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Removal of ethylbenzene and p-nitrophenol using combined approach of advanced oxidation with biological oxidation based on the use of novel modified prepared activated sludge

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ABSTRACT

The treatment of a synthetically prepared wastewater containing ethylbenzene and p-nitrophenol has been investigated using combined treatment schemes based on the advanced oxidation process followed by the conventional aerobic oxidation process (using primary activated sludge (PAS), modified prepared activated sludge (MPAS) based on the use of combined sludge from different treatment sources and activated sludge (AS)). The operating conditions for the pretreatment scheme have been optimized and it has been observed that initial pH of 3–3.5, a Fe^{2+} dosage of 2.0 $g L^{-1}$ and a H_2O_2 dosage of 1.5 $g L^{-1}$ in combination with ultrasound gives the best performance. Approximately, 55–70% reduction in the chemical oxygen demand (COD) was obtained at optimum conditions after pretreatment from initial conditions of COD as 3642 and 3417 $mg L^{-1}$ and BOD as 881 and 533 $mg L^{-1}$ for the wastewater containing ethylbenzene and p-nitrophenol respectively. From an initial BOD_5/COD (BI) value of around 0.15–0.2, the ratio was found to increase to about 0.30–0.35 after pretreatment, which is considered good for the aerobic treatment. In the case of aerobic oxidation, promising results were obtained for the modified prepared activated sludge giving better conversion ability of intermediates into solid residue and higher biomass yield that could be separated by simple filtration as compared to the primary activated or the activated sludge treatment. The best treatment approach as established in the work was ultrasound assisted Fenton process as the pretreatment followed by biological oxidation using MPAS.

1. Introduction

Environmental pollution is mainly attributed to the improper discharge of industrial organic effluents. Aromatic compounds such as ethylbenzene and p-nitrophenol are the principal pollutants usually found in industrial wastewater streams from petrochemical, plastics, resin, rubber, textile, pharmaceuticals manufacture as well as tanning industries (Nagda et al., 2007; Pradhan and Gogate, 2010a; Ma et al., 2000). Nitrophenols exhibit moderate to high toxicity in the aquatic environment though the concentrations in the actual water streams can be significantly higher. Similarly, ethylbenzene concentration should be typically less than 1 $\mu g L^{-1}$ in drinking water from ground or surface sources though for the surface water in industrial and urban areas, the level of ethylbenzene can be as high as 15 $\mu g L^{-1}$ (WHO, 1996, 2000). Due to very slow rates for possible biotic and photochemical decomposition, nitrophenols present in water could pose significant risk to

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sensitive aquatic organisms, particularly under surface water conditions which are not favoring elimination pathways. It is also important to remove ethylbenzene from wastewater due to highly hazardous nature and as it can cause many serious health effects to humans (Bina et al., 2012; Cost et al., 1993).

There are different possible treatment approaches such as sonication, ozonation, photolysis, Fenton chemistry, electrochemical oxidation, photocatalytic degradation and adsorption on activated carbon, ion exchange resins and silicates that can be applied to remove aromatic compounds such as ethylbenzene and other phenolic compounds from industrial wastewater (Cost et al., 1993; Xu et al., 2005; Nagda et al., 2007; Goncharuk et al., 2002; Aisien et al., 2013; Pham et al., 2013) but these methods result either in incomplete degradation or the treatment costs are significant. Biological oxidation using different types of bacterial strain which are isolated from soil, sewage or water under aerobic, anaerobic or combined aerobic and anaerobic conditions can also be applied though the treatment may be significantly slow and may not be effective at higher loadings of the biorefractory compounds (Lobo et al., 2014; Yi et al., 2006; Chakraborty et al., 2005; Stepnowskia et al., 2002). The approach of oxidizing the pollutants seems to be more viable as compared to the adsorption using activated charcoal considering the fact that adsorption leads to secondary pollution and also the costs especially with biological oxidation are expected to be lower. Biological oxidation can be based on use of different microorganisms though significant work has been carried out on bacterial species of *Pseudomonas* which are known for their capacity to decompose the various aromatic compounds as single source of carbon and energy (Huang and Li, 2014; Seo et al., 2009; El-Naas et al., 2014; Prenafeta-Boldu et al., 2002). Pretreatment using advanced oxidation processes can lead to rearrangement of the molecules enhancing the biodegradability and hence leading to the enhanced effectiveness of the biological oxidation. Using mixed culture of microorganisms can be another option for effective treatment considering the specific action of microorganisms on different compounds. The present work has focused on these two aspects of improving the biological oxidation for specific case of pollutants as ethylbenzene and nitrophenol.

Advanced oxidation processes (AOPs) are defined as the processes that generate hydroxyl radicals in sufficient quantities to oxidize majority of the complex chemicals present in the effluent water (Gogate and Pandit, 2004). Fenton based oxidation works on the principle that ferrous irons together with H_2O_2 produce aggressive chemical reaction generating hydroxyl radicals which are strong oxidizing agents (Yap et al., 2011; Stepnowskia et al., 2002). The use of Fenton's reagent for wastewater treatment is attractive because iron is a cheap and non-toxic element, while hydrogen peroxide is easy to handle and will rapidly decompose to yield oxidants (Jones, 1999). It is also important to understand that use of Fenton oxidation is often hampered by the requirement of acidic conditions for optimum operation as well as generation of toxic sludge creating disposal problems. Using Fenton oxidation in combination with ultrasound and only as a pretreatment to biological oxidation is expected to yield lower problems as compared to the use of Fenton oxidation alone since lower quantum of oxidants will be required.

Use of ultrasound also results in the formation of hydroxyl radicals through the cavitational events and this can also be effectively applied in wastewater remediation (Pham et al., 2013). Ultrasound alone however may not result in a sufficient rate of degradation to be of practical use. Also, the time-scale and the dissipated power necessary to obtain complete mineralization of the pollutants in the case of ultrasound treatment are not economically acceptable. One way to increase its efficiency is to combine ultrasound with an advanced oxidation process such as Fenton chemistry (Cravotto et al., 2005). Ultrasound based processes have been applied in the past for removal of p-nitrophenol from wastewater with about 57–67% removal (Pradhan and Gogate, 2010b; Ma et al., 2000; Cost et al., 1993; Xu et al., 2005; Sivakumar et al., 2002). The present work depicts the use of the oxidation processes (Fenton, ultrasound (US) or US/H_2O_2) for pretreatment to convert pollutant into intermediates which can be easily digestible by aerobic microbes in biological process.

In conventional biological process, microbial populations obtained from municipal sludge or anaerobic digesters show limited capability of degrading aromatic compounds. Aromatic compounds such as ethylbenzene and p-nitrophenol are well known to be toxic to biological treatment processes and their presence limits the biodegradability of many wastewaters (Jahan et al., 2014). Most of the earlier studies have involved single microbial species which may have limitations in field application due to the variety of contaminants present in the waste. There are different approaches that can be adopted in biological treatment as well with different *Pseudomonas* sp. strains being used in combination with anaerobic digestion (Seo et al., 2009; El-Naas et al., 2014). It has been well established that various *Pseudomonas* sp. are able to degrade aromatic compounds and remove the color in a variety of wastewaters, probably through their capacity to excrete various extracellular enzymes. Hence, a mixed community of microbes may be more effective to give enhanced mineralization, although many reports on aromatic degradation generally deal with pure species of microorganisms (Vazquez and Rial, 2014; Nwekel and Okpokwasili, 2014; Stoilova et al., 2006). Activated sludge is considered as natural microbial consortium which is generated from the biological activities that can be readily used for treatment of wastewaters (Sofer et al., 1990; Nwodo et al., 2012). There have been some earlier works focusing on the use of microbial consortium for COD removal or in general wastewater treatment (Thawornchaisit and Pakulanon, 2007; Hu et al., 2005) but the studies have mainly concentrated on biological oxidation. The present work has focused on the improvements that can be obtained in the biological oxidation based on the use of different sludge and by using advanced oxidation based pretreatment. The different activated sludge used for aerobic biological treatment process include primary activated sludge (PAS) as obtained directly from the effluent treatment plant, pure inoculated sludge based on the use of single microorganism species and called as activated sludge (AS) and modified prepared activated sludge (MPAS), which has been prepared specifically in this work based on the different activated sludge obtained from commercial sources. Overall, the present study reports the use of a novel combined biological (based on mixed culture) and advanced oxidation method for the treatment of ethylbenzene and p-nitrophenol containing wastewater.

Initially, the work was focused on the study of the performance of several oxidation processes such as only H_2O_2, only Ultrasound (US), US/H_2O_2, Fenton and US/Fenton as a pretreatment approach and subsequently the pretreated samples were treated further by aerobic activated sludge process. Aerobic biological treatment of the wastewater was carried out using the three different sludge namely primary activated