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Electrochemical oxidation of pulp and paper making wastewater assisted by transition metal modified kaolin

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Abstract

The electrochemical oxidation of pulp and paper making wastewater assisted by transition metal (Co, Cu) modified kaolin in a 200 ml electrolytic batch reactor with graphite plate as electrodes was investigated. H_2O_2, which produced on the surface of porous graphite cathode, would react with the catalysts to form strong oxidant (hydroxyl radicals) that can in turn destruct the pollutants adsorbed on the surface of kaolin. The transition metal (Co, Cu) modified kaolin was also characterized by XRD and SEM before and after the modification and the results showed that the transition metals were completely supported on kaolin and formed a porous structure with big BET surface. The mechanism was proposed on the basis of XPS analysis of the catalyst after the degradation process. Series of experiments were also done to prove the synergetic effect of the combined oxidation system and to find out the optimal operating parameters such as initial pH, current density and amount of catalyst. From the results it can be founded that when the initial pH was at 3, current density was 30 mA cm^{-2}; catalyst dose was 30 g dm^{-3}, COD (chemical oxygen demand) removal could reach up to 96.8% in 73 min.

Keywords: Electro-catalysis; Pulp and paper making wastewater; Modified kaolin

1. Introduction

Water is used extensively in the paper and pulp making industry in wood preparation, digester house, pulp washing, pulp bleaching and paper making [1]. One of the main characteristics of the wastewater discharge from the pulp and paper making industry is the high load of organic materials, such as organic sulfur compounds, pulping chemicals, organic acids, chlorinated lignins, resin acids, phenolics, unsaturated fatty acids, terpenes, etc. [2,3]. The pulp and paper making industries produce wastewater with high organic compounds and refractory organics that is not completely removed by physiochemical preliminary treatment (i.e., coagulation/flocculation and sedimentation) or biological processes (i.e., anaerobic and aerobic attack) [4–6]. In China, the pulp and paper industries accounts for a major portion of wastewater generation. However, small paper making mills do not have satisfactory and adequate wastewater treatment facilities and are a cause of serious environmental concern.

Many researches [7,8] have demonstrated that the new advanced oxidation technologies, which are based on the in situ formation of OH radicals, have been successfully applied to the complete mineralization of different kinds of organic compounds that come from the lignin degradation. Among them, electrochemical technologies used to treat various wastewaters have been extensively investigated, research works have been focused on the efficiency in oxidizing various pollutants on different electrodes, improvement of the electrocatalytic activity and electrochemical stability of electrode materials. Until now, many works have been done to develop high performance anodes in respect of high catalytic activity, long life, etc. including glassy carbon electrode [9], carbon felt [10], Pt/Ti and graphite [11]. However, the use of electrochemical treatment for the removal of soluble and colloidal organics from pulp and paper mill effluents has not been investigated so far.

Catalytic electrochemical oxidation of wastewater has been extensively studied so far. Most of the degradation processes were conducted in aqueous phase using porous graphite cathode in the presence of Fe^{2+} to form an electro-Fenton system. Others like anodic oxidation, also called electrochemical incineration, are using the adsorbed hydroxyl radicals ($OH^{\bullet}$) that formed on

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the anode surface to destroy organics. Hydroxyl radicals is a very powerful oxidizing agent that react with organics giving dehydrogenated or hydroxylated derivatives, until achieving their complete mineralization. Nowadays a single process alone may not be adequate for the treatment of all various organic compounds. Electrochemical remediation of various wastewaters combined with activated carbon adsorption [12], photo-catalysis [8] have been reported recently.

Transition metals modified kaolin as catalyst used in the electrochemical system is a new and effective approach in our previous studies when treating the oil produced water and anionic surfactants wastewater [13–15]. Kaolin, traditionally used to stabilize heavy metals [16] and catalyze organic reactions [17], was rarely reported to catalyze degradation of wastewater in electrochemical systems.

In this paper, the combined electro catalytic oxidation of pulp making wastewater in the presence of Cu_2O–CoO–PO_4^{3-} modified kaolin was investigated. Two processes are involved in the whole degradation process: catalysts' adsorption and synergetic oxidation process. By adsorption process, pollutants can be immediately adsorbed on the catalyst due to its high BET surface and porous structure. By combined electrochemical oxidation process, strong oxidants produced through decomposition of electro-generated H_2O_2 can destruct organic pollutants and convert them into CO_2 and H_2O. Near carbon anode, the evolution of O_2 with high yields can immediately reduced on the porous graphite cathode to form H_2O_2:

$$2H_2O - 4e^- \rightarrow O_2 + 4H^+ \quad (1)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$

In the presence of transition metal modified kaolin, oxidant formation is as follows: (M: Cu^+, Co^{2+})

$$H_2O_2 + M^{n+} \rightarrow M^{(n+1)+} + HO^\bullet + OH^- \quad (3)$$

$$H_2O_2 + M^{(n+1)+} \rightarrow M^{n+} + HOO^\bullet + H^+ \quad (4)$$

Table 1
Selected properties of raw wastewater

Characteristics	Value
pH	13.5
COD (mg/l)	1669.7
BOD (mg/l)	460
BOD/COD ratio	0.27
Total solids (mg/l)	1860
Suspended solids (mg/l)	40
Dissolved solids (mg/l)	1790
Chlorides (mg/l)	0.112–10,121
Conductivity (μs/cm)	870
Color (platinum cobalt units, PCU)	290
Turbidity (NTU)	120

This process is similar to the electro-Fenton process. However, in the Fe^{2+} existed homogeneous aqueous phase, electro-generated H_2O_2 can diffuse onto the anode forming O_2:

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e \quad (5)$$

The aim of this work is to study the conjunctional effect when integrating the catalyst (modified kaolin) into the electrochemical system and find out the optimal operating parameters in treating the pulp and paper making wastewater.

2. Materials and methods

2.1. Materials

All chemicals used in the experiment were analytically pure reagent.

The wastewater used in this study was collected from Kraft cooking section of an agri-based paper mill, which manufactures Kraft paper with wheat straw as the raw material. The wastewater was characterized for BOD, COD, pH, total solids, suspended solids, dissolved solids and color using the standard methods [18] and the data can seen in Table 1. The used wastewater was

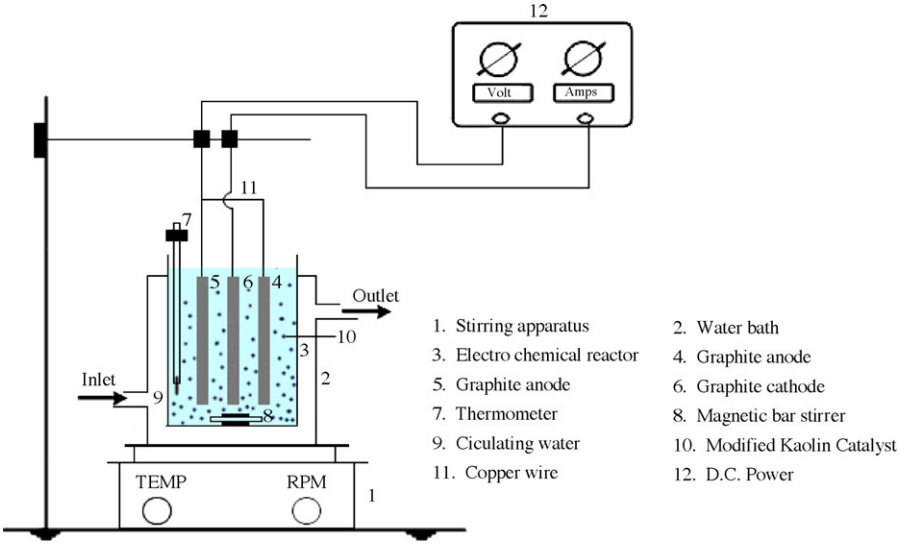

Fig. 1. Schematic diagram of experimental setup.