissolved and colloidal organic matter in the MWW. Since the photopromoted reactions are expected to occur on the surface of the TiO_2 there was a concern that only dissolved organic matter would be effective. Probably the adsorptive capacity of the silica gel support is bringing the colloidal organic matter to the reactive zone.

Subsequent studies on samples taken from a mill acid stream, a mill basic stream, and waters from a biological treatment pond continue to confirm attractive reaction rates for TiO_2 based photocatalytic treatment. Monitoring was extended to the common control parameters of TOC, DOC, and colour and effective reduction of all of these was demonstrated.

OPTIMIZATION OF PHOTCATALYSTS

The favourable results of the studies of treatability of streams from pulp mills recommends some basic studies to learn what parameters might be involved in rational rather than empirical optimazation of catalyst systems. An important hint came from an early study by Xu and Langford (1995) of various methods of loading TiO_2. It was observed that maximum activity could be achieved with a small amount of TiO_2 (~3% by wt.) if it was applied as a thin film on a silicate support. The film exhibited x-ray powder patterns suggesting very small TiO_2 crystallites, or even a nearly amorphous phase. It was important to learn what fraction of the surface of the silicate was covered by TiO_2 and how that changed with increase of TiO_2 loading.

Vaisman et al. (2000) reported a novel cross polarization solid state NMR method to monitor the surface of a silicate using Si signals resulting from polarization induced by the H atoms of the surface OH groups so that surface Si atoms dominated the NMR spectra. Then the extent of surface coverage by TiO_2 could be estimated by the decrease of the Si signal on addition of TiO_2. The optimum photoactivity is already developed (2.5% loading) at a surface coverage that is incomplete but corresponds to a "monolayer" coverage by TiO_2 (anatase) unit cells. As the TiO_2 loading increases (5%), initially there is not further coverage of the zeolite. The TiO_2 grows out from the surface. At 10% loading, it appears that the TiO_2 falls over to begin to increase surface coverage. The higher surface coverage does not enhance reactivity. The location of the Ti on the surface can be identified from energy filtered transmission electron microscopy by taking the difference between images formed just below and just above a Ti transition energy. The Ti appears to be distributed over edges, steps, and defects as theory of crystal growth suggests. This is leading us toward exploration of new ways to load TiO_2 slowly in thin layers as the rational improvement of catalyst design.

A second issue is whether supported catalysts with TiO_2 supported on silicates (zeolites) change reaction pathways compared to TiO_2 in ways that will present special problems for the goal of mineralization of organic contaminants as rapidly as possible. This issue was examined by Chen et al. (2001). Using phenol as a well-studied model substrate, the pathways on commercial TiO_2 were compared to those on a 3% by weight TiO_2 loaded ZSM-5 zeolite. In general reaction rates and pathways were very similar with the TiO_2 exhibiting slightly greater rates of oxidation of early intermediates than the supported catalyst. However, one significant problem was identified in basic solutions. The catalyst support, presumably because of its adsorption capacity, promoted coupling reactions between radicals and production of a polymer that can prove refractory. Since reactions mediated by hydroxyl radicals will commonly produce phenols form aromatic constituents, this observation indicates a limitation on use of the supported photocatalysts for basic streams without neutralization.

The final catalyst optimization issue is not so much a matter of the catalyst chemistry as catalyst engineering. For use in practical reactors, it is highly desirable for the catalyst particles to be larger than the <50 μM dimensions of TiO_2 and zeolite powders. At least 250μM is desired for handling. The literature reports a variety of efforts to attach TiO_2 to macroscale supports including sand and glass beads. Our initial effort supported the catalyst on silica gel particles. These did not prove sufficiently mechanically robust for use in the fluidized bed reactors to be described below. Reflection led us to what we like to call the "golf ball" concept. The TiO_2 loaded zeolite particles should be anchored in indentations in the surface of a robust support so that they are not exposed for attrition. Our "golf ball" is a porous glass material or a specially prepared porous ceramic. The condition is a requirement for low light absorption in the 350 nm range. The "golf ball" implementation has been used in the fluidized bed reactor described below. It is also the conceptual parent of a floating ball catalyst that has promise for use in passive solar applications on waste ponds.

DESIGN OF REACTORS

The fundamental limitation that has frustrated commercialization of TiO_2 based photocatalytic systems is the cost of electric power for the uv lamps. The figure of merit for a photocatalytic system is electricity cost per decade of reduction of contaminant concentration. Consequently, only those applications that can accept a slow process driven by natural light (e.g. sunlight in treatment ponds) have been economically fully attractive. The limitation can be translated into photochemical language as an insufficiently large intrinsic quantum yield for the reactions. A good deal of research ahs been directed toward enhancement of quantum yields. There has been some success but an order of magnitude increase has remained elusive. Thus, a solution must be sought elsewhere. For dilute contaminant streams, the apparent quantum yield at a given concentration is approximately a linear function of concentration as indicated by Fig. 1

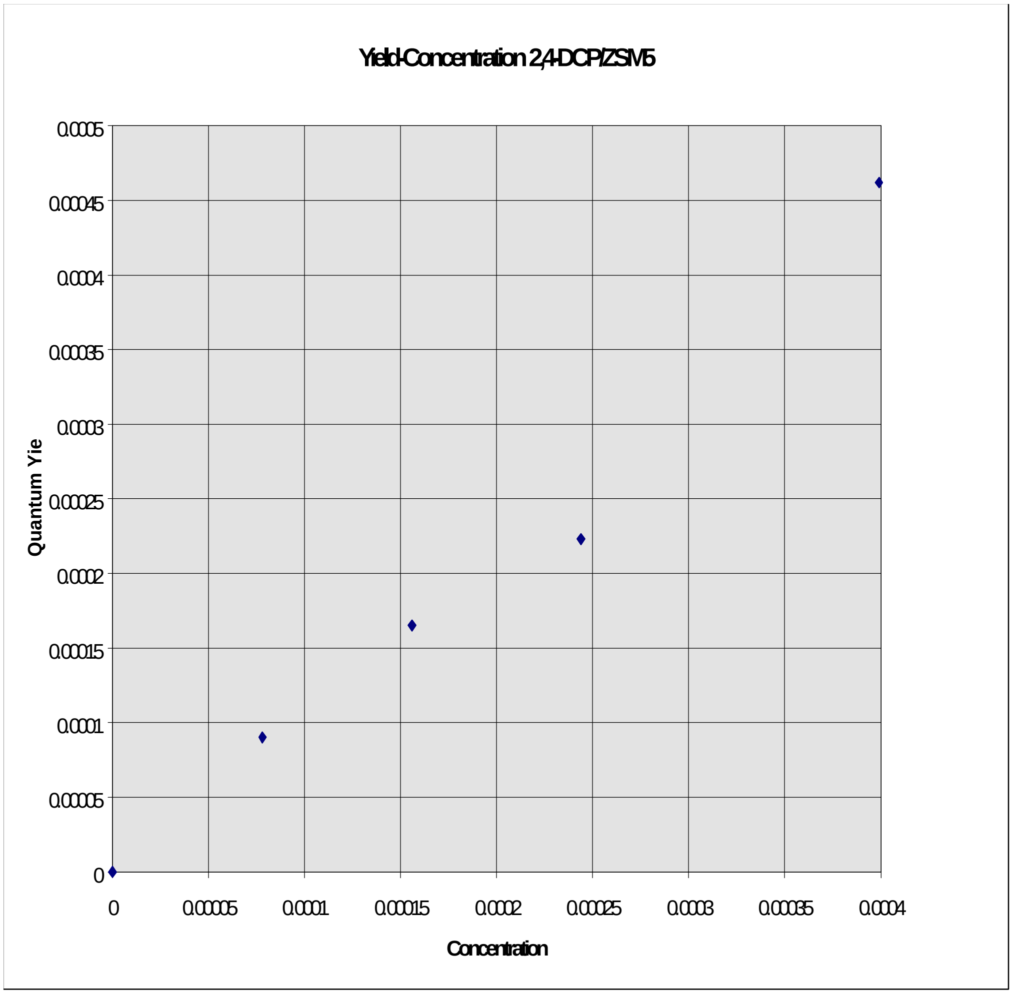
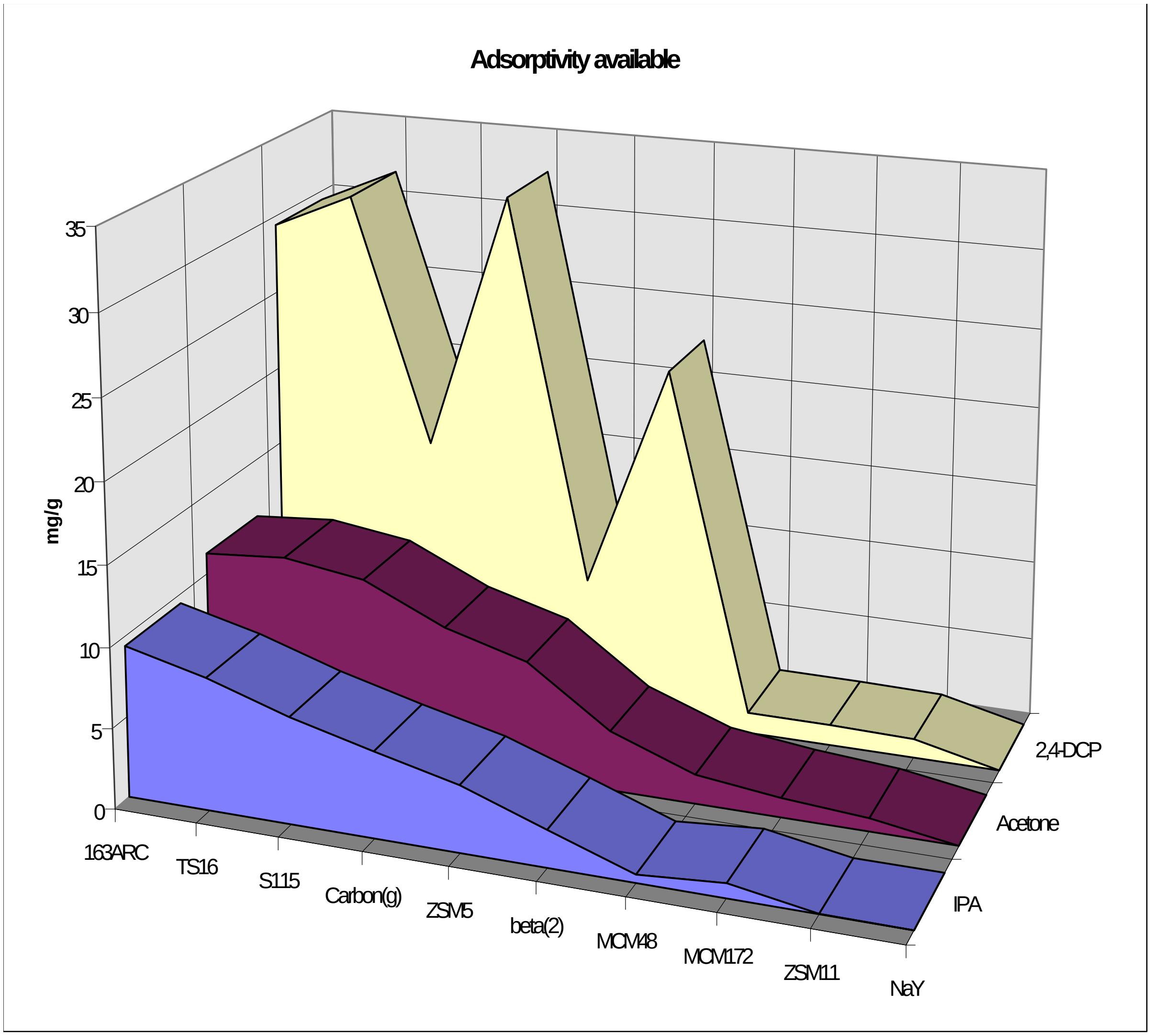


Figure 1 Typical yield vs. concentration curve

This means that pre-concentration of the substrate by a factor of ten can reduce electricity cost for contaminant oxidation by a factor of 10. This is the major advantage of the combination of a photocatalyst with an adsorbent support. The reactor should be designed for two stage operation. In the first stage, a stream to be treated is passed through the adsorbent bed. As breakthrough is approached, the flow is terminated and the adsorbent is photocatalytically regenerated taking advantage of the photocatalyst supported at low loading on the adsorbent material. The system can be though of as an analog of activated carbon that can be regenerated with the added advantage that the products are CO_2, water, and inorganic ions. Of course, this analogy only holds if the adsorbent is competitive with activated carbon. A number of high silica zeolites do offer such adsorption capacity. Fig. 2 shows the relative adsorption of 2,4-dichlorophenol, acetone, and *iso*-propanol on a series of zeolites compared to activated carbon.

Figure 2 Adsorption capacities of zeolites

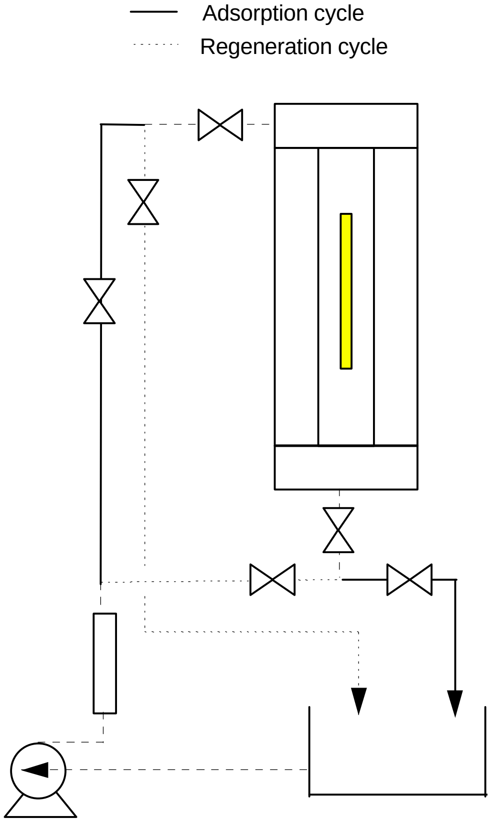


A second important problem confronts the design of industrial photoreactors. Light absorption follows Beer's law and light intensity decreases exponentially as it passes into an absorbing medium. Photoreactors that exploit fixed beds of photocatalyst are severely limited in their ability to achieve uniform treatment of a reactant stream. Commonly, this leads to build up of refractory intermediates on the surface of photocatalysts distant from the lamps. Consequently, we have chosen to explore fluidized bed reactors.

A design study with both empirical and theoretical components was undertaken to develop a fluidized bed photoreactor at small pilot scale that would achieve uniform illumination of all of the photocatalytically active material. The TIPM (Tomographic Imaging and Porous Media) Laboratory at Calgary directed by Dr. A Kantzas provided the capacity to determine particle pathways in the reactor using Radioactive Particle Tracking (RPT) (Kantzas et al. 1999).

A photocatalytic particle was tagged with ^{99m}Tc in the form of technecium macroaggregated albumin and tracked in a series of runs in the fluidized reactor. (Bhargava et al. 1999). Conditions were readily identified where fluidization achieved uniform illumination of photocatalyst particles. A schematic of the photoreactor is shown in Fig. 3. Notice that for these experiments recirculation through a reservoir was employed.

Figure 3
Fluidized bed photoreactor schematic



The reaction chamber had a central chamber for the lamp with a diameter of 7 cm. This was enclosed in a water cooling jacket of 12 cm thickness. The reaction zone surrounded this lamp assembly with a diameter of 20 cm. The height of the reaction zone was 81 cm. The lamp was supplied by Trojan Technologies, Inc. which uses a power supply from American Ultraviolet Company drawing 40 A at 230V. In one trial, a 100 L charge of 43.9 mg/L phenol was reduced by an order of magnitude in 20 mins of irradiation. Given volume ratios of reactor and reservoir, this corresponded to 12 mins in the irradiation zone (Bhargava 2000).

The reactor described above is now entering pilot trials that will determine its economics. We were unsuccessful in our efforts to interest any network partners in trials on streams within the mill. However, both the Calgary Waterworks and an oil contamination control firm are now working with PERM Environmental, Inc. to conduct the pilot trials that will allow accurate treatment economics to be derived.

There is an additional opportunity to exploit photocatalysis in the pulp mill environment. This is a very low cost implementation that uses natural light (sunlight) to enhance the performance of existing biological treatment lagoons. In this application there is the longer time available to exploit passive energy supply. Two advantages deserve evaluation. One is the use of photocatalysis to oxidize biologically refractory components such as resin acids. The other is simply to enhance capacity or reduce effluent levels without the need to expand the lagoon. Phototcatalytic treatment is effective for reduction of colour, TOC, and DOC. Table 2 reports one of the experiments with irradiation equivalent to 10 h. of sunlight on samples taken at the input and output points of a lagoon. (We are indebted to Alberta Pacific Forest Industries for the samples.)

Table 2
Reduction in control parameters after irradiation
equivalent to 10 h. of sunlight (air mass one)

Sample	Colour % reduction	TOC % reduction	COD % reduction
Effluent before treatment lagoon (pH=6-7_	129	43	44
Effluent after treatment lagoon	108	56	87

Two possible implementations of a treatment scheme for supplementing performance of Lagoons have been explored. One is an elaboration of an installation used to enhance a treatment lagoon at a Volkswagen plant. In this version, a plate exposed to the sun (or to uv lamps for evaluation) is coated with a TiO_2 loaded adsorbent. As in the two stage system, the adsorbent does result in pre-concentration. Water is pumped form the lagoon over the photocatalytic plate and recycled to the Lagoon. A lab scale pilot of this scheme with fluorescent lamps for lab evaluation is shown in Fig. 4.

Figure 4
Lab pilot of solar reactor

CONCLUSIONS AND FUTURE DEVELOPMENT

At the completion of this study, two opportunities have emerged for the pilot testing of advanced oxidation in the pulp mill stream using TiO_2 based photocatalysis. The adsorption-regeneration two-stage reactor has promise for handling the large flows that arise within the mill. A particularly encouraging result that was quite surprising is the observation that colloidal organic matter was oxidized at a rate comparable to dissolved organic matter. The limitation our study of pathways implies is that treatment of acidic streams is more promising than treatment of basic streams where polymerization may become significant. Base streams may require neutralization. The second opportunity is the use of photocatalysis as a supplement to effluent treatment lagoons. This is an opportunity of great promise since it can exploit solar radiation without the cost of electricity for uv light generation. The advantages include effective treatment of compounds that are refractory toward the biological treatment (e.g. resin acids) and a low cost contribution to overall rate of reduction of values of effluent control parameters. (The addition of solar photocatalytic units is expected to be highly cost effective as compared to expansion of lagoons.) Our lab scale pilot (solar) reactor remains available to any partner company that wishes to conduct trials. A two stage reactor for use on a stream within the mill is available from PERM Environmental, Inc.

Despite the current lack of interest in the pilot phase of development of photocatalytic advanced oxidation within the network partner group, the work conducted within the NCE program will not be without consequence. A pilot project to evaluate economics of adsorption-photocatalysis for treatment of drinking water is now underway under the management of the spin out company, PERM Environmental. The project has Calgary Waterworks and the Alberta Heritage Foundation for Medical Research as partners and has its scientific monitoring dimension accepted as a project in the new Clean Water NCE. As well, negotiations are well advanced to evaluate the photoreactor described here for clean up of waters contaminated in the context of washing soils contaminated with hydrocarbons.

REFERENCES

Bhargava, A. Langford, C.H. and Kantzas, A. 1999 Hydrodynamic study of a novel photocatalytic reactor for wastewater treatment.

Bhargava, A. 2000. A novel photocatalytic reactor. M.Sc. thesis, University of Calgary.

Chen, J, Eberlein, L. and Langford, C.H. 2001, Pathway differences in photooxidation: TiO_2 powder compared to TiO_2 supported on a zeolite. Photochem. Photobiol. A: Chemistry, submitted.

deJong, E. Wong, K.K.Y. and Saddler, J.N. 1997, The mechanism of xyianase prebleaching of kraft pulp: an examination using model pulps prepared by depositing lignin and xylan on cellulose fibres. Holzforschung, 51(1) 19-26.

Kantzas, A. Hamilton, K. Zarabi, T. Bhargava, A. Wright, L. Brook, G. and Chen, J. Application of gamma ray camera imaging and SPECT systems in chemical processes. 1999. 1st World Congress on Industrial Process Tomography, Buxton, Greater Manchester, UK. April 14-17, 1999.

Vaisman, E. Starosud, A. and Langford, C.H. 1999. Application of photocatalysis for oxidation of organica and decolourization of pulp mill effluents. Proceedings of the 1999 Sustainable Forest management Network Conference. Edmonton , AB. 14-17 February. p 301-306.

Vaisman, E. Cook, R.L. and Langford, C.H. 2000 Characterization of a composite photocatalyst. J. Phys. Chem. 104, 8679-8684.

Xu, Y-M. and Langford, C.H. 1995, Photoactivity of TiO_2 supported on zeolites A and ZSM5. J. Phys. Chem. 6, 3115-3121.