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.
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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[•]) 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:

$$2H_2O - 4e^- \rightarrow O_2 + 4H^+ \tag{1}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{2}$$

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

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

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

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:

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e \tag{5}$$

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
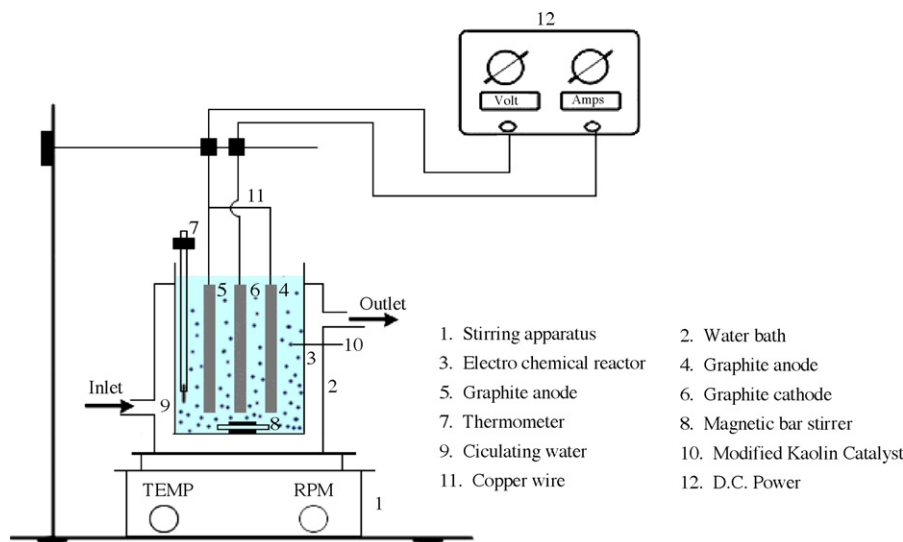

Fig. 1. Schematic diagram of experimental setup.

made alkaline or acid by the addition of sodium hydroxide and sulphuric acid, respectively.

2.2. Electrolysis system

Fig. 1 shows the schematic diagram of the experimental apparatus. The experiments were conducted by batch process using undivided cell of 200 ml capacity under constant temperature conditions. Electrodes were served by porous graphite. The anode and cathode were positioned vertically and parallel to each other with an inner gap of 0.5 cm. The superficial surface of the working electrode (3.2 cm × 6 cm) was 19.2 cm^2. 30 g dm^{-3} smashed catalyst was added into the system to form an oxidizing electrochemical reactor. The solution was constantly stirred at 200 rpm with a magnetic stirrer in order to maintain uniform concentration of the electrolyte solution. The electric power was supplied with regulated dc power supply, WYK302b, Xi'an, China.

2.3. Analytical method

All the experiments were carried out in duplicate and analysis of each parameter was done in triplicate for each run. The coefficient of variation obtained was not more than 5% for the three determinations and for the experiment runs carried out in duplicate. The initial pH of the solution was measured using an Orion 290 pH meter. COD was chosen as a parameter in order to evaluate the process of oxidation and was determined according to standard methods for the examination of water and wastewater. And the concentration of H$_2$O$_2$ accumulated in the system was obtained by titration with KMnO$_4$. BET surface area of the catalyst was measured via the N$_2$ sorption method using a Quantachrome Autosorb Automated Gas Sorption System. The crystallinity of the catalyst was determined by powder X-ray diffraction (XRD) D/Max-3c model (Rigaluc, Jp) using a scanning diffractometer of D/MAX-RA with Ni-filtered Cu Kα radiation (λ = 1.5406 Å). Solid morphology and average crystal size were determined by scanning electron microscopy (SEM, Quanta 200, Holland) and a gold film was sputtered onto the sample prior to observation (ISI DS-130). X-ray photoelectron spectroscopy (XPS) was carried out to analyze the chemical state of the surface elements for the catalysts. PHI ESCA 5700 instrument, with a Al Kα X-ray source (1486.6 eV) and pass energy of 29.5 eV operating at a pressure of 7 × 10^{-10} Torr, was used. Cobalt and copper ions that leaching from the catalyst were measured using Perkin-Elmer inductively coupled plasma-atomic emission spectroscopy (ICPAES).

3. Catalyst preparation and analysis

3.1. Catalyst preparation

The Cu$_2$O–CoO–PO$_4$$^{3-}$ modified kaolin was prepared as follows: adding 50 g Cu(NO$_3$)$_2$, 20 g Co(NO$_3$)$_2$ and 50 g Na$_3$PO$_4$ into 250 ml distilled water (pH 7.1), 10 ml H$_3$PO$_4$ was added to dissolve nitrate salt of metal (Cu, Co), then the solution pH was adjusted with NaOH solution to a neutral conditions. Two
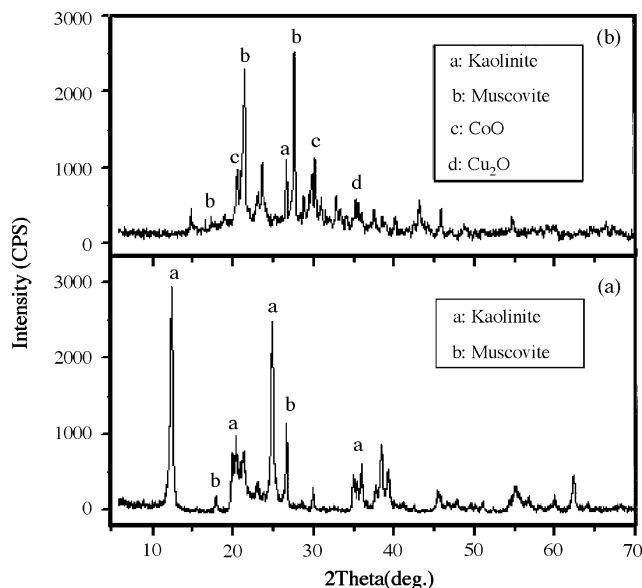

Fig. 2. XRD patterns of neat (a) and modified kaolin (b).

hundred grams of kaolin powder, which was used as support, was impregnated into the solution with mechanical stirring in a water bath at 50 °C for 4 h. After that, the solution was aged at room temperature for 48 h and filtrated, washing, the deposit was dried at 100 °C for 4 h. To immobilize the metals, the prepared dried slurry was sent to calcine at 600 °C.

3.2. XRD pattern of neat and modified kaolin

The patterns of XRD for the neat kaolin and modified kaolin are shown in Fig. 2. Two diffraction peaks that related to kaolinite and muscovite can be clearly observed in Fig. 2(a), the presence of peaks as an attributive indicator of kaolinite and of muscovite is detected. Two common trends can be seen in contrast of Fig. 2(a) and (b): first, the intensity of the peaks characteristic of kaolinite decreases at 600 °C, which indicates the stable Al–O octahedron structure in neat kaolin has broken and the losses in crystallinity and the structural deformation. Meanwhile, the characteristic peak for muscovite has been strengthened; Co and Cu related species can be also clearly seen in Fig. 2(b).

3.3. SEM analysis of neat and modified kaolin

The morphology of Cu$_2$O–CoO–PO$_4$$^{3-}$ modified kaolin examined by SEM and representative photographs were shown in Fig. 3. It can be observed that the previous flaky structure of neat kaolin (seen in Fig. 3(a)) has changed into granular structure through the modification process; intercalation of Cu$_2$O–CoO–PO$_4$$^{3-}$ into kaolin has resulted in an increase in the stacking disorder of the kaolin. After the modification and calcinations, the layer bonds of neat kaolin are broken, which lead to more micro-sized particles and pored structure (seen in Fig. 3(b)) has formed. This was consistent with the results of that the enlarged BTE surface of modified kaolin (38 m^2 g^{-1}) compared with the neat kaolin (20 m^2 g^{-1}).
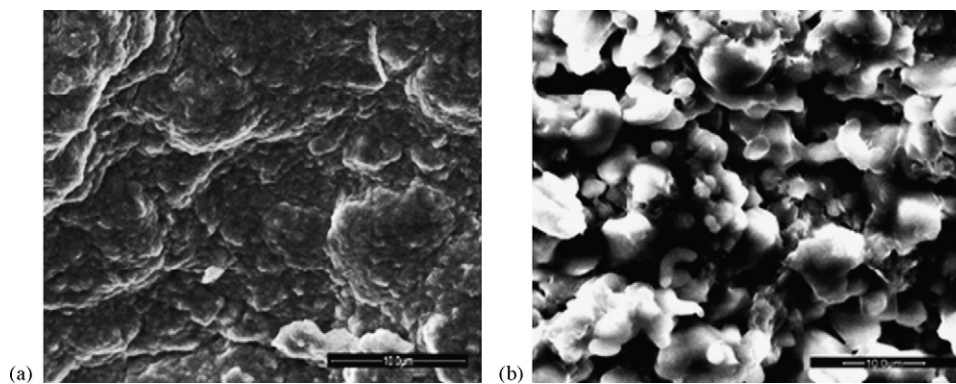
Fig. 3. Morphologies of neat (a) and modified kaolin (b) by SEM (magnification 1500×).

4. Results and discussion

4.1. Synergetic effect

In the presence of catalyst (modified kaolin), organic pollutants can be degraded by electrolysis and removed by adsorption. To evaluate the feasibility of adding catalyst into the electro-catalysis process, the efficiencies of COD removal by only modified kaolin, electro-catalysis and their combined process were compared in the same reactor, respectively. Effect of kaolin's adsorption was performed at the same conditions except the absence of current. The tendency of COD value variation during the whole electrolysis, adsorption process and combined processes in the first 73 min was shown in Fig. 4. It can be seen that COD was removed by catalyst adsorption more rapidly than that of by electro-catalysis. Such a combined process obtained a 96.8% COD removal compared with 56.7% and 30.9% COD removal in catalyst adsorption process and electrochemical process, respectively. However, the two processes were not environmentally equivalent due to the accumulation of unconverted contaminants on the solid phase by adsorption. Moreover, the whole combined process is a mass transfer process and its COD

removal rate may depend on the stirring speed, particle size and also the solution conditions.

Fig. 4 also shows the specific energy consumption (SEC) as a function of electrolysis time. The SEC is defined as the amount of energy consumed per unit mass of COD removal, expressed in kW h kg of COD removal and is given as

$$\text{energy consumption} = VIt/\Delta\text{COD} \tag{6}$$

It was found that SEC was the highest when no catalyst was added to the solution. A significant reduce in SEC was observed when 10 g catalyst was added into the electrochemical system. Compared with pure EC process, SEC was reduced in the combined process from 23 to 8.48 kW h (kg of COD removed)$^{-1}$ in 65 min, which indicated that the introduction of modified kaolin can both improve the degeneration speed and reduce the consumption cost. This may bring a certain industrial application prospect.

4.2. Influence of initial pH values

Since the pH of the solution plays a very important role in influencing the electrochemical processes (such as the concentration of electro-generated H_2O_2, oxidizing strength of $\cdot$OH radicals and the structure of organic compounds) the effect of the initial pH in the range of 3–10 has been investigated.

To evaluate the ability of system to accumulate H_2O_2 generated by the porous graphite cathode during reaction under different pH, electrolysis of 200 ml pulp mill wastewater was carried out with a cell voltage 10 V applied. From Fig. 5 it can be found that the concentration of H_2O_2 was higher when pH 3.0, but when the initial pH was adjusted to 10, the concentration of electro-generated H_2O_2 dramatically decreased. This lower steady concentration may be due to that the diffused oxygen can hardly get electrons in the alkaline solutions.

The pH value perhaps influences not only the processing capacity of the system but also the stability of organic compounds in the wastewater. In the experiments, a series of pulp mill wastewater of different pH were studied towards the stability and the degradation rate of COD. Observation of UV–vis spectra of the wastewater during 24 h shows that pulp mill wastewater possesses good stability in acidic environment at room temperature. Fig. 6 shows the influence of the initial pH on the COD removal
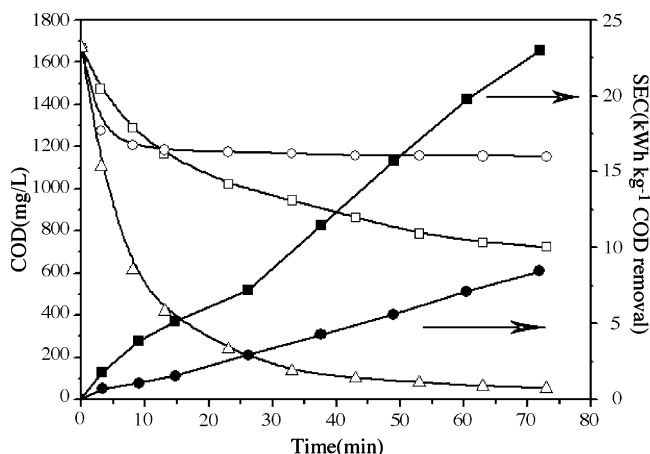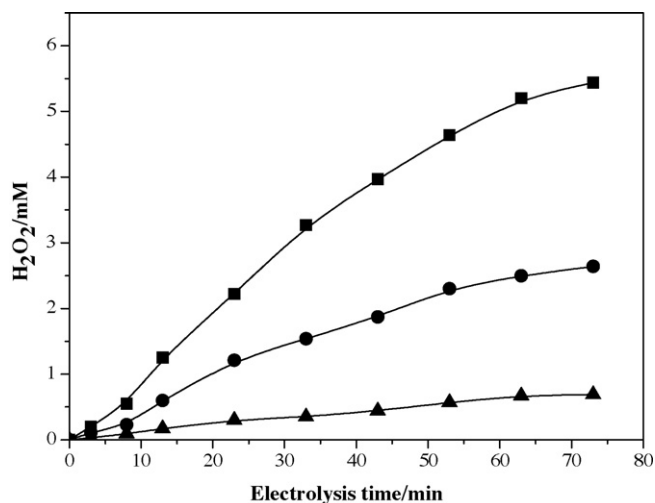

Fig. 4. Synergetic effects on COD removal and SEC variation in the combined process (□: catalyst adsorption process; ○: EC process; △: electro-catalysis combined process; ■: EC process; ●: electro-catalysis combined process (COD$_0$: 1669.7 mg dm^{-3}; cell voltage: 10 V; current density: 30 mA cm^{-2}; initial pH: 3)).

Fig. 5. Change of H_2O_2 concentration with time in the presence of Cu–Co-modified kaolin (■: pH: 3; ●: pH: 6.5; ▲: pH: 10).

rate and pH changes as the function of time during the oxidation of pulp mill wastewater in the combined electrolysis batch. The results were compared in terms of the time required for COD changes.

As can be seen from Fig. 6, the maximum COD removal efficiency (96.3%) was achieved when initial pH was 3, while the similar COD removal efficiency (95.7%) could also be achieved when pH was 5. The better effectiveness at pH 3.0 agrees with the fact that the maximum rate for $OH^\bullet$ generation from Eq. (3), inferred that the optimal pH operating condition should be in acid solutions, while the diffused oxygen may get electrons easily in this pH region. In alkaline solution, hydroxide, bicarbonate and carbonate can scavenge hydroxyl radicals [19]:

$$HO^\bullet + {}^-OH \rightarrow H_2O + O^{\bullet -} \qquad (7)$$

which influence the oxidizing property of the free radicals to degrade the organics K and the result was similar to our previous
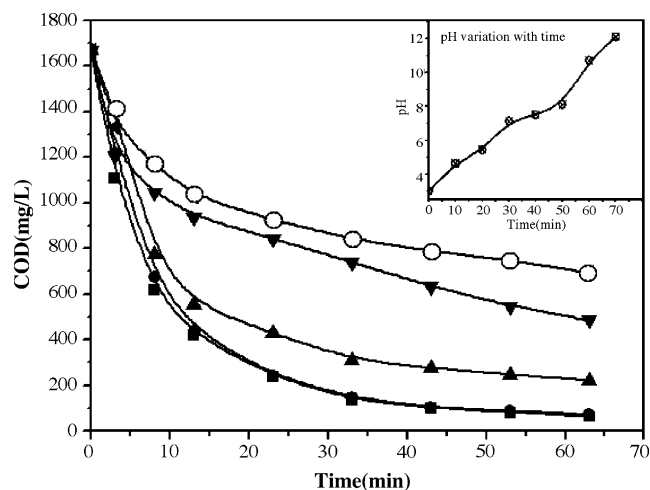

Fig. 6. Influence of initial pH on the evolution of COD (■: pH: 3; ●: pH: 5; ▲: pH: 6.5; ▼: pH: 8; ○: pH: 10) T: room temperature; cell voltage: 10 V; current density: 30 mA cm^{-2}.
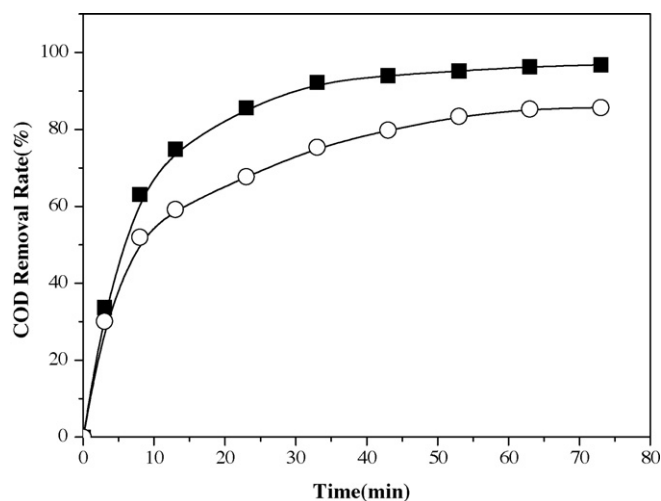

Fig. 7. Comparison of electro-Co–Cu-modified kaolin heterogeneous system (■) and electro-Co–Cu homogeneous system (○) on COD removal efficiency (COD_0: 1669.7 mg dm^{-3}; cell voltage: 10 V; current intensity: 30 mA cm^{-2}; initial pH: 3).

study [15] that the catalyst displays higher catalytic activity in the acid or moderate acid solutions.

Since the solution pH was not buffered, the pH may changes as the function of time elapsed and the results were shown in Fig. 6. With the time prolong pH elevated and the end pH was about 12 after 70 min treatment, which may be due to that H_2 produced resulted in pH value shifted to the alkaline region. Moreover, with pH elevated, the degradation rate obviously slowed down after 30 min treatment.

4.3. Comparison with homogenous Co and Cu combined system

To evaluate the effect of $Cu_2O–CoO–PO_4{}^{3-}$ modified kaolin in electrochemical system concerning the ability to degrade pollutants, the homogenous electro-Co–Cu combined system was applied. 30 g dm^{-3} $CoSO_4$ or $CuSO_4$ was added into the solution
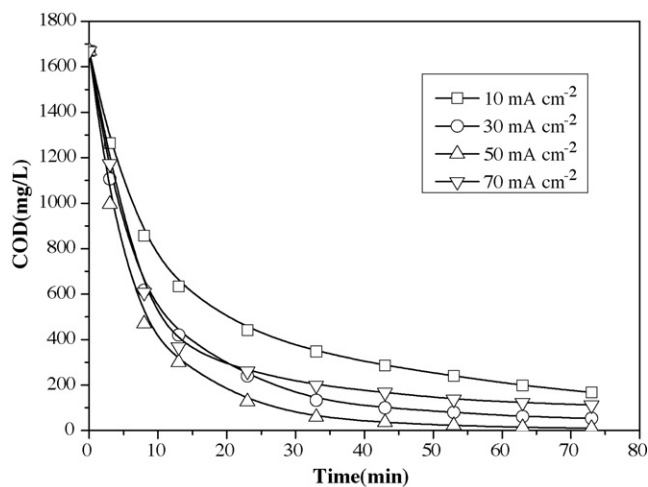

Fig. 8. Influence of applied current density on COD (T: room temperature; initial pH: 3).

instead of modified kaolin and the COD removal as the function of time in different electrochemical systems was shown in Fig. 7. It can be clearly seen that the COD removal rate was faster in electro-Co–Cu-modified kaolin combined heterogeneous system than that of in electro-Co–Cu catalyzed homogenous electrochemical system.

The multi-transition metals modified kaolin gains more advantages than Co–Cu catalyzed electrochemical system when treating pollutants in aqueous phase, this probably due to its ability to condense pollutants and electro-generated H_2O_2 onto its big surface and make the reaction more easily to occur. Moreover, because modified kaolin existed electrochemical system is heterogeneous; the adsorbed multi-metal compounds was stable and friendly environmental pollution, and the percentage of leaching metal ions less than 2 ppm was detected with plasma-atomic emission spectroscopy in the final treated wastewater.

4.4. Effect of current density on COD removal

The current density, a surrogate parameter, also influences the treatment efficiency of the electrochemical degradation processes. Therefore, the applied current density was varied ($10–70\,mA\,cm^{-2}$) to examine its effect on the COD removal (Fig. 8). As can be seen, current density varied in the region of $10–30\,mA\,cm^{-2}$ resulted in a faster COD removal, however, slow COD removal efficiency was observed when the current density varied in the region of $30–70\,mA\,cm^{-2}$. This result was consistent with the results that Mahesh had reported [20], which might be attributed to that the increase in the size of the emanating bubbles and these bubbles resulted in quick flotation of kaolin particles, lowering the chances of the pollutants interacting with the catalyst. Furthermore, higher current density could bring high electric energy consumption and operating cost.

4.5. Effect of the amount of catalyst on catalytic activity

The influence of the amount of $Cu_2O–CoO–PO_4^{3-}$ was studied to analyze the relationship between the amount of catalyst and COD removal rate (Fig. 9). It was shown that COD degradation rate becomes faster with the increases of the amount of catalyst: when the catalyst dose reaches $30\,g\,dm^{-3}$, the variation of COD removal rate becomes unapparent. The reasons may be lie in that, when the catalyst reaches a certain amount, it will reach equilibrium with electro-generated H_2O_2, so the generation of $OH^\bullet$ was mainly determined by the concentration of H_2O_2. Moreover, because the whole degradation processes is mass transfer controlled, its COD removal rate may depend on stirring speed, particle size and also solution conditions. When the catalyst reaches a certain amount, the COD reduction rate may further influenced by other factors. Moreover, SEC was also analyzed as the function of the amount of catalyst.

As can also be seen, when the catalyst dose increases from 1 to $30\,g\,dm^{-3}$, the SEC reduces significantly from 20.10 to $10.54\,kW\,h\,kg^{-1}$ COD removal, energy consumption saved by 47.6% when operated for 73 min.
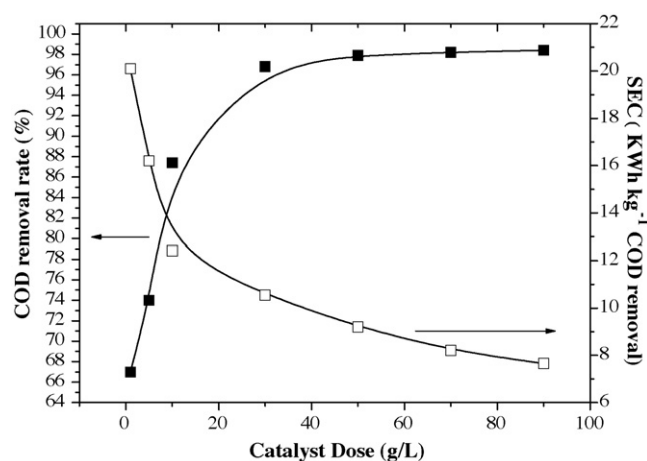

Fig. 9. Influence of the amount of catalyst on COD removal and energy consumption (T: room temperature; initial pH: 3; cell voltage: 10 V; current density: $30\,mA\,cm^{-2}$, 73 min).

4.6. XPS analysis of the catalyst after the reaction

XPS analysis was preformed to get a better understanding of proposed mechanism on the catalyst surface. Fig. 10 shows XPS survey spectra of the catalyst after the reaction. It can be seen clearly that Co, Cu and O peaks, including C species was involved, which can be explained the adsorption of pollutants on the catalyst.

Fig. 11 presents Co 2p and Cu 2p XPS spectra and their deconvolution curves, respectively. The normal binding energy of the Co, CoO and Co_2O_3 were 777.9, 780.6 and 779.4 eV, respectively, and the testing result was 781.0 eV, inferred that the valence of the cobalt was the mixture in the catalyst. The normal binding energy of the Cu, CuO and Cu_2O were 933.1, 933.8 and 932.6 eV, respectively, while the testing result was 932.8 eV, indicted that the valence of cuprum was also the mixture in the modified kaolin.

To understand the chemical state of cobalt and cuprum well, the deconvolution curves of the cobalt and cuprum was made to analyze their valence distribution. It can be seen from Fig. 11(c), the peaks at 780.5 and 779.3 eV are attributed to Co^{2+} and Co^{3+}, Co^{2+} accounted for the proportion of 69.49% while Co^{3+} accounted for 30.51%. Compared to Co^{2+} occupied 100% of the total cobalt element before the combined electrochemical
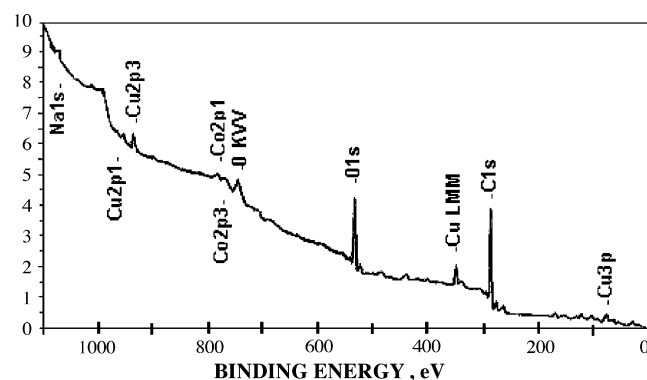

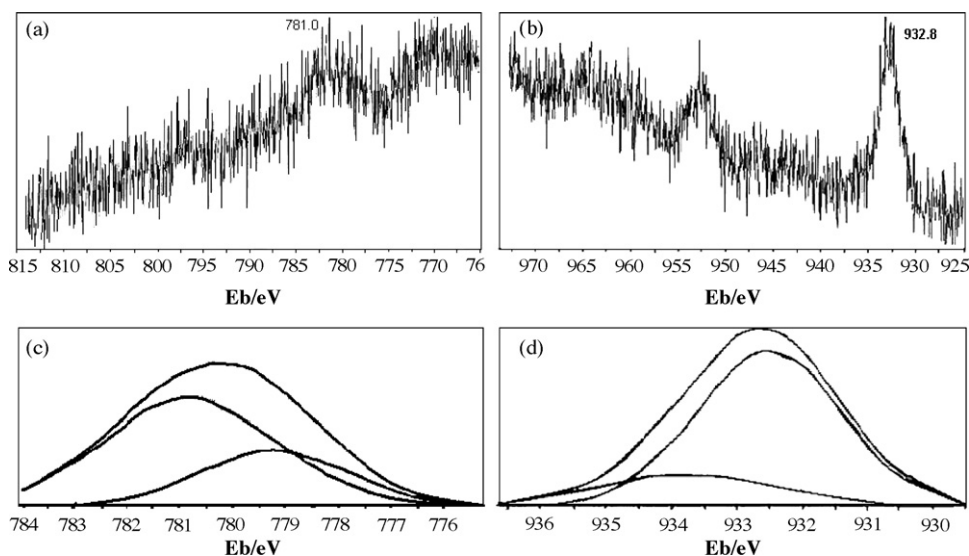Fig. 10. XPS spectra of modified kaolin after reaction.

Fig. 11. Binding energy of Co 2p$_{3/2}$ (a and c) and Cu 2p$_{3/2}$ (b and d) in the modified kaolin after the degradation process.

process, it can be concluded that CoO had been partly oxidized to Co$_2$O$_3$ via the decomposition of H$_2$O$_2$. Furthermore, from Fig. 11(d), previous existed Cu$^+$ in modified kaolin had changed into multi valence compound including Cu$_2$O and CuO, the peaks at 932.5 and 933.7 eV are attributed to Cu$^+$ and Cu^{2+}, Cu$^+$ accounted for the proportion of 79.72% while Cu^{2+} accounted for 20.28%. This means that Cu$_2$O–CoO–PO$_4$$^{3-}$ modified kaolin have good catalytic activity in the electrochemical degradation process.

5. Conclusion

The combined electro-catalysis of pulp mill wastewater assisted with Cu$_2$O–CoO–PO$_4$$^{3-}$ modified kaolin catalyst was performed in the single undivided cell. The morphology and phase structure of kaolin before and after modification were studied. Optimal operating conditions such as initial pH, current density were also studied. It was found that when the initial pH was 3, current density was 30 mA cm^{-2} and the catalyst dose was 30 g dm^{-3}, the COD removal rate can reach 96.8%. No significant increase in the COD removal was observed as the current density exceeded 50 mA cm^{-2}. The removal of organics from pulp mill wastewater might be attributed to strong oxidant that produced from the synergetic effect of between modified kaolin and electrochemical system.

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