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The WRC operates in terms of the Water Research Act (Act 34 of 1971) and its mandate is to support water research and development as well as the building of a sustainable water research capacity in South Africa.

TECHNICAL BRIEF

Industrial wastewater

Improving industrial wastewater treatment for production of biogas

A completed Water Research Commission (WRC) study investigated the integrated photo-catalytic and anaerobic treatment of industrial wastewater for biogas production.

Background

Anaerobic treatment of high strength wastewater is a widely accepted practice in the industry due to the fact that it converts the organic pollutants into biogas, which is a mixture of methane and carbon dioxide. As a result, this process leads to the reduction in chemical oxygen demand (COD) of industrial wastewater.

Moreover, the biogas produced is a source of energy which can be used in industry or for domestic purposes to offset the ever increasing energy demand. Waste removal and methane yield are the key parameters used in the evaluation of an anaerobic digester (AD) performance in the anaerobic digestion process.

The performance of ADs is inadequate in removing some biorecalcitrant wastes effectively. For this reason, advanced oxidation processed (AOPs) such photocatalytic degradation as well as integrated techniques have attracted a lot of interest in the recent years.

Several photocatalysts have been investigated, of which TiO_2 is most commonly applied. The catalyst and liquid mixture can be in form of slurry. The material in the slurry could be could be of nano- or macro-size TiO_2 particle.

Used in this way, the photocatalysts pose an additional challenge with regard to the separation of the mixture. To address this problem, the catalysts can be deposited onto a support material such as zeolite. In such an application, zeolite has a dual function of adsorption and that of providing support for the catalyst.

However, this creates yet another set of problems. One of such problems is that, in some cases, the degradation of the toxic wastes through photocatalysis results in compounds that are more toxic than the original one.

The structures of the intermediate and final products are influenced by the operating conditions. It is important to identify the intermediate products in order to determine the photodegradation pathway which depends both on the properties of the parent compound, the characteristics of the support material and those of the reaction mixture.

The presence of ions in the solution influences the properties of both TiO_2 and the toxic waste. Also, given that adsorption processes depend on the adsorbent surface area available and the presence of the active sites, the interaction between the support material and the catalyst influences both the adsorption and photo-degradation processes.

The other problem is the light penetration in a system that has non-transparent liquid and opaque support materials. These problems are compounded by the fact that mass transfer limitations increase with an increase in biomass support loading.

Aims and methodology of WRC project

The aim of this WRC project was to analyse the performance of the AD and advanced oxidation process (AOP) systems separately in degrading high strength wastes and to develop an integrated AD-AOP system to improve biogas production rate and methane yield.

The treatment of high strength wastes such as molasses, textile, heavy metals and pharmaceutical was investigated under different experimental conditions.

The approach was such that the work started with the preparation of catalysts and testing them on desk top experimental set ups at the Vaal University of Technology (VUT) and Tshwane University of Technology (TUT).

Preliminary anaerobic digestion studies focused on molasses wastewater (MWW), pharmaceutical wastes and methyl blue (MB) dye. The photocatalyst (TiO_2) was attached onto zeolite and silica adsorbents. The adsorbents served two purposes of supporting both the catalyst (in the photodegradation process) and the microorganisms (in anaerobic digestion).

In the photodegradation process ultraviolet lamps and sunlight were the sources of irradiation. For the solar photodegradation experiments, fluidised bed reactors (FBR) were employed to adsorb and photodegradate pharmaceuticals.

The TiO_2 was attached to powdered activated carbon (PAC) using silica xerogel. The PAC was used instead of clinoptilolite due to its favourable adsorption of pharmaceuticals and also due to the fact that it could be easily fluidised in the fluidised bed reactor.

Main results of the study

The investigation has been steadily increasing in depth and complexity in the aspects of the microbiology, photochemistry, design and modelling. This has resulted in an exponential growth in the number of researchers progressing from master to doctoral degree studies.

The final report is a summary of the results obtained by these young scholars. The biodegradation of MWW was observed to increase with an increase in the initial substrate concentration.

However, the degradation of MB, a model textile wastewater, was inhibited at high concentrations (concentrations above 2000 mg/L). In both wastewater types, it was found that the use of zeolite as biomass support material improved biodegradation efficiency.

Specifically, biogas production improved by five folds when treating MB and ten folds when treating MWW when zeolite was used in the FBR compared to reactors without zeolite. Similarly, chemical oxygen demand (COD) removal also showed the same trend with zeolite improving COD removal by about 20% in both cases.

However, biodegradation was found to be suitable for colour removal only for the MB but not MWW. Colour removal of about 80% was achieved with the MB while an increment in colour was observed for MWW after the biodegradation process. Due to the fact that AD treatment could not remove the colour of the MWW and also due to the toxic nature exhibited by the MB dye, photodegradation of these kinds of wastewater was studied.

For the photodegradation studies, composite photocatalysts comprising TiO_2 and an adsorbent (zeolite, silica or activated carbon) was prepared and the proportion of TiO_2 in the composite ranged between 10-20%, depending on both the adsorbent and the pollutant to be removed. Given the energy cost associated with the application of UV, the use of solar irradiation was investigated.

Solar photodegradation experiments were performed in fluidized bed battery of reactors, in which 90% removal of the pharmaceutical substrates was realized. This system was employed to study the hydrodynamics of and adsorption in the solar fluidised bed reactor.

The optimum hydrodynamic condition was obtained when the reactor inclination angle and superficial air velocity were 75° and 0.014 m/s, respectively. However, a reactor inclination angle of 75° and a superficial velocity of 0.007 m/s gave the best adsorption and photodegradation of the substrates.

These results show that the use of the synthesised composite catalyst in the fluidised bed reactor provided a stable and efficient system capable of long term use. The results from this work also show that this system can be used for the removal of pharmaceutical substrates at low concentrations.

However, with zeolite TiO_2 was detaching with repeated use whilst silica was found to be a better binder than zeolite. Further, effects of ions on photodegradation were investigated using the UV reactor and silica as a binder for TiO_2 for the treatment of mixed dye and Cr(VI) wastewater.

It was found that there was a good dispersion of TiO_2 on the surface of silica. The degradation of dye/TiO_2-silica binary system proceeded faster than that of the respective ternary dye/Cr(VI)/ TiO_2-silica system at neutral pH.

Results showed that the photo reduction of Cr(VI) was much faster in the mixed system than in the single one. The studies using separate photodegradation and biodegradation revealed limitations and advantages of each process, which were further employed by integrating the two processes.

Conclusion

An Integrated AD and AOP using South African zeolite was applied in the treatment of methylene blue dye in up-flow fixed bed bioreactor and UV photoreactor. The optimal operating conditions obtained in the separate AOP and AD were applied in the treatment of methylene blue dye in an integrated up-flow fixed bed bioreactor and photoreactor.

Results showed that, compared to the separate systems, the integrated AOP-AD system achieved better degradation with colour and COD reductions of 81% and 80%, respectively.

Moreover, it was found that UV photodegradation pretreatment improved the biodegradability of the MB dye by 3- folds after irradiation time of 60 minutes. Thus integration of the two processes in such a way that UV photodegradation precedes the AD process led to higher biogas production than that of the stand-alone AD process.

Further reading:
To order the report, *Integrated photo-catalytic and anaerobic treatment of industrial wastewater for biogas production* (**Report No. 2105/1/14**) contact Publications at Tel: (012) 330-0340, Email: orders@wrc.org.za or Visit: www.wrc.org.za to download a free copy.