JOURNAL OF ENVIRONMENTAL SCIENCES XX (2017) XXX–XXX

Available online at www.sciencedirect.com
ScienceDirect
www.elsevier.com/locate/jes

ELSEVIER

JES
JOURNAL OF ENVIRONMENTAL SCIENCES
www.jesc.ac.cn

Pre-treatment of pyridine wastewater by new cathodic–anodic-electrolysis packing

*Yang Jin, Qinyan Yue**, *Kunlun Yang, Suqing Wu, Shengjie Li, Baoyu Gao**, *Yuan Gao*

Shandong University, Jinan 250100, China

ARTICLE INFO

Article history:
Received 5 November 2016
Revised 24 February 2017
Accepted 27 February 2017
Available online xxxx

Keywords:
Cathodic–anodic-electrolysis packing
Pyridine wastewater
pH
Hydraulic retention time
Air–liquid ratio
Initial concentration

ABSTRACT

A novel cathodic–anodic-electrolysis packing (CAEP) used in the treatment of pyridine wastewater was researched, which mainly consisted of 4,4′-diamino-2,2′-disulfonic acid (DSD acid) industrial iron sludge. The physical properties and morphology of the packing were studied. The CAEP was used in a column reactor during the pretreatment of pyridine wastewater. The influence of pH, hydraulic retention time (HRT), the air–liquid ratio (A/L) and the initial concentration of pyridine were investigated by measuring the removal of total organic carbon (TOC) and pyridine. The characterization results showed that the bulk density, grain density, porosity and specific surface area were 921 kg/m^3, 1086 kg/m^3, 43%, and 29.89 m^2/g, respectively; the removal of TOC and pyridine could reach 50% and 58% at the optimal experimental conditions (pH = 3, HRT = 8 hr, A/L = 2). Notably, the surface of the packing was renewed constantly during the running of the filter, and the handling capacity was stable after running for three months.

Introduction

Pyridine, a type of heterocylic compound, is a chemical raw material (Zhao et al., 2011). Pyridine has been widely used in cooking, chemical synthesis, pharmaceutical, and pesticide industries, and so on (Sun et al., 2011; Wen et al., 2013). Compared with other aromatic hydrocarbons, pyridine is more difficult to degrade (Li et al., 2016). As a refractory organic nitrogen heterocyclic compound, pyridine's derivatives mainly include alkyl pyridines, halogenated pyridines and amino-pyridines, which have been widely used as industrial solvents, agriculture herbicides and pesticides (Shen et al., 2015). Pyridine causes stench, nerve toxicity, and serious damage to the cornea (Li et al., 2014). With the rapid development of the economy and chemical industry, pyridine has become a common organic pollutant which can cause serious damage to human health. Because pyridine has high volatility and solubility in water, pyridine wastewater is produced during the process of production and application of pyridine and its derivatives. This kind of wastewater is highly concentrated and refractory to biodegradation.

According to the currently utilized technologies, pyridine wastewater can be treated by coagulation, adsorption, chemical oxidation, Fenton oxidation, photocatalytic oxidation, and direct incineration methods (Bai et al., 2010; Tian et al., 2013). However, coagulation and adsorption methods cannot remove the pyridine-class pollutants effectively. Although chemical oxidation methods can remove COD, the degradation efficiency for pyridine is too low, and these methods also result in secondary pollution. Fenton oxidation may oxidize recalcitrant pollutants and refractory organics in the chemical oxidation process. Unfortunately, the Fenton reagent method

* *Corresponding authors*. E-mails: qyyue58@aliyun.com (Qinyan Yue), baoyugao_sdu@aliyun.com (Baoyu Gao).

http://dx.doi.org/10.1016/j.jes.2017.02.016
1001-0742/

has some shortcomings, such as high-cost reagents, complex processes, large amounts of waste residues, and inevitable secondary pollution. Photocatalytic oxidation processes have been widely developed as a new research field in the past decade. However, the related research is still in the experimental stage, and few photocatalytic oxidation processes have been applied in practical industrial operations (Qiao and Wang, 2010). Accordingly, the most important purpose of the current study is to find an effective method to solve the problem of pyridine wastewater treatment. This research offers new approach using micro-electrolysis technology for the pretreatment of pyridine wastewater.

Micro-electrolysis technology, also referred to as internal electrolysis, is a kind of novel reaction based upon an electro chemical mechanism, which was acknowledged in China in 1980s (Liu et al., 2012; Ning et al., 2015). It is based on the primary battery between Fe^0 and carbon (C). During the reaction of the primary battery, Fe^0 acts as the anode, losing electrons, and C as the cathode, where H^+ gains electrons. The working mechanism of micro-electrolysis technology is the following: (1) the reduction of Fe^0 and evolution of new [H^0]; (2) the flocculation of $Fe(OH)_x$ produced by the reaction; (3) the sedimentation of cathodic–anodic-electrolysis products; (4) adsorption by the packing.

According to recent research, micro-electrolysis technology has been chosen by more and more industries in the water treatment process, such as for electroplating wastewater, petrochemical industry wastewater, printing and dyeing wastewater, and other industry wastewater that is hard to degrade. The structure of many organic pollutants can be degraded during the micro-electrolysis treatment process, while some biological methods are not able to accomplish this. This treatment could increase the ratio of BOD_5 to COD_{Cr} (B/C) in wastewater, which is helpful for subsequent biological treatment, enabling treated wastewater to reach the national discharge standard (Li et al., 2008; Luo et al., 2014; Ying et al., 2012b; Zhang et al., 2015). In the conventional micro-electrolysis reaction, the contact area between the wastewater and the packing could be decreased during operation due to hardening of the packing during the working process, which reduces the treatment efficiency toward contaminants. What's more, this hardening also suspends the micro-electrolysis reaction (Lai et al., 2013; Ruan et al., 2010; Ying et al., 2012a; Zhang et al., 2014). As a consequence, development of a novel kind of unhardened cathodic–anodic-electrolysis packing is urgently needed (Wang et al., 2013).

Iron sludge produced during chemical production processes is a hazardous waste. There are many kinds of iron sludge, and 4,4′-diamino-2,2′-disulfonic acid (DSD acid) iron sludge is one of them. According to the requirements for the treatment of hazardous waste, the iron sludge must be transported to a hazardous waste disposal center to be safely solidified and landfilled. In recent years, some research on the treatment and re-use of iron sludge has been carried out. One idea has been to recover the iron content for iron-making. Even though this method is cheap, there are often many organics in iron sludge that can impact the quality of iron. In another development, iron sludge was used as the raw material of pigment. However, the related production process is very complex. In addition, some researchers have used iron sludge to produce inorganic salts and nanomaterials, which is not efficient. Even though these studies provide some ideas for the treatment of the iron sludge, the processes would be difficult to achieve during actual production. Most of this research involves Fenton iron sludge. DSD acid industrial iron sludge is generated during the production process of DSD acid. The DSD acid industrial iron sludge is rich in iron because the iron serves as a catalyst during the production process of DSD acid. What's more, the DSD acid industrial iron sludge also contains many organics. Therefore, the DSD acid industrial iron sludge is not only a hazardous waste but also a potential resource. Research on the treatment of DSD acid industrial iron sludge has been rare.

The current study used the iron and organics in DSD acid industrial sludge to produce micro-electrolysis packing. The iron and organics were transformed into Fe^0 and C by pyrolysis, the Fe^0 and C served as the raw materials for the micro-electrolysis packing. Then the packing was used to treat refractory organic wastewater, which not only achieved reuse of the DSD acid industrial sludge and realized resource recovery, but also accomplished the aim of treating waste with waste. In recent years, many granular packing materials consisting of sewage sludge and solid pollutants have been studied: for example, using novel ceramic particles consisting of sludge and fly ash in the treatment of synthetic wastewater (including glucose, soluble starch, sodium acetate trihydrate, ammonium sulfate, peptone, potassium biphosphate) (Han et al., 2009); utilizing ultra-lightweight ceramics fabricated from sewage and clay (Qi et al., 2010); using ceramic-corrosion-cell fillers made from clay and sewage sludge in the treatment of cyclohexanone industry wastewater (Wu et al., 2011); and using micro-electrolysis ceramic packing that consisted of clay, scrap iron, and powdered activated carbon in the treatment of acrylonitrile wastewater (Huang et al., 2016). In the current study, a novel kind of cathodic–anodic-electrolysis packing made from DSD acid industrial iron sludge and clay was produced using pyrolysis technology.

This novel packing has improved adsorption ability because of its porosity. On the other hand, this packing is good at avoiding the problem of hardening in the operation of the cathodic–anodic-electrolysis process due to the renewal of the surface during use. Importantly, all of materials utilized are waste products. Additionally, the use of DSD acid industrial iron sludge technology could reduce the amount of iron powder needed due to its high iron content, making it much cheaper than other materials. A simple and easy operation process with low secondary pollution could be obtained by using a column reactor (Chen et al., 2011; Huang et al., 2013). This method not only achieved the recycling of clay and industrial iron sludge, but also provided a novel method and material for the pretreatment of pyridine wastewater. The crucial factor in the production process of this packing is maintaining the proper intensity. In this case the iron can be consumed during the process of treatment of wastewater, which destroys the structure of the surface of packing; as a consequence, the surface layer of the packing is shed and the surface of packing is continuously renewed. This characteristic can delay the hardening of the packing and improve the back-washing process effectively. Thus, the problem of hardening and channeling was solved and the effectiveness

Please cite this article as: Jin, Y., et al., Pre-treatment of pyridine wastewater by new cathodic–anodic-electrolysis packing, J. Environ. Sci. (2017), http://dx.doi.org/10.1016/j.jes.2017.02.016