Techniques of Wastewater Treatment

2. Future Technologies

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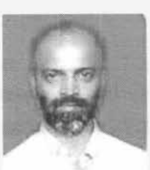

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In the first part of this article, we have learned about the need and importance of wastewater treatment and conventional methods of treatment. Currently the need is to develop low power consuming and yet effective techniques to handle complex wastes. As a result, new and advanced techniques are being studied and in the second part of the article, we give a brief description about each of such techniques, their principles of operation, merits and demerits.

1. Wastewater Treatment by Sonication

Chemical activation for the occurrence of the reaction can be achieved by thermal, photochemical, electrochemical, and sonochemical activation. All these techniques can be considered as supplying energy to make an active oxidizable species of the pollutants. Generally speaking, sonochemistry is a term related to the effect of ultrasonic waves on these reactants.

Basics of Sonochemistry:

1. Transducers are used for the generation of ultrasound and they are liquid driven or magnetostrictive or piezoelectric transducers. It is only ultrasound that is useful for chemical reactions.

2. Similar to the transmission of the normal sound waves, in ultrasound (frequency > 16 KHz) during the rarefaction stage of the wave, the liquid molecules are torn apart causing cavitation to occur i.e. formation of voids. These spots or cavities violently collapse during the next compression cycle. Thus propagation of ultrasonic waves in the liquid promotes the

formation of cavitation bubbles which can grow and implode under the periodic variation of the pressure fields.

Part 1. Introduction to Effluent Treatment and Industrial Methods, *Resonance*, Vol.5, No. 10, pp. 56-68, 2000.

Method and Mechanism

The generation of oxidative species is an effect of cavitational collapse. During collapse of a cavitational bubble, though the process remains locally adiabatic, inside the cavity, temperature shoots up to few thousand degrees. At such high local temperature, the weak intermolecular forces (in the form of bonds) are disrupted. This thermal dissociation or breakage of molecules gives oxidative species like HO^{o}, HO_2^{o}, O^{o} and peroxy compounds H_2O_2 and O_3 inside the cavity. These short lived species react with solute molecules which is nothing but the organic compounds in wastewater at the outer shell of cavity. Synergized effect of presence of highly oxidative species with high local temperature causes the organic molecule to undergo oxidative degradation. For oxidation to occur the species should be thrown out of the cavity and hence the rate of collapse of cavity should be marginally greater than the life of the oxidative species.

Wastewater Treatment

When ultrasound is applied to effluent, water undergoes thermal dissociation to H atoms and OH radicals. OH is highly reactive and can oxidise almost all contaminants in water. This primary oxidation is the reason for the degradation of contaminants in water. Sonochemical reactions are normally characterised by the simultaneous occurrence of pyrolysis and radical reactions, especially at high solute concentrations. Volatile solutes undergo direct pyrolysis reactions within the gas phase of the collapsing bubbles or within the hot interfacial (cavity-liquid) region.

Phenols, chloro-phenol, nitrophenol, parathion, etc. are among a few regularly observed contaminants in an industrial effluent, which are known to get degraded by the cavitation phenomenon. *Figure* 1 shows one of the mechanisms of the cavitational

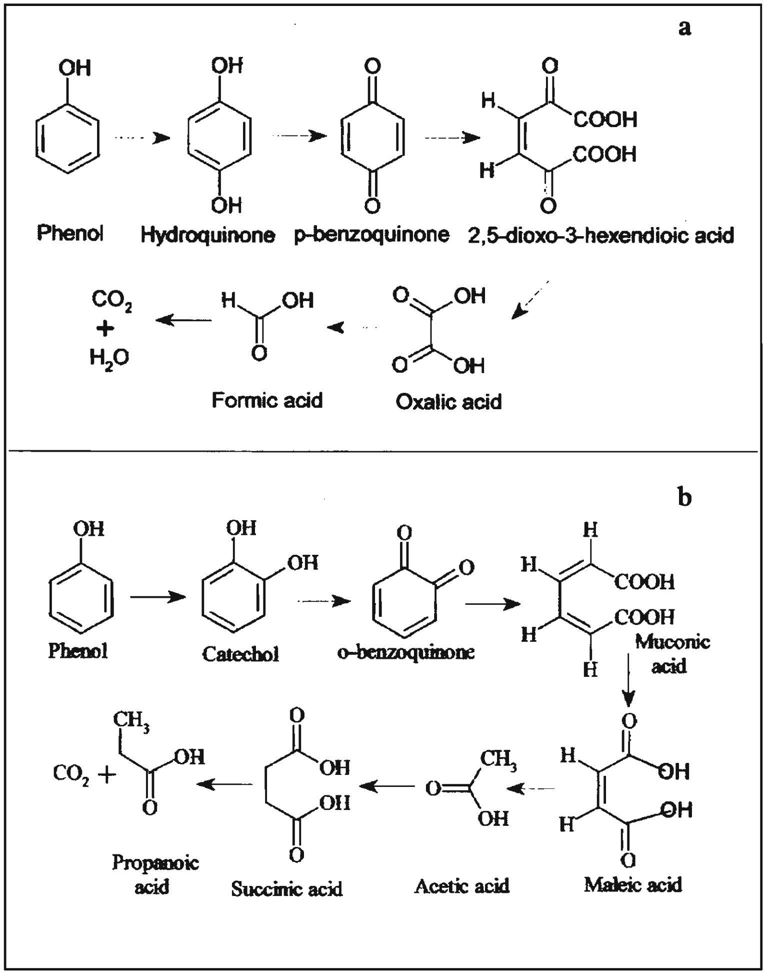

Figure 1. Phenolic oxidation scheme by sonication.

oxidation of phenol in wastewater. Degradation pathway is likely to change with the change in the intensity of ultrasound, concentration of the contaminant in water, etc. An unanticipated advantage is that sonication also kills some microorganisms and hence disinfects water.

Recent Advances

a) Catalytic Sonicative Degradation of Wastewater: Since sonolysis is a very slow process, catalytic modifications have been tried out to enhance the rates along with sonication. Solid catalysts, which can be separated by filtration, are used for this purpose. Catalysts like Raney Ni, V_2O_5, Pt, AgO and Fenton reagent, which help the oxidation reactions, are applicable in these cases.

b) Chemi-sonication of the wastewater (CAVOX): Radical attack degrades and oxidises a number of organic contaminants. This homogeneous destruction of compounds like CCl_4, CH_2Cl_2, $C_2H_2Cl_4$, at 100-1000 ppm is possible in conjunction with the strongly oxidising chemicals such as H_2O_2 and ultrasound. Depending upon the quantity of the entrained gas and concentration of H_2O_2 used along with intensive cavitation, the destruction process takes 1-4 hours for the above mentioned concentrations.

c) Synergism of sonication with conventional methods: Coupling of ultrasound with ultraviolet (UV) radiation or electrostatic forces or with WAO (Wet Air Oxidation) gives synergetic improvements in the treatment efficiency as discussed below in brief:

1. *Photocatalytic* action with the ultrasound has resulted in higher degradation rates of the contaminants. This is due to the mechanical effects of cavitation involving photocatalyst surface cleaning and increased mass transfer of the polluting species to the powdered catalyst surface.

2. *Electrochemical* effects: Effective oxidation rate of aromatics is significantly increased when employed with ultrasound. When a salt solution is present with aromatic compound, it has been observed that the reaction becomes faster via formation of intermediate such as chlorinated hydrocarbons.

3. *SONIWO* : Sonication followed by WAO gives an economic hybrid model and an efficient process. Sonication in the presence of the catalytic WAO including catalysts like $CuSO_4$ and $NiSO_4$ is more effective than without a catalyst. Sonication can breakdown large molecular weight compounds which are then easily oxidised by WAO.

Thus it can be concluded that the effluent treatment by sonication is an excellent polishing step. Though the process looks simple, it is rather slow and for scale-up, extra energy cost is the major drawback. The success of the process has been demonstrated on the laboratory scale and lot of technological issues need to be solved before it becomes industrially applicable.

2. Photocatalytic Oxidation of Industrial Effluent

Photo-oxidation is a promising technique among few newly developed but yet to be industrially employed techniques. Photocatalytic oxidation uses UV radiation and a catalyst for the destruction of the pollutants. Catalyst life is also long and it can be reactivated once used.

Fundamental Concept Behind The Decontamination

The reaction that occurs during the photocatalyst mediated destruction of wastewater is a radical reaction and the radical formation occurs due to the activation energy supplied by the highly energetic UV radiation to the catalyst surface and the water molecules in the effluent. A number of semiconductor oxides can be used as catalysts for this particular purpose. The semiconductor oxide molecules on illumination with radiation having energy greater than its optical band gap transfers an electron to the conduction band leaving a hole in the valence band. At the solid-liquid interface the electron transfer occurs either from the conduction band to an acceptor in the solution or from a donor in solution to the valence band. These processes compete with the recombination of electron and hole to produce thermal energy, which is not useful for decontamination. In the absence of suitable electron and hole scavengers, the stored energy is dissipated within a few nanoseconds by recombination. The valence band holes are powerful oxidants (1.0 to 3.5 V) while conduction band electrons are good reductants (0.5 to – 1.5 eV). This eventually leads to photocatalytic redox processes ultimately leading to the destruction of the organic molecule. The most important thing that can lead to the reaction is the reacting substance remaining in contact with the surface of the catalyst.

Generally transitional metal compounds are proven useful for photocatalysis. They include TiO_2, ZnO, Fe_2O_3, CdS, W_2O_5, ZnS, etc. There are few reasons behind the use of TiO_2 as a photo-oxidant as compared to other transition metal oxides. Other oxides act as sensitizers for light induced redox processes due to their electronic structure. ZnO is a suitable alternative for TiO_2 but it is very unstable with respect to non-uniform dissolution. TiO_2 exists in two crystalline forms, namely, anatase and rutile. It has been observed that generally anatase is suitably catalytically photoactive while rutile is catalytically inactive. But it has also been observed that rutile is highly active in the case of degradation of CN^- and it competes with standard photocatalysts viz. Degussa, Sachtleben, Kimera (which are the trade names of the catalysts from different manufacturers having different composition of anatase and rutile type TiO_2) are normally preferred in the application of photo-oxidation. Following reaction scheme shows the stepwise photocatalysis using TiO_2.

$$TiO_2 \longrightarrow TiO_2\,(e^- + h^+)$$

$$h^+ + RX_{ad} \longrightarrow RX_{ad}^{\cdot +}$$

$$h^+ + H_2O_{ad} \longrightarrow HO_{ad}^{\cdot} + H^+$$

$$h^+ + OH^-_{ad} \longrightarrow HO_{ad}^{\cdot}$$

$$e^- + O_2 \longrightarrow O_2^{\cdot -}$$

$$e^- + H_2O_2 \longrightarrow OH^- + HO^{\cdot}$$

Where R indicates the solute organic molecule and the subscript 'ad' indicates the adsorbed species on catalyst surface. One more generalised oxidation scheme for the organic compounds (viz. alcohol) can be given as

$$R\text{-}(CH_2)_2\text{-}OH \rightarrow R\text{-}CH_2CHO \rightarrow RCH_2COOH \rightarrow RCH_3 + CO_2 \rightarrow$$
$$R\text{-}CH_2OH \rightarrow R\text{-}CHO \rightarrow R\text{-}COOH \rightarrow R\text{-}H + CO_2 \rightarrow CO_2 + H_2O$$

Methods of Catalyst Loading

During the process of catalytic oxidation of the toxic contaminants the active surface area of the catalyst is very important but simultaneously one has to consider the catalyst stability, recovery and reuse since it is expensive and can cause solid pollution if disposed off as such. The loading can be done in two ways, in the free form i.e., slurry or in an immobilised form i.e. attached to a transparent surface. Since the catalyst life is very long (>5 years, it also depends up on the catalyst composition) the cost of operation in immobilisation mode is economically feasible.

Catalyst Activation By Doping: The properties of the catalyst particles can be modified by selective surface treatments to enhance the interfacial charge transfer reactions of TiO_2 in the bulk phase and the colloidal particles. Typical dopants that are widely accepted are Fe(III), Cr(III), Mo, V, T(IV), Ti/Fe, etc. The results obtained in the decontamination of different compounds based on doping are contradictory but certainly it enhances the selective degradation of particular compounds.

Factors Affecting The Process Efficiency

Since the photocatalysis is a radical reaction the completion of the reaction depends on a number of parameters like catalyst loading, pH of the effluent, intensity of the incident radiation, type of the catalyst, type and composition of the effluent, etc. It has been observed that the maximum destruction of the contaminants occurs at an optimum amount of the catalyst, which is found to be 350-460 ppm depending on the concentration of the contaminants in the effluent. It is always preferred to have an acidic effluent (tending to pH 7). An alkaline pH effluent oxidises slower than the acidic one as the contaminants easily undergo fast destruction in the acidic conditions. Since the radical generation is a two-parameter dependent (catalyst loading and composition of effluent) process, intensity of irradiation affects significantly in reaction initiation step and at higher intensities, the rate is found to be more. Specifically in the range of 340-450 nm wavelength the effect is very pronounced. Single (only one component is present) effluent is always better to be decontaminated as compared to the mixed (number of contaminants is more than one) effluent since it creates a competition for absorbance of the radicals and overall COD reduction rate may be less than a single component system.

Developments in the Photocatalytic Oxidation Treatment

a) *Cavitational oxidation in vacuum* (*VACAVOX*): At 185-190 nm the UV is absorbed very effectively in *vacuum* condition and when combined with sonication gives better results.

b) *Photo-induced electron transfer*: Here, the chemicals, which produce large number of solvated electrons (generally called chromophores) are used. They play an important role in giving superoxide anion. This comprises three steps as

i) electronic excitation of the organic contaminant in aqueous medium,

ii) photocatalyzed electron transfer process and

iii) oxidation through the generated hydroxyl radicals.

c) *Cavitation induced photo-oxidation*: Photo-oxidation intrinsically helps in increasing the rate of the oxidation reaction along with intermittent cavitation helping in increasing the local temperature and the local rates of oxidation reaction.

Though the process of photocatalysed oxidation of the industrial effluent looks very effective, the scale-up (design on large scale based on laboratory data) is a major difficulty in its implementation. Also the recovery of the catalyst in slurry mode of operation and reduction in the efficiency in immobilised mode pose a problem in designing proper reactor system. Solar radiation can be effectively used in the place of UV lamps to make the process more economical. In Indian context, this method offers an exciting opportunity due to the abundance of sunlight.

3. Effluent Treatment by Super Critical Oxidation

Thermal technique of effluent treatment using super critical fluids (SCFs) as a technology is challenging. SCFs are fluids raised to temperatures and pressures beyond their critical point when they exist as a single phase. These processes are initially being considered for the destruction of highly toxic materials, which are costly to dispose off. Few of the known chemicals, which can be used at SC condition, are water, CO_2 and linear alcohols like ethanol, propanol, etc. *Box* 1 gives the general information about the properties of a fluid at its SC condition. Here we discuss the direct application of respective SCF for wastewater treatment.

Super Critical Water (SCW)

Water becomes a super critical fluid above 374°C and 22 MPa. Under these conditions, the hydrogen-bonded structure is largely broken down. It is therefore much less polar and can dissolve relatively large amounts of non-polar organic compounds making them available for chemical reaction in the liquid phase. The loss of structure also means that the medium is more like a collection of light mobile molecules and diffusion rates are rapid. For this reason reactions, which are diffusion controlled, are much faster. Hence super critical water can be a reaction medium for the oxidation reactions of organic compounds.

Box 1. General Properties of Super Critical Fluids

They have properties between gases and liquids. Thus mixing of two fluids becomes very feasible by reduction of mass transfer limitations.

There is a better control of diffusion properties and phase behaviour.

Control of product selectivity is rendered facile.

They are cheap, non-toxic and non-inflammable solvents.

Reaction conditions can be maintained milder.

The basic compounds for these fluids are environmentally safe and easily available in large quantities.

Organic compounds can be rapidly and almost completely converted by molecular oxygen to benign small species like CO_2, H_2O, N_2, Cl^-, SO_4^-, etc. Conversion of pollutants into more benign species can also take place rapidly by the hydrolysis in supercritical water without the presence of oxygen.

Catalytic SCWO

The reaction scheme for SCWO of an effluent follow a stepwise process in two different ways like homolytic pathway where radicals are formed and heterolytic path where ionic species are formed in the initiation step. Further oxidation of organic compounds follows the same steps as in earlier methods of oxidation. The addition of a heterogeneous catalyst during SCWO is effective in promoting complete oxidation. Here the crucial step lies in finding out the proper catalyst which should be active and stable in supercritical water. Among the catalysts, mainly TiO_2, V_2O_5/Al_2O_3, MnO_2/CeO_2, CuO/ZnO have been found useful.

Method of Treatment

The reaction scheme is almost identical to the wet-air oxidation (WAO) except that the reaction conditions are much severe. Heat recovery and feed preheating can be done from the hot reaction mass before it is discharged. Once established, it may be a viable alternative to *wet air oxidation* if the smaller residence times can offset the other higher costs of the technology. In addition, the greater corrosion problems of the reaction vessels in super critical water oxidation due to the presence of oxygen and water at high temperatures must be solved. Efficiencies of SCWO are around as high as 99.9% and few large-scale plants are running very efficiently. Apart from water as a SCF, CO_2 is also very widely used for the same purpose of effluent treatment. CO_2 becomes SC at ambient temperature 31°C and 6.9 MPa. The oxidation mechanism is same as for SC water and results are comparable. A large-scale plant at Baltimore Municipal sewage treatment runs using SC CO_2 since the last one decade with excellent results. Thus it can be taken as a conversion of ideas into reality or rather invention to an economical innovation.

Conclusion

By now the reader must have got an idea about the importance of wastewater treatment. Today, biological method (aerobic) is the most widely used method because of its simplicity and relatively low cost but is less successful when the effluent contains highly toxic organic pollutants. It occupies a large space and this could be a severe limitation. Thus for treatment of a highly contaminated and toxic effluent there is no option other than advanced techniques like WAO, SCWO, sonication and photocatalytic oxidation using solar energy at least in a supplementary role. An economic and reliable way of using solar energy for effluent treatment is a very attractive option for Indian industries since the life of the catalyst is long. Also many possible synergism of these techniques promise a good pollutant destruction rate that helps in maintaining the environment clean. In the curious mind of an undergraduate reader these papers would have surely generated a long series of questions and possibly many innovative ideas about the wastewater treatment could emerge. In fact this is not the end, it is just the beginning of thought process which is prompting the reader to think about the existence of a global ecological balance, which is in danger of destabilising. Balancing the hydrological cycle is not an easy task. Our job is to let nature do it in its own way without disturbing the balance by adding any waste in any form and if it is inevitable for the progress then look at the above mentioned options. Thus everybody needs to remember that "*conservation of our environment and other living species including the microbes will help us to live a longer and healthy life*".

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17 year old Gauss recorded in his diary his discovery: "Eureka! triangle + triangle+ triangle= number" (every integer is a sum of three triangular numbers).

The Mathematical Intelligencer,
Vol.17, No.4, 1995, Springer-Verlag, New York