Chapter 2
Recovery and Recycling of Industrial Wastewater by Hybrid Processes

Farhang Shadman

Abstract Modern industries demand large quantities of water at purity levels that are unprecedented in industrial applications. Unless water usage is changed, these processes will not be sustainable. The key solution to reducing water usage and wastewater discharge in the ultra-pure water (UPW) plants is the development of suitable technology for water reuse and recycling. In particular, successful water conservation strategies will require innovations in a number of areas.

The ultimate solution to water conservation and sustainability for industrial use lies in some form of reuse and recycling strategy. However, the recycling process is not trivial and involves some challenges. Typically, the success in implementing recycling depends on two major factors:

1. The first requirement would be the availability of robust and low-energy purification processes. This is critical because the environmental issues associated with water usage and wastewater discharge cannot be solved simply by recycling water if the recycling process consumes large amounts of energy. Large energy usage, in addition to being costly, would cancel any environmental gains that may be achieved by water saving. There is no merit in water recycling if for every unit of water recovered and recycled we end up using large amounts of energy. This is particularly important because many of the existing purification methods were not originally developed and optimized to accommodate recovery and reuse. In this article, some novel approaches and technologies based on the use of hybrid systems, their principle of operation and design, as well as the methods for selection and optimization of these promising hybrid systems are presented.

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2. The second requirement is the availability of fast-response, real-time, and on-line sensors, and the associated process control strategies to monitor the quality of purified wastewater and protect the system against any unexpected upsets or surges in impurities. In particular, there is a need for robust metrology methods to prevent potential risks associated with water recycling as well as to demonstrate that recycling, when properly designed and implemented, can save water, reduce cost, and improve water quality. The concept of comprehensive and integrated metrology combined with process control is key in both performance improvement and in cost reduction. The application of sensors and advanced process-control are particularly critical for the operation of the hybrid systems. The available technologies in this area, as well as the remaining challenges that would need further research and development, are reviewed.

2.1 Introduction

There is an ever increasing demand for high purity water in many industries. For example, the water usage in modern semiconductor manufacturing plants easily reach 2–3 million gallons of ultra-pure water per day. The production of ultra-pure water from various feed water sources is a complex process that involves a large number of steps and process units. A generic version of a typical ultra-pure water system is shown in Fig. 2.1.

The feed water goes through three stages of *pretreatment*, *primary treatment*, and *final polishing*. The pretreatment steps typically involve the following steps:

- Softening
- Coagulation
- Sedimentation
- Filtration
- Carbon-bed filtration
- pH adjustment

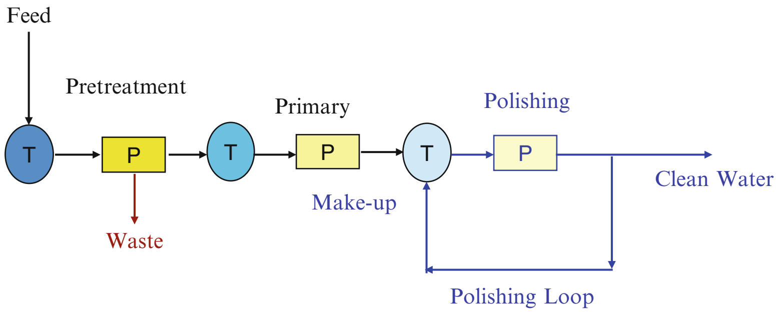


Fig. 2.1 General layout of typical water purification plants

- Chlorination (NaClO)
- Multi-media filtration

The typical feed water has a hardness of 4–110 mg/l and total dissolved solid (TDS) of 10–200 mg/l. The output of the pretreatment stage is conductivity of about 100 μ-siemens/cm.

The primary treatment typically consists of the following steps:

- Ion exchange: cation and then anion, sometimes followed by mixed bed
- RO units
- UV 254 sterilization
- Filtration
- Heat exchange

Front-stage reverse osmosis (RO) units, with typical recovery of about 75–90%, usually are either cellulose acetate, which is a chlorine resistant material, or polyamide thin film composites, with essentially no chlorine resistance. Two arrangements for RO are possible: double pass (product staging) and double stage (reject staging). It should be noted that RO does not remove any low molecular weight organics

Finally, the polishing stage consists of the following unit processes:

- Mixed-bed ion exchange
- Ultra filtration (UF)
- Ultra-violet radiation – UV185 (oxidizer)
- Ultra-violet radiation – UV254 (sterilizer)
- Ozonation

In addition to the above main steps, there are a number of other supplementary treatment processes used in the UPW plants. These include use of additives such as acrylic acid polymers as anti-scaling agents as well as HCl, H_2SO_4, and NaOH during ion-exchange regeneration.

The key solution to reducing water usage and wastewater discharge in the ultra-pure water (UPW) plants is the development of suitable technology for water reuse and recycling. The conservation of water is linked to the usage of chemicals and energy. Consequently, successful water conservation strategies will require innovations in a number of areas. The strategies of decision on recycle or reuse and the overall picture determining the overall environmental impact are shown in Fig. 2.2.

The major factors in design and operation of UPW plants for sustainability are:

- Environmentally-friendly wastewater treatment: This includes lowering both energy and chemical usage.
- Decision on "*reuse*" vs "*recycle*"*:* Cost, environmental impact, and local constraints affect this decision.
- Process control to avoid disturbances and upsets: Sensors and related hardware for recycle control, as well as process control software (process simulator) are key elements of process control.
- Design of recycle configuration: The best use of recycled water

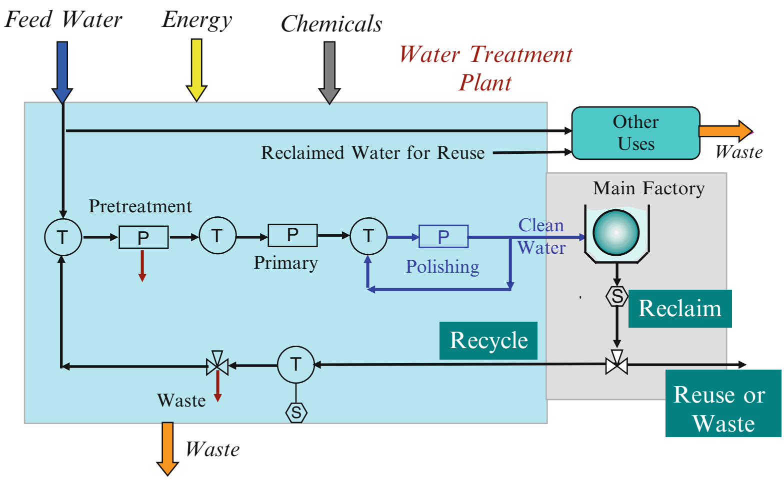


Fig. 2.2 Input, output, and general configuration of UPW systems

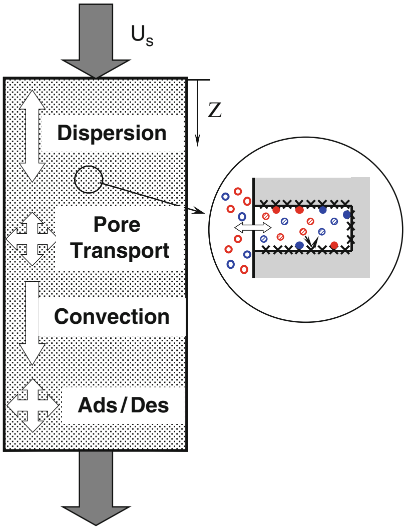
2.2 Issues and Problems in Conventional Water Purification Systems

In this section some of the key issues in purification that require novel approaches and new process innovations will be discussed. For this analysis the treatment processes for removal of organics from water and wastewater can be divided into two categories:

1. Removal by phase separation (capture): The main examples are packed-bed sorption, filters (regular, UF, charge-assisted), and membranes. The main issue for this class of treatment processes is that the impurities removed from water remain in the system.
2. Removal by chemical reactions: The reactions include oxidation, reduction, and decomposition. The main challenge for this class of treatment processes is that these reactions are often slow and require large amounts of energy and chemicals. The fundamentals of impurity removal by capture and the basic equations that form the foundation of any process analysis are shown in Fig. 2.3. Examples of results are shown in Fig. 2.4.

Typically there are four stages in any adsorption bed during the operations:

- Stage 1 is the initial washout period during which bulk flow characteristics and mass transfer effects dominate.
- Stage 2 represents early stages of the operation during which fresh adsorbent exist in some parts of the packed bed.



Adsorbed Phase Conservation:

$$\frac{\partial s_i}{\partial t} = k_{ai}\, p_i \left(\frac{s}{1 + a\, s_i}\right) - k_{di}\left(\frac{s_i}{1 + a\, s_i}\right)$$

Pore Phase Conservation:

$$\varepsilon_p \frac{\partial p_i}{\partial t} + \frac{\partial s_i}{\partial t} = \alpha\, k_{pi}(c_i - p_i)$$

Bulk Fluid Phase Conservation:

$$\varepsilon_b \frac{\partial c_i}{\partial t} + \varepsilon_p(1-\varepsilon_b)\frac{\partial p_i}{\partial t} + (1-\varepsilon_b)\frac{\partial s_i}{\partial t} = -U_s \frac{\partial c_i}{\partial z} + D\frac{\partial^2 c_i}{\partial z^2}$$

Sites Conservation:

$$s_o = s + \sum_i s_i$$

Fig. 2.3 Fundamentals of impurity removal by capture

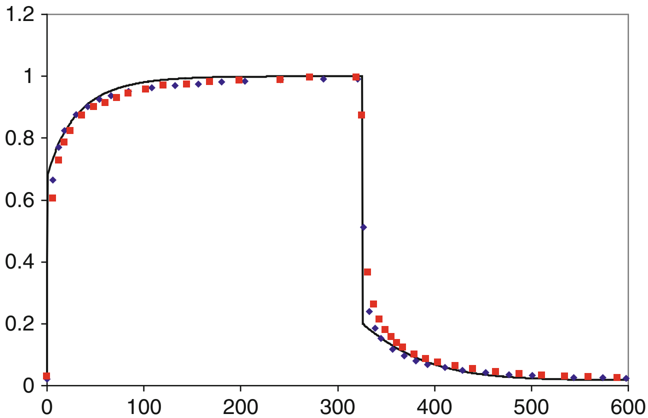


Fig. 2.4 Typical profiles of adsorption and desorption

- Stage 3 is when partial adsorbent deactivation has taken place in all parts of packed bed.
- Stage 4 represents the total bed exhaustion.

These stages are shown in the example illustrated in Fig. 2.5.

One of the key issues in the capture process is the fact that the removal efficiency of the process is highly compound-dependent. For example, Fig. 2.6 shows the difference between the capture efficiency of activated carbon for two

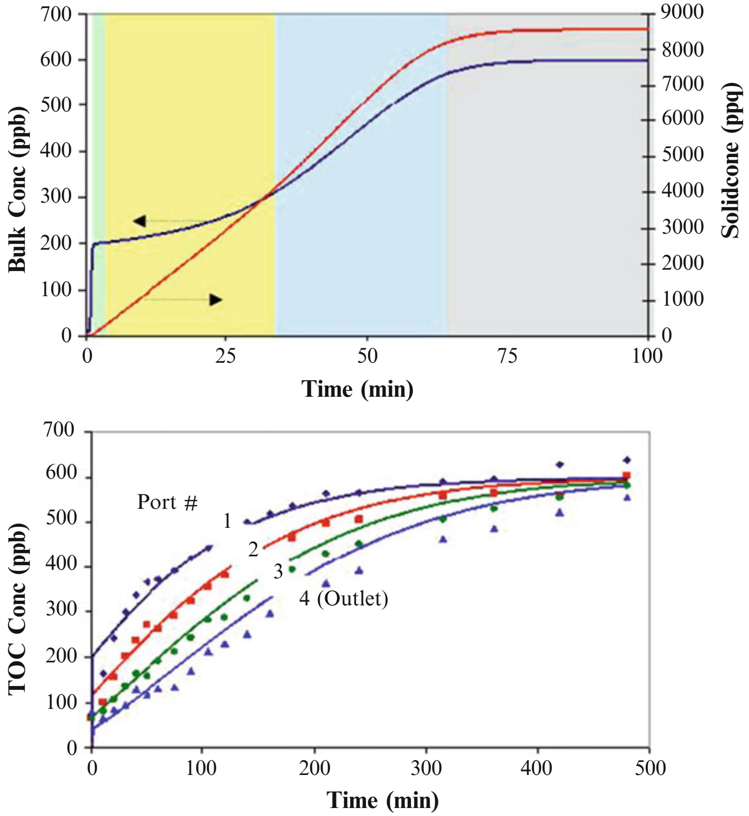


Fig. 2.5 Stages and zones in adsorption beds

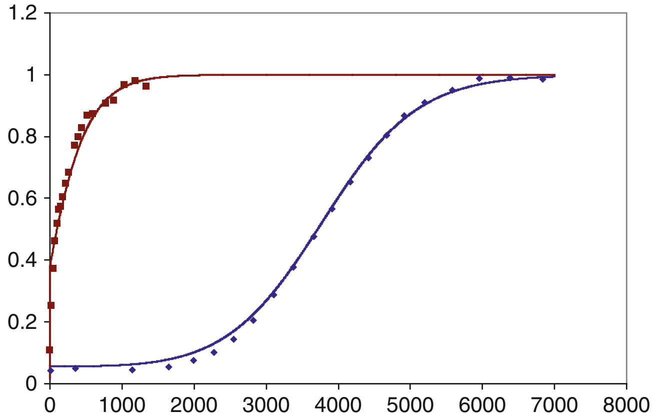


Fig. 2.6 Compound dependence of capture process

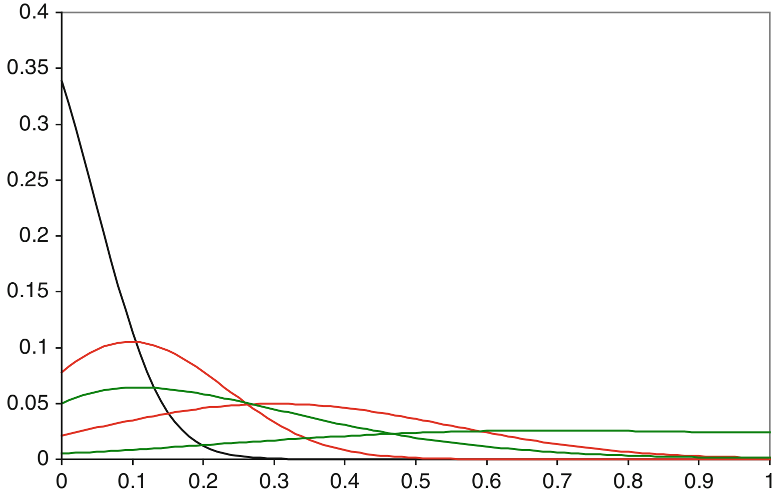


Fig. 2.7 Mobility of captured impurities

organic impurities: isopropyl alcohol (IPA) and chloroform. Multiple beds or multiple sorbents may be required to remove a wide range of impurities present in feed water. The impurities captured in typical adsorption beds are not permanently immobilized. A key issue related to the capture processes is their reversibility of the process and the risk of the release of captured impunity and the re-contamination of water triggered by changes in the operating condition or properties of the feed water. The mobility of impurity in the adsorbed phase is illustrated in Fig. 2.7. This is of particular concern in manufacturing processes where steady and reliable quality of process water is required, and at the same time transient situations causing upsets in the operation are inevitable. An example is shown in Fig. 2.8, where a small change in the water pH due to a spike of pH in water causes the release of organic impurities measured as TOC (total organic or oxidizable carbon).

The other complicating issue is the multicomponent interaction among adsorbates during adsorption of various impurities competing for the sites on the adsorbent. As shown in Fig. 2.9, during the simultaneous adsorption of ethylene glycol and FC-93 on granular activated carbon (GAC); the presence of FC-93 causes the ethylene glycol concentration to overshoot above its equilibrium value.

2.3 Creating Synergy Among Processes by Application of New Hybrid Systems

In this section, examples of new ideas for solving the issues discussed above will be presented. One such idea is the use of a hybrid system, which would combine a number of conventional processes and create more efficient integrated processes

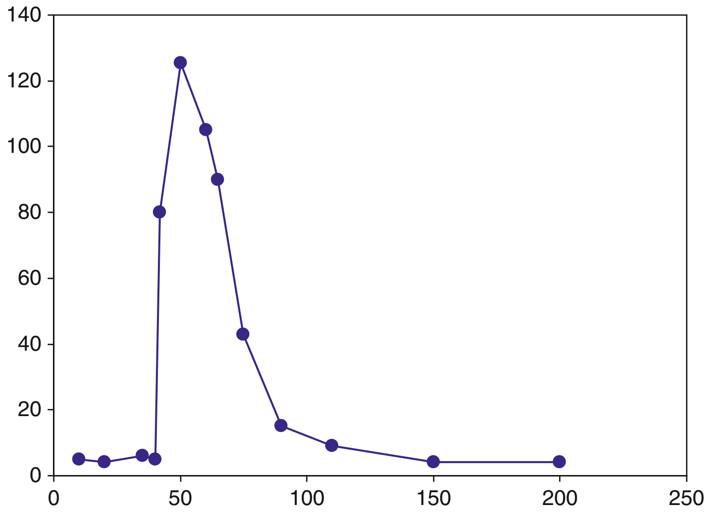


Fig. 2.8 Leakage of impurities from adsorption bed

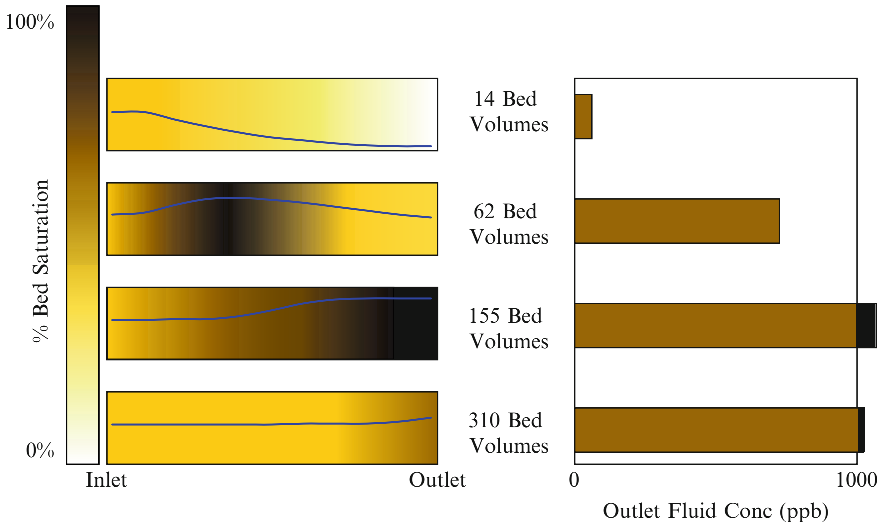


Fig. 2.9 Complex interactions in multi-impurities separation

showing synergistic effects. The synergy basically means that the efficiency of the hybrid combined process is significantly greater than the simple additive effect of individual processes that make the overall system.

In the development of such hybrid processes, the key step is to recognize the primary weaknesses and strength of each conventional unit process. For example,

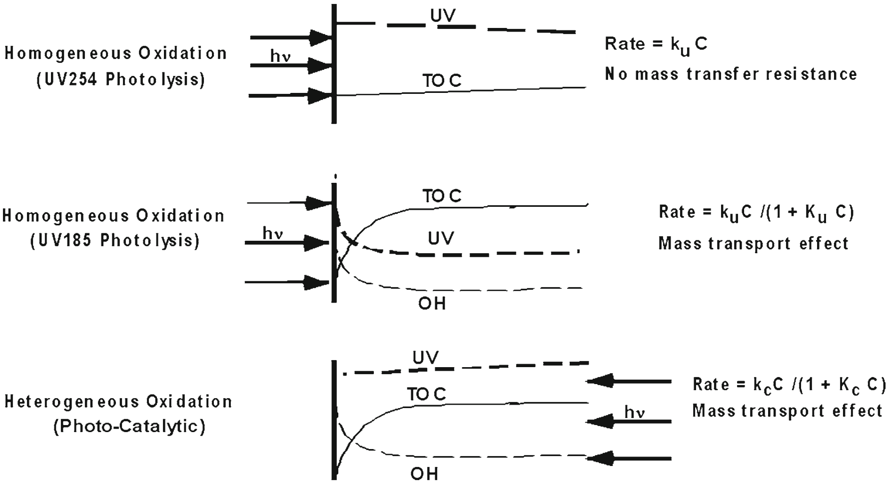


Fig. 2.10 Mechanisms of UV action for TOC removal

considering the removal of total organics (measured as TOC) in water, the removal processes are as follows:

- Capture: Adsorption on packed beds, filters, and membranes.
- Oxidation by ozone: Action through formation of oxidizing radicals causing the lysing of cells.
- Oxidation by other oxidizers: Action through formation of oxidizing radicals.
- Treatment by ultra-violet (UV) radiation: primarily coming in two forms: UV 185 (oxidizer) which causes lysing through radical formation, and UV 254 (sterilizer) which stops cell growth and reproduction. The effect of various forms of UV is illustrated in Fig. 2.10.
- Others: Examples are bio-reactions and reduction reactions.

In general, all options mentioned above fall in two general groups: Removal by capture and removal by chemical reaction. The advantages of removal by capture are fast removal and the availability of well-established unit operations, whereas the disadvantages are the inevitable retention of captured impurities in the system and potential release and re-contamination. The advantages of removal by chemical reactions are possible total removal with no retention of impurities whereas the disadvantages are slow removal rate and potentially higher energy and chemicals consumption.

An example of a hybrid system that combines the advantages of the capture and reaction strategies and essentially eliminates the disadvantages of both is the application of what we call *reactive filtration*. Figure 2.11 shows a specific embodiment of this type of system as a photo-catalytic membrane. In this system the removal process starts with first capture of organics by the membrane, then with complete removal (destruction) of organics by oxidation reaction which takes place on catalytic

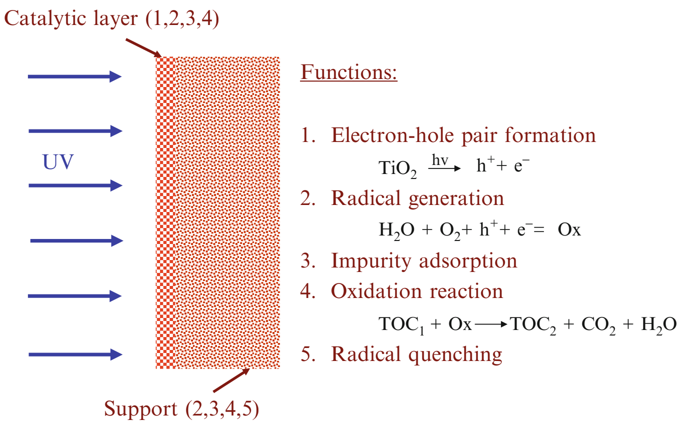


Fig. 2.11 Hybrid system: reactive filtration

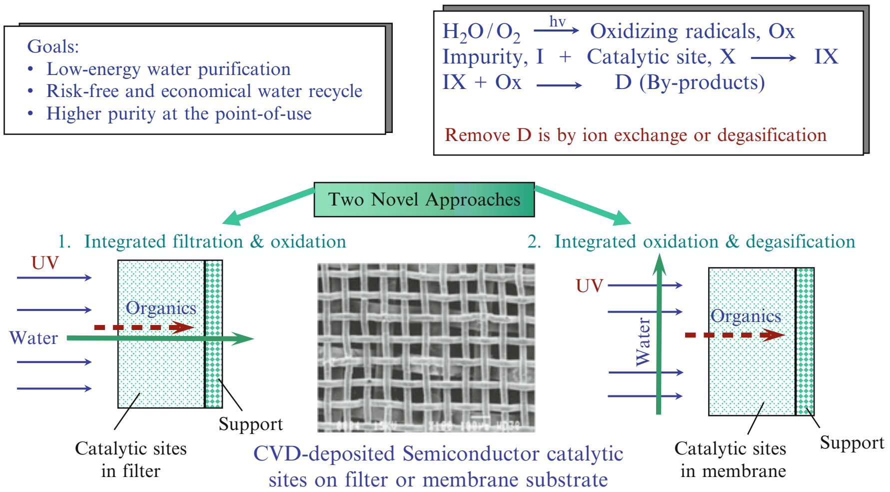


Fig. 2.12 Photo-catalytic membrane

sites incorporated in the membrane and energized by the UV light. A more detailed description of this hybrid system that combines separation and reaction is shown in Fig. 2.12. In this illustration, two flow patterns and configurations are illustrated: one for integrated filtration and oxidation and the other for integrated oxidation and degasification.

Photo-catalytic membranes are a very promising and attractive method of removing low level organics from water in ultra-pure water systems, particularly in the final stages of purification process, as well as for cases where impurities are hard to remove (recalcitrant). Figure 2.13 shows a special experimental setup for testing these membranes used for photo-catalytic oxidation or organics and removal by degasification.

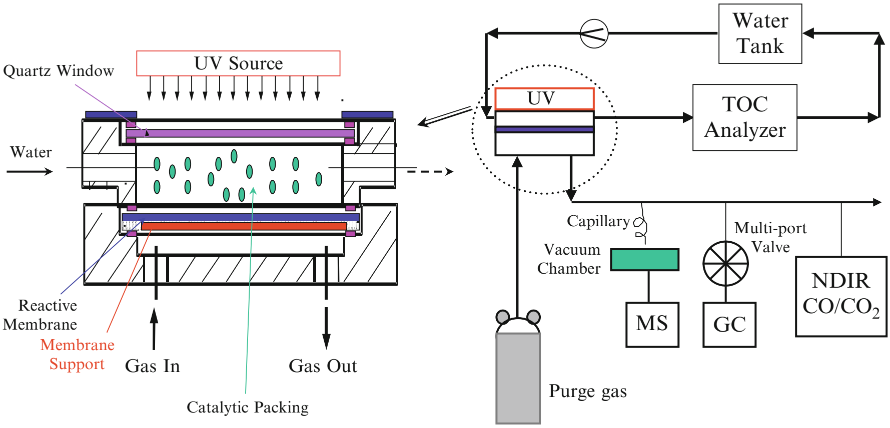


Fig. 2.13 Catalytic membrane test setup

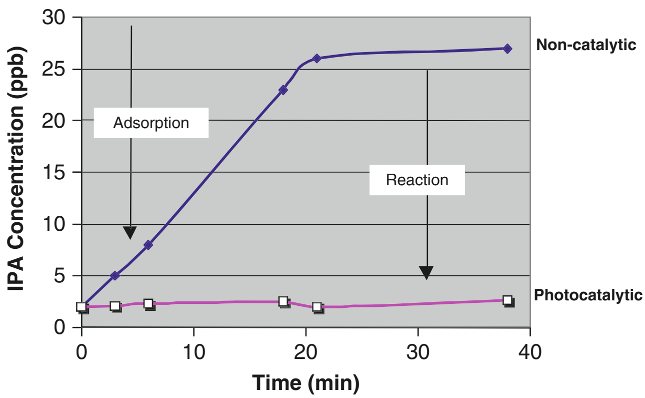


Fig. 2.14 Typical test results for photo-catalytic membranes

The key component of the setup is a test cell which holds the membrane. Figures 2.14 and 2.15 show the test results, using the catalytic membrane for removal of iso-propyl alcohol (IPA) from water. IPA is an organic contamination used in semiconductor fabs which end up in the rinse water discharged from these fabs. It is also a good model compound representing organics with moderate to slow rate of oxidation.

The application of photo-catalytic oxidation for removal of organic from water is an active area of research [5, 8]. In particular, work is going on by a number of research groups to find better catalytic or promoters to enhance the catalytic effect of conventional catalysts such as titanium oxide. A key idea for improvement of catalytic action is the use of promoters. Figures 2.16 and 2.17 illustrate the primary function and mechanism of action of promoters in suppressing the undesirable hole–electron recombination process. As shown in Fig. 2.18, the use of promoters

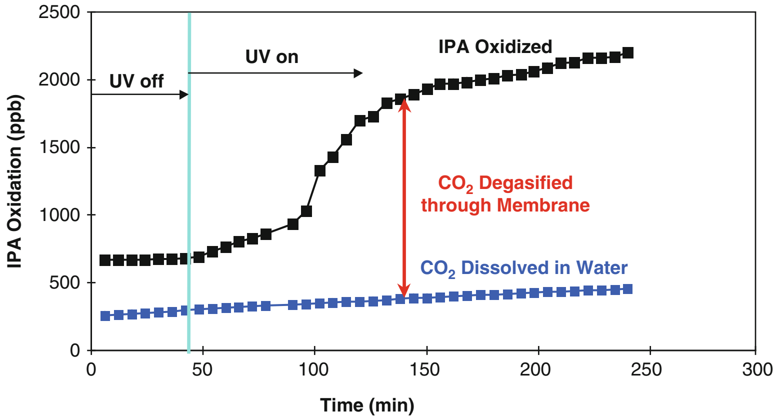


Fig. 2.15 Catalytic oxidation of IPA

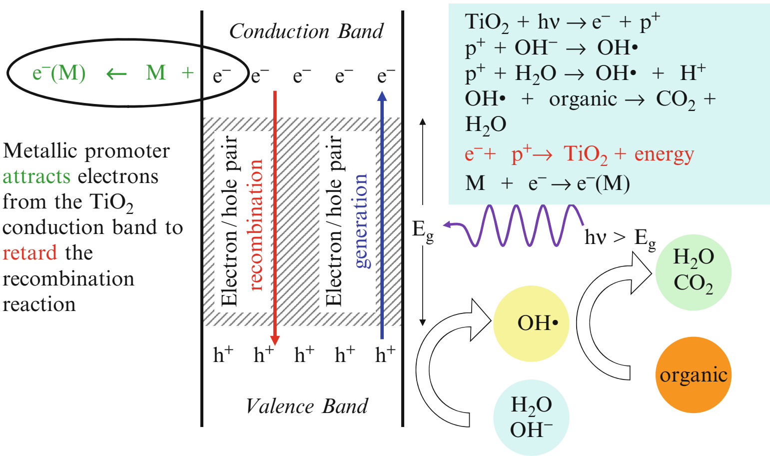


Fig. 2.16 Role of promoters in TiO_2 catalytic oxidation

$TiO_2 + h\nu \rightarrow e^- + p^+$	photogeneration of electron / hole pair
$p^+ + OH^- \rightarrow OH\bullet$	production of radicals
$p^+ + H_2O \rightarrow OH\bullet + H^+$	
$OH\bullet$ + TOC → intermediates $\rightarrow CO_2 + H_2O$	radical oxidation of organic compound
$e^- + p^+ \rightarrow TiO_2$ + energy *(undesirable reaction)*	recombination of electron / hole pair
$M + e^- \rightarrow e^-_M$ *(desirable reaction)*	Noble metal, M, attracts free electron slows recombination, and promotes radical generation

Fig. 2.17 Role of promoters in catalytic oxidation

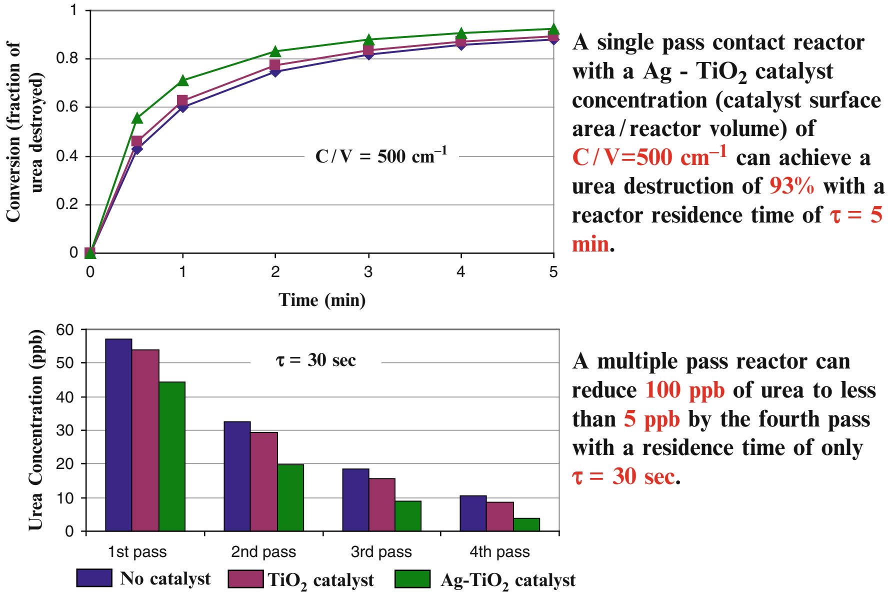


Fig. 2.18 Comparison of catalytic and non-catalytic oxidation

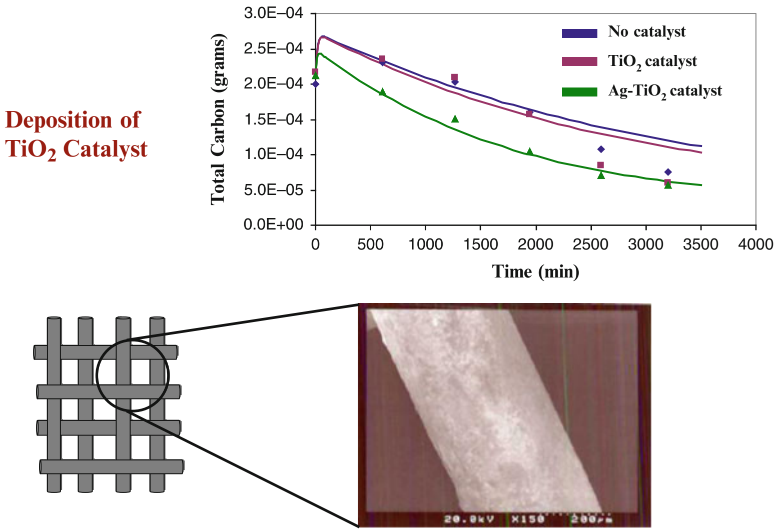


Fig. 2.19 Fabrication of catalytic filters by atomic layer deposition

is a very effective way of enhancing the efficiency of catalytic reactors treating and removing traces of urea (a relatively recalcitrant organic impurity) from water. As shown in Fig. 2.19, these filters can be fabricated by depositing the catalyst using atomic layer deposition (ALD) method.

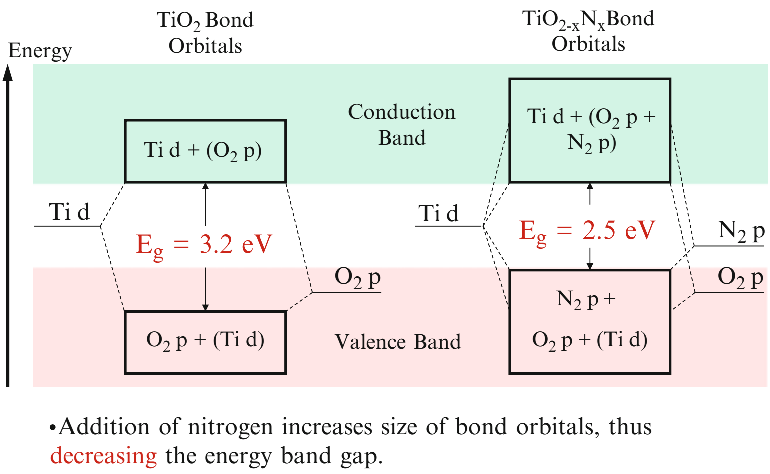


Fig. 2.20 New concepts in TiO_2 catalysis

$$O_3 + H_2O \xrightleftharpoons{\text{High pH}} O_2 + 2OH^* \quad \text{pH controlled}$$
$$O_3 + OH^* \rightleftharpoons O_2 + HO_2^*$$
$$O_3 + HO_2^* \rightleftharpoons OH^- + 2O_2$$
$$O_3 + OH^- \rightleftharpoons HO_2^- + O_2$$
$$O_3 + HO_2^- \rightleftharpoons OH^* + {}^*O_2^- + O_2$$
$$O_3 + {}^*O_2^- \rightleftharpoons {}^*O_3^- + O_2$$
$${}^*O_3^- + H_2O \rightleftharpoons OH^- + OH^* + O_2$$
$$OH^*, HO_2^*, {}^*O_2^-, {}^*O_3^-, O_3 + CH_n \longrightarrow CH_m + CO_2 + H_2O$$

Fig. 2.21 Hybrid system: UV – ozone combination

Another approach to enhancing the catalytic effect is by modification of the substrate to lower the band gap energy needed to activate the sites for the hole generation [1, 3, 4, 6]. In case of titanium oxide, the incorporation of nitrogen in the titanium oxide matrix to convert oxide to oxi-nitride has proven to be a promising method to lower the band gap energy; an example of such results is shown in Fig. 2.20.

The hybrid treatment effect can also be obtained by combining the UV with ozone. The combination is shown to be synergistic. The mechanism of this combined synergistic process in shown in Fig. 2.21.

The concept of combining conventional processes to get new integrated systems with synergistic effect can be extended beyond what has been discussed to systems that involve more than two process units [2, 7]. An example of this in a three-stage process is shown in Fig. 2.22. In this three-stage process, the catalytic oxidation is used in stage 1 to completely oxidize (mineralize) some TOC impurities and, at the

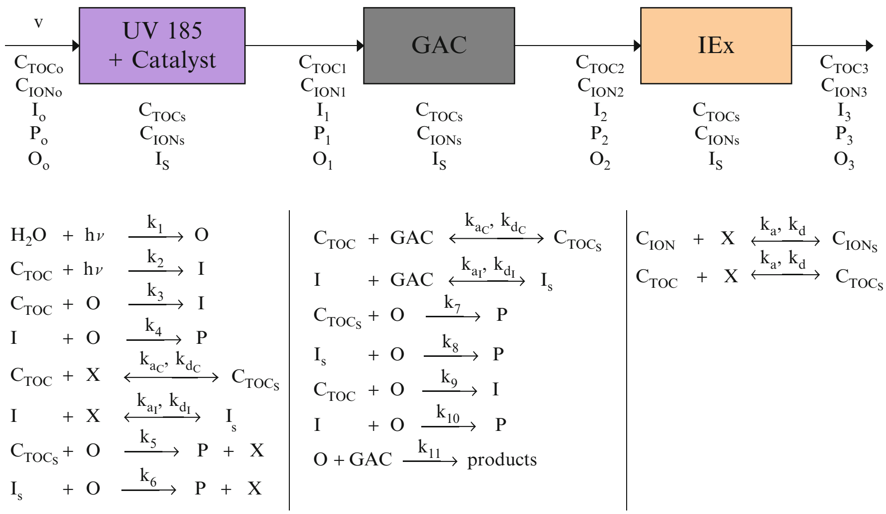


Fig. 2.22 Three-stage hybrid system

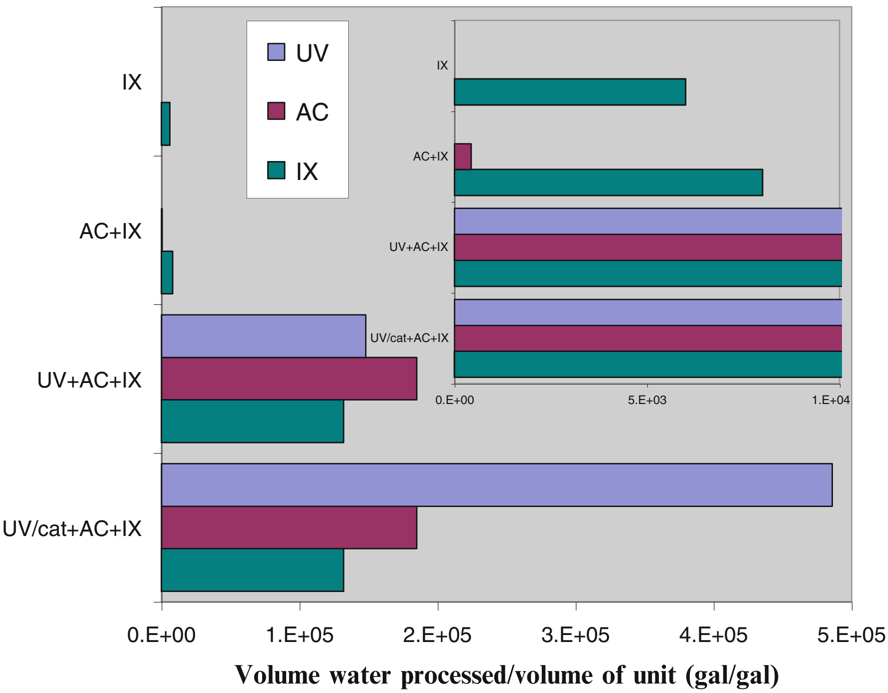


Fig. 2.23 Hybrid purification system performance

same time, partially oxidize or reform other impurities which are recalcitrant to total oxidation. Partial oxidation of these recalcitrant impurities would make them more absorbable on GAC or similar capture process units that follow the first stage. Finally in the third stage, ion exchange is used to remove any ionic impurity that has not been removed in the first two stages and to increase the resistivity of the final ultra-pure water. The role of each unit in this three-stage hybrid process is shown in Fig. 2.23.

2.4 Summary and Conclusions

The key to green technology for water purification is the application of low-energy and low-waste water purification methods. To facilitate this application, novel purification techniques are needed. This does not exclude the conventional processes; in fact, innovative combination of well-proven conventional methods and their usage in hybrid systems can create synergistic efficient processes. The usage of these hybrid new processes can be greatly promoted by the application of a robust metrology method using on-line, real-time, and fast response sensors as well as a process control algorithm.

References

1. Sato S, Asahi R, Morikawa T, Ohwaki T, Aoki K, Taga Y (2002) Photo-catalysts sensitive to visible light. Science 295(5555):626–627
2. Castro ME (2006) Kinetics and mechanism of ion exchange process and resin deactivation during ultra-purification of water, PhD dissertation, Chemical Engineering, The University of Arizona
3. Burda C, Lou Y, Chen X, Samia A, Stout J, Gole J (2003) Enhanced nitrogen doping in TiO2 nanoparticles. Nano Lett 3(8):1049–1051
4. Ihara T, Miyoshi M, Iriyama Y, Matsumoto O, Sugihara S (2003) Visible-light-active titanium oxide photo-catalyst realized by an oxygen-deficient structure and by nitrogen doping. Appl Catal B Environ 42(4):403–409
5. Kusakabe K, Aso S, Wada T, Hayashi J, Morooka S, Isomura K (1991) Destruction rate of volatile organochlorine compounds in water by ozonation with ultraviolet radiation. Water Res 25(10):1199–1203
6. Sankatani Y, Koike H (2001) Novel photo-catalytic oxidation materials, Japanese Patent no. 2001072419
7. Schmotzer M, Castro ME, Shadman F (2002) Activated carbon removal of organic contaminants in ultra-pure water. Clean Technol Environ Policy 4:125–132
8. Wei T, Wang Y, Wan C (1990) Photo-catalytic oxidation of phenol in the presence of hydrogen peroxide and titanium dioxide powders. J Photochem Photobiol A Chem 55(1):115–126

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