Photodegradation of Waterpollutants

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What is Photodegradation?

- Photodegradation and Photokatalysis are usually oxidations of organic compounds in exoergic processes, in which the absorption of light energy is the driving reaction force.
Direct photochemical degradation.

• In direct photochemical degradation the electrons of an organic compound are excited. This can lead to decomposition of the organic molecule into two radicals, which are extremely reactive. More often the excited point of the molecule is attacked by oxygen molecules, which then oxidise the organic compound.

• As the reactivity of ground state triplet oxygen with the singlet ground state of the most compounds is very low, the excitation of oxygen to singlet is even more important for the oxidation of organic compounds.
Direct photochemical degradation.

Degradation of phenol by singlet oxigene to maleinate
Addvanced oxidation process:

As the photodegradation of many microorganisms and compounds is very slow and lead to oxidation or degradation of organic compounds, the addvanced oxidation process by combining UV illumination with ozone or \( \text{H}_2\text{O}_2 \) supply is much more effective often leading to complete mineralisation.

This is achieved especially by the photolytic reaction of \( \text{H}_2\text{O}_2 \).
Indirect photochemical oxidation:

In the indirect photochemical oxidation radicals are formed by photolysis, which then attack the organic compounds. As an example the reaction of $H_2O_2$ is drown:

$$H_2O_2 \xrightarrow{hv} 2OH.$$ 

As hydroxide radicals need an electron to obtain an octate, they are very electrophilic and that for attack electron rich areas of any molecules.
Photocatalysts

A couple of semiconductive materials can be used as photocatalites. Most popular is $TiO_2$ because of it’s chemical stability and high efficiency.

$TiO_2$ has a band gap of 3.2 eV, equivalent to about 400nm. By this reason $TiO_2$ can be excited by illumination in the range of 300 to 400 nm.

Driving force for catalysis of photochemical reactions is the excess of free energy in the electron-hole thus produced.

$$TiO_2 \xrightarrow{h\nu} e_{cb}^- + h_{vb}^+$$
Photocatalysts

By this reaction $Ti^{3+}$ centers act as electron holes while $e^-$ partially go to the surface, where they can be taken up by other molecules.

Examples for possible reactions forming highly reactive radicals:

$$h^+ + H_2O \rightarrow H^+ + OH\cdot$$

$$O_2 + e^- \rightarrow O_2^-$$

$TiO_2$
Sensitizer dyes are photoactive organic compounds like for example methylene blue, which are resistant to photodegradation by releasing the absorbed energy to neighboring molecules and in this way activating them.

\[
\text{Farbstoff} \xrightarrow{\text{Licht}} \text{Farbstoff}^* \quad (1)
\]
\[
\text{Farbstoff}^* + \text{Sauerstoff} \rightarrow \text{Farbstoff} + \text{Sauerstoff}^* \quad (2)
\]
\[
\text{Sauerstoff}^* + \text{Schadstoffe oder Keime} \rightarrow \text{Zersetzung bzw. Entkeimung} \quad (3)
\]
Photokatalysts can be used as particles dispersed in the water. In this way the surface of the catalyst is used most efficiently but the dispersed particles disturb illumination. Additionally the particles have to be removed after the treatment.

Another method is a fixed bed covered with $TiO_2$.

For the dye sensitization most popular are granulated polymers careing the dye.
Comperance with other oxidation methods

• Ozonation:
Effective to many organic compounds, but ineffective to halomethanes, triazine herbicides and other compounds. Ozone combination with $H_2O_2$ or UV illumination can overcome this problem.

• Biodegradation:
Most important purification method for purification of municipal wastewater. However, xenobiotics as methyl vinyl ketone, pentachlorophenol and 2,4-dichlorophenol can inhibit the respiratory activity of activated sludge. In this case aclimation of microorganisms is necessary.
Comparison with other oxidation methods

•Chlorination:

Chlorination is the major factor of prevention of water borne diseases.

Chlorination may cause the formation of trihalomethane as carcinogenic chloroform.
Direct UV disinfection:

Classicly photoreactions has been used for desinfection of drinking water and it still being the easiest and chaapest way to disinfect water.

The illuniation with sunlight for five houres kills most coliform MOs.
Direct UV desinfection:

- Direct desinfection by denaturisation of DNA and photolytic reactions on the surface
- Indirect desinfection by oxidation of cellwalls or cell membranes and through this destruction of cellwall/membrane properties or even cell lysis. This effect is achieved by radical production.
Direct UV disinfection:

Such reactors are used in the drinking water disinfection in addition to chlorination in the Black Mountain Irrigation District.
Enhanced UV disinfection:

At the Japan Gulch Water Treatment Plant the drinking water disinfection is done by a chain of UV reactors with $\text{H}_2\text{O}_2$ supply.

Beside the disinfection by the advanced oxidation process, chlorine reconfiguration is achieved.
Other application examples:

- Disinfection of water, rainwater, drinking water in containers, tanks, small wells, open systems
- Protection of germ build up of surfaces (e.g. on watersoluble lacques)
- Disinfection of tanks before filling

Underground water tank with an immersion lamp and aeration

- Disinfections in air washers for air conditioning systems (coolant recovery)
Photochemical detoxination

$CN^-$ degradation: $CN^-$ is used in previous metal processing, for example to recover gold-mill tailing.

$CN^-$ is usually oxidized by alkaline chlorination or with $H_2O_2$ but the hexacyanoferat(II) and hexacyanoferat (III) from gold-mill tailing are resistent to the treatment.
Photochemical detoxination

Also they undergo photodegradation by releasing $CN^-$ and recombining after the end of the illumination.

Degradation can be achieved by addition of $TiO_2$ to alkaline solution (pH 10) and illumination by sun for 1.5 h.
Photochemical detoxination

Cr(VI) is very stable, good water soluble, carcinogenic and extremely toxic. Cr(III) is much less toxic and precipitating in neutral and alkaline solutions.

Chrome polutions origins e.g. from chrome plating, leather tanning and metallurgical processes.

Photocatalitic reduction of chrome in alkaline solution by $TiO_2$ to $Cr(OH)_3$ which strongly addsorbs to $TiO_2$ and thus is removed from solution by removeing the catalyst.

In presence of oxygene the reduction is inhibited because of competiton with $O_2$ molecules for conduction-band electrons.
Photochemical detoxination

Main reaction:

\[ CrO_4^{2-} (aq) + 4H_2O + 3e^- \xrightarrow{hv} Cr(OH)_3(ads) + 5OH^- \]

\( N_2 \) - purging necessary because of \( O_2 \) production:

\[ 4OH^- + 4h^+ \rightarrow O_2 + 2H_2O \]
Conclusions

- The advanced oxidation process is highly suitable for disinfection for drinking water purposes.
- As groundwater has usually low load of pollutants, the advanced oxidation process with or without photocatalysts is also suitable for detoxification of herbicide contaminated water.
- As seen on cyanides and chrome removal, some photochemical methods require special conditions not suitable for drinking water purposes.
Conclusions

- As photodegradation and photodetoxination are not suitable for highly differentiated waste water and high loads it can be used for partial waste water streams containing special contamination.
References

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Thank You for Your Attention !!!