



## Research article

# Pretreatment technologies for industrial effluents: Critical review on bioenergy production and environmental concerns

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## ABSTRACT

The implementation of different pretreatment techniques and technologies prior to effluent discharge is a direct result of the inefficiency of several existing wastewater treatment methods. A majority of the industrial sectors have known to cause severe negative effects on the environment. The five major polluting industries are the paper and pulp mills, coal manufacturing facilities, petrochemical, textile and the pharmaceutical sectors. Pretreatment methods have been widely used in order to lower the toxicity levels of effluents and comply with environmental standards. In this review, the possible environmental benefits and concerns of adopting different pretreatment technologies for renewable energy production and product/resource recovery has been reviewed and discussed.

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## 1. Introduction

The rapid increase in the establishment of different industrial sectors entails detrimental effects on the environment due to their inability to meet the effluent discharge standards and regulations. Several studies have reported the genotoxic effects of such effluvia on all living forms. Consequently, the range of toxicity of major industrial effluents was found to reach as high as  $10^{12}$  revertant per liter (in *Salmonella*), which includes severe mutagenic hazards. In order to mitigate such hazards, several pretreatment methods have been adopted and proposed over the past few years. Besides, among the numerous industrial establishments, five major players have proven to inflict the highest level of hazard to both the surroundings as well as all life forms (Tong et al., 2017; Shobana et al., 2017). These include effluents from the paper and pulp industry, coal manufacturing facilities, petrochemical, textile and the

pharmaceutical industry. The effluents generated by these industries are highly toxic in nature. The complexity of the outflow contaminants impedes the effects of effluents treatments to reduce its toxicity and makes the treatment expensive. Therefore, proper pretreatment method should be selected in order to achieve cost-effective secondary treatment of the effluent. A thorough understanding of the pretreatment technologies used to treat these industrial effluents is particularly of high-priority to alleviate environmental concerns.

With regard to the paper and pulp mill effluents, the fatality induced to aquatic life forms owing to the disruption of carbohydrate metabolism, ion balance and biotransformation activity of enzymes has been well documented in the literature. In order to dilute such anomalies, several pretreatment methods for paper and pulp industrial effluents have been recommended in the literature (Kinnarinen et al., 2016; Kong et al., 2016; Shankar et al., 2014; Yunqin et al., 2010). Among them, thermochemical precipitation, advanced oxidation processes, adsorption, electrocoagulation and enzymatic pretreatment have been tested at the laboratory scale (Hakizimana et al., 2017; Koyama et al., 2017; Garg et al., 2005;

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Shankar et al., 2014; Liu et al., 2011). The pretreated paper and pulp discharge has also found application for biomethane production. For instance, Baba et al. (2013) reported a 2.6-time increase in methane yield using waste paper pretreated with rumen fluid. However, in recent years, several studies have focused on integrated pretreatment approaches, especially, by combining UV pretreatment to existing techniques (Jaafarzadeh et al., 2016, 2017).

Another industrial effluent that can cause mutagenicity to even the purest forms of water bodies is the petrochemical industry (Siddique et al., 2017; Salehi et al., 2014). Several pretreatment methods have been tested to mitigate the toxicity levels preceding its environmental discharge. The most widely reported pretreatment techniques for effluents from the petrochemical industry are ozonation (Wu et al., 2017a; Kameswari et al., 2011; De los Santos Ramos et al., 2009), coagulation (Wang et al., 2014; Verma et al., 2010; Hakizimana et al., 2017), photocatalytic degradation (Saïen and Nejati, 2007), filtration (Salehi et al., 2014; Ko and Fan, 2010) and adsorption (Shobana et al., 2017; Hakizimana et al., 2017). Electrocoagulation as a pretreatment option was studied by Garg et al. (2014) and it was found that under optimized conditions (pH - 8.2, pretreatment time - 180 min, current density - 125 A/m<sup>2</sup> and inter electrode distance - 1 cm), the chemical oxygen demand (COD) removal was 66%. Another interesting pretreatment method, i.e. the combination of fungi and bacteria for the degradation of 2-naphthalensulphonic acid polymers (2-NSAPs) from petrochemical wastewater (Gullotto et al., 2015), showed a COD removal of 62%.

It is noteworthy to mention that exploring the use of such pretreated wastes for direct consumption in other fields is of extreme interest for creating circular economy within different industries. For instance, purified terephthalic acid wastewater has been investigated for its ability to be used as a suitable substrate for biohydrogen production (Zhu et al., 2010). Recently, a pretreatment strategy that combines ultrasonication and microwaves to enhance biomethane production was reported by Siddique et al. (2017). Li et al. (2017a) adopted a one-step carbonization and ZnCl<sub>2</sub> activation pretreatment to fabricate a novel polymer binder-free nanocomposite based electrode using waste activated biological sludge from petrochemical industries and this product was reported to have widespread applications in energy storage.

Moreover, the use of a wide range of chemicals and dyes in the textile industry adds to the complex and variable characteristics of its discharge, thereby necessitating the implementation of adequate pretreatment strategies. Such complex industrial outflows usually interfere with the photosynthesis of plants and marine life forms (Ezechi et al., 2015) and also causes cancerous effects on animals and humans (Almasian et al., 2015). Different pretreatment approaches have been tested for the removal of dyes from aqueous solutions, namely electrochemical treatment (Basha et al., 2012; Haque et al., 2015), coagulation and flocculation (Hakizimana et al., 2017; Liang et al., 2014; Wei et al., 2015), photocatalytic oxidation (Kernazhitsky et al., 2015) and adsorption (Tan et al., 2015).

Recently, advanced oxidation processes (AOP) that has the potential to generate hydroxyl radicals have been shown to intensify the decolorization of textile effluents (Jorfi et al., 2016). The effective removal of the contaminants from wastewaters offers the advantages of reusability and procurement of valuable elements from such textile effluents (Koseoglu-Imer, 2013; Bhaskar Raju et al., 2009).

Despite its inevitable role in energy generation, the coal industries have effectively implemented different pretreatment methods for its effluents. One of the predominant emission from coal manufacturing namely the fly ash, contains high amount of heavy metals which necessitates pretreatment in order to prevent its leaching into the groundwater (Blissett and Rowson, 2012; Chen

et al., 2008; Hsu et al., 2008). In this regard, the pretreatment of fly ash with hydrogen peroxide and carbonation (Ecke et al., 2003) to immobilize the heavy metals has been reported. Moreover, coal gasification wastewater that is poorly biodegradable has also been subjected to several pretreatments, among which the acid/alkali method is most commonly used at the industrial scale (Koyama et al., 2017; Lin et al., 2009). Additionally, the conversion of coal industrial waste for an array of applications such as zeolite synthesis (Iyer and Scott, 2001), CO<sub>2</sub> capture (Arenillas et al., 2005) and the manufacture of adsorbents (Hsu et al., 2008) have been attributed to the selection of a suitable pretreatment method. Current research shows a shift to the application of more integrated approaches utilizing biologically pretreated coal gasification wastewater for advanced wastewater treatment processes (Hou et al., 2016; Xu et al., 2015).

The incremental uptake of drugs in recent times has often led to bulk production of pharmaceuticals and as a consequence, an increase in their proximity to aquatic life forms. Several toxicity studies have reported the acute and chronic toxicity of wastewater from the pharmaceutical industry to algae, fish, daphnia and bacteria. In order to overcome such ill effects, pretreatment methods have been adopted to minimize the effects due to hazardous pollutants from pharmaceutical industries. Some of the pretreatment methods are Fenton oxidation, wet-air oxidation, coagulation/flocculation and filtration (Hakizimana et al., 2017; Wang et al., 2012; Tekin et al., 2006; Torres et al., 1997). Qiu et al. (2011) reported wet air oxidation as a pretreatment for fosfomycin pharmaceutical wastewater and recorded a 99.9% phosphate recovery along with a surge in the biodegradability ratio, i.e. BOD<sub>5</sub>/COD from 0 to >0.5. Besides, cephalosporin bacterial residues have been examined for its potential for biomethane production via thermo-alkaline pretreatment (Li et al., 2017b). The results obtained from that study proved the capacity of pretreated wastewater (6% NaOH at 105 °C for 15 min) for renewable energy generation owing to a ~255% increase in yield in comparison to that of the un-treated waste.

The aim of this review is to provide a holistic view on the beneficial aspects of pretreatment in five major industries, namely the paper and pulp mills, coal manufacturing facilities, petrochemical, textile and the pharmaceutical industry. The argument for such a preference are based on the aforementioned toxic effects caused by the effluents of these highly polluting industries. Moreover, a comprehensive knowledge of the different pretreatment methods is crucial in order to comply with effluent discharge standards and at the same time to seek possible benefits by enhancing its applicability. Anew, the characteristics of the pretreatment methods and its subsequent role in renewable energy production have also been discussed with certain propositions for large-scale implementation. Such an exclusive analysis over the dominant industrial sectors will facilitate the integration of pretreatment technologies with conventional wastewater treatment plants for resource recovery.

## 2. Importance of key industrial sectors

Several industrial establishments produce benefits for the society, yet they also contribute to certain baleful effects. In this regard, among the five selected industries, the products from the paper and pulp industries contribute the most in our day to day lives. The utilization of products from these industries is of personal importance for the manufacture of vital commodities such as newspapers and books. It is one of the key industry that consumes large quantities of natural cellulosic resources and the manufacture of pulp, paper and paper products ranks among the world's largest industries (De los Santos Ramos et al., 2009). Secondly, energy

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