Application of molybdenum and phosphate modified kaolin in electrochemical treatment of paper mill wastewater

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Abstract

Pulp and paper mill wastewater is characterized by very high chemical oxygen demand (COD) values that inhibit the activity of microorganisms during biological oxidations. The electrochemical degradation of pulp and paper mill wastewater catalyzed by molybdenum and phosphate (Mo–P) modified kaolin with graphite as anode and cathode was investigated. The catalyst was characterized by XRD, XPS and SEM spectra and the effects of pH, metal ion and introduction of NaCl on the efficiency of the electrochemical degradation process were also studied. It was found out that the modified kaolin loaded with Fe^{3+} had higher electrochemical catalytic activity in the electrochemical degradation of paper mill wastewater at pH 4. A 96% COD removal efficiency was obtained in 40 min of electrochemical treatment of the wastewater at current density $30 \, mA \, cm^{-2}$. A possible mechanism for degradation of the mill wastewater constituents was also proposed.
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1. Introduction

The pulp and paper industry is a water-intensive industry and consumes over $60 \, m^3$ of freshwater per ton of paper produced [1]. Wastewater from pulp and paper mills has high biochemical oxygen demand (BOD), chemical oxygen demand (COD) and turbidity. In addition, pulp and paper mill effluents contain variable amounts of lignin, sulphides, sulphates and chlorides that are toxic and non-biodegradable [2]. Consequently, a novel approach should be developed to face more stringent environmental regulations on the quality of effluent discharged into water bodies.

Many studies have been carried out on the treatment of pulp and paper mills wastewater, including biological treatment [3–5], wet oxidation [6,7], ozone treatment [8–11] and chemical coagulation [12–14]. However, in the biological processes, the lignin and its derivatives show high stability to degradation [15] and the inhibition potential of phenolics and the presence of other organic and inorganic are a major drawback of the process [16]. Wet air oxidation (catalytic and non-catalytic) has been found to reduce COD in a large extent. However, the energy requirement and the use of high-pressure reactors and associated equipment make the wet air oxidation of large volume of wastewater unviable and uneconomical [17]. Chemical coagulation, using alum, ferric chloride, ferric sulphate and lime have been studied [13,14]. As an option, electrochemical technologies can be efficiently applied to the treatment of wastewater containing organic pollutants and exhibits improved performance over conventional coagulation method. Compared with traditional flocculation and coagulation, electrochemical degradation has an advantage of removing even the smallest colloidal particles, because they have a greater probability of being coagulated due to the electric field that sets them in motion. It also has the advantage of producing a relatively smaller amount of sludge [18].

Nowadays, there is a remarkable reemergence of interest in the preparation of pillared layered materials [19,20]. It has been demonstrated that pillared mineral compounds have good properties, such as Al_{13}-pillared layered materials that exhibit high catalytic, absorption, ion-exchange properties [21]. Theoretically, the correct choice of the intercalated compound and the pillaring procedure and activation is essential not only for properly "cementing" the layers and therefore providing high mechanical and thermal stability, but also for generating active

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sites for uses [22–24]. Therefore, the application of pillared or modified mineral compounds derived from kaolin has aroused a lot of interests in new material synthesis.

The objective of this paper is to report on the study carried out on Mo–P modified kaolin materials, which highly reduces COD of the pulp and paper mill wastewater. The study synthesized and characterized the minerals and looked at the effect of pH, salts and different metal ions on electrochemical degradation in the paper mill wastewater.

2. Materials and methods

2.1. Materials

The chemical reagents used and kaolin, composed of $Al_4[Si_4O_{10}](OH)_8$ (surface area: $20\,m^2\,g^{-1}$ and pore volume: $0.5\,cm^3\,g^{-1}$), were of analytical grade and employed without further purification.

The effluents used in this research were supplied by Xi'An Wan Long paper mill, obtained from the equalization tank in the wastewater treatment plant and used without any pretreatment. The wastewater was maintained at $5\,°C$ to conserve its characteristics (Table 1).

2.2. Experimental set-up

The experiments were conducted with undivided cell of $500\,mL$ capacity with constant temperature of $25\,°C$. Two porous graphite electrodes were fixed vertically and parallel to each other with an inter gap of $1.0\,cm$. The true surface of graphite electrode ($3.2\,cm \times 6\,cm$) was $19.2\,cm^2$. Ten grams of catalyst was packed around the graphite electrode, forming a multi-phase electrochemical oxidation packed bed. Uniform concentration of the electrolyte was maintained by constantly stirring the solution at 200 rpm using a magnetic stirrer. Electric power was supplied by regulated DC power supply, WYK302b, Xi'An, China. Current and voltage were varied between 0 A and 2.5 A and 0–35 V, respectively.

2.3. Preparation of the catalyst

Mo–P modified kaolin catalyst was prepared as follows: into 30% (w/w) NaOH solution 0.02 mol $(NH_4)_6Mo_7O_{24}$ and 20% (w/w) NaH_2PO_4 solution were added with stirring at room temperature, then kaolin was added and stirred at $80\,°C$ for 4 h. The solution was allowed to age at room temperature for 24 h. The precipitate obtained was filtered, washed and dried at $105\,°C$ for 4 h, then calcined at $600\,°C$ for 4 h.

The prepared Mo–P modified kaolin was immersed into the same concentration ($0.2\,mol\,L^{-1}$) of ferric chloride solution, cobalt chloride solution or copper chloride solution for 3 h respectively, and then dried at $70\,°C$ for 4 h to obtain Mo–P-modified kaolin loaded with M^{x+} catalyst.

2.4. Characterization of the catalyst

The crystallinity of the catalyst was determined by powder X-ray diffraction (XRD) D/Max-3c model (Rigaluc, Japan) using a scanning diffractometer of D/MAX-RA with Ni-filtered Cu Kα radiation ($\lambda = 1.5406\,\text{Å}$). X-ray photoelectron spectroscopy of the catalyst loading metal iron before and after electrochemical oxidation process were recorded by an X-ray photoelectron spectrometer equipped with a Mg Kα (1253.6 eV) source. 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).

The initial pH of the solution was measured using an Orion 290 pH meter. COD was determined using a standard method [25].

3. Results and discussion

3.1. Characterization of the catalyst

3.1.1. XRD spectra

XRD patterns of original kaolin, Mo-modified kaolin, Mo–P-modified kaolin and Mo–P-modified kaolin loaded with Fe^{3+} after electrochemical process are shown in Fig. 1. It was found that the original kaolin consisted primarily of kaolin and a little amorphous component. However, the crystallinity of Mo-modified and Mo–P-modified product were relatively high and some new spatial lines were observed, which could be attributed to Mo or Mo–P modified structure formed in respect to the original kaolin. When kaolin was modified with molybdenum, a significant change occurred in that one band was spilt into two or three peaks between $20°$ and $30°$ were observed and the band between $30°$ and $40°$ weakened, and some new bands were observed. These indicated that a kaolin–Mo–kaolin structure has been formed. When kaolin was modified with molybdenum and phosphate, more intercalated structure of modified material was constructed between $10°$ and $30°$. While the structure of Mo–P-modified kaolin loaded with Fe^{3+} changed greatly, the peak at $10–20°$ almost disappeared and some bands between $20°$ and $30°$ were weakened. However, the structure of the catalyst maintained the primary structure of kaolin.

3.1.2. Morphology

The morphology of Mo–P modified kaolin examined by SEM and representative micrographs are shown in Fig. 2. It was observed that the morphologies of Mo–P modified product were different from that of the starting material and that a

Table 1
Characteristic of the pulp and paper mill wastewater

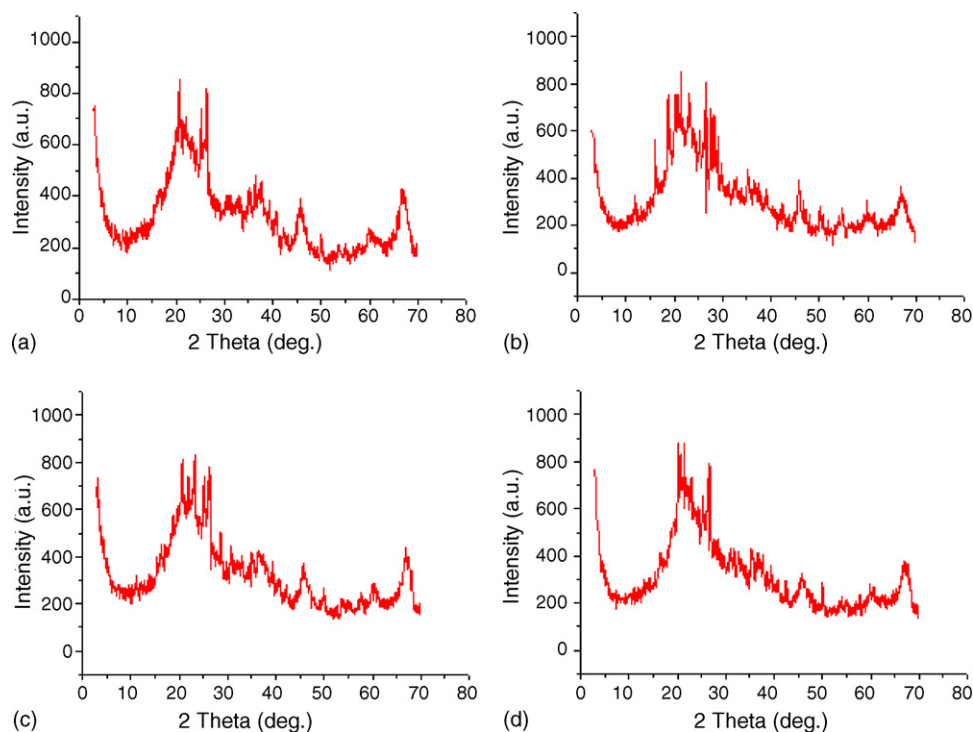| Characteristics	Value
pH	10.0
COD (mg/L)	1620
BOD (mg/L)	450
Total solids (mg/L)	1336
Suspended solids (mg/L)	280
Dissolved solids (mg/L)	1056

Fig. 1. XRD patterns of modified kaolin: (a) kaolin, (b) Mo-modified kaolin, (c) Mo–P-modified kaolin, and (d) Mo–P-modified kaolin loaded with Fe^{3+} after electrolysis.

porous structure with bigger surface was formed after the modification.

3.1.3. XPS spectra

Fig. 3 shows the X-ray photoelectron spectra of Mo–P modified kaolin loaded with Fe^{3+} after electrolysis. The spectra (a) showed the XPS signals of Mo 3d in Mo–P modified kaolin loaded with Fe^{3+} after electrolysis. In spectra (a), the band at 233.09 eV was attributed to Mo^{6+} (232.7 ± 0.2 eV), that combined with some organics, the band at 232.2 eV and 231.73 eV might be $Mo^{\delta+}$ ($5 < \delta < 6$), indicating that Mo is related with some organics. The binding energies at *ca.* 231.2 eV might correspond to Mo^{5+} species. The spectra (b) shows the XPS signals of Fe 2p in Mo–P modified kaolin loaded with Fe^{3+} after electrolysis. Three signals at about 708.6 eV, 710.9 eV and 713.1 eV are attributed to Fe^{3+}, Fe-modified kaolin, and Fe^{2+} combined with organics, respectively. The spectra (c) shows XPS signals

of O 1s in Mo–P modified kaolin loaded Fe^{3+} after electrolysis. The bands at 533.2 eV, 531.0 eV and 529.6 eV correspond to SiO_2, Al_2O_3, and MoO_3, respectively. The band at 532.1 eV and 527.9 eV could be attributed to O species of the organics adsorbed on the catalyst, indicating that the catalyst was involved with degradation of mill wastewater.

3.2. Application of the catalyst in the electrochemical degradation of pulp and paper mill wastewater

3.2.1. Influence of current density on the COD removal

The effect of current density on COD removal with time during oxidation of the wastewater catalyzed by modified kaolin loaded with Fe^{3+} at pH 4 was investigated. The COD removal at current density 10, 20, 30 and 40 mA cm^{-2} at 40 min were 65%, 89%, 95% and 96%, respectively, indicating a higher current density caused a faster COD removal. It was further noted
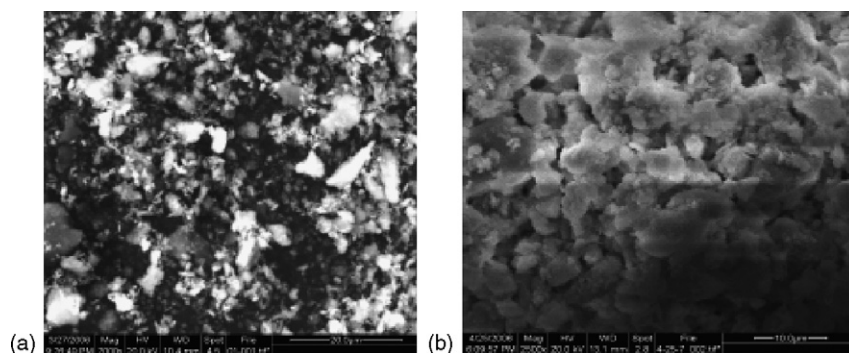

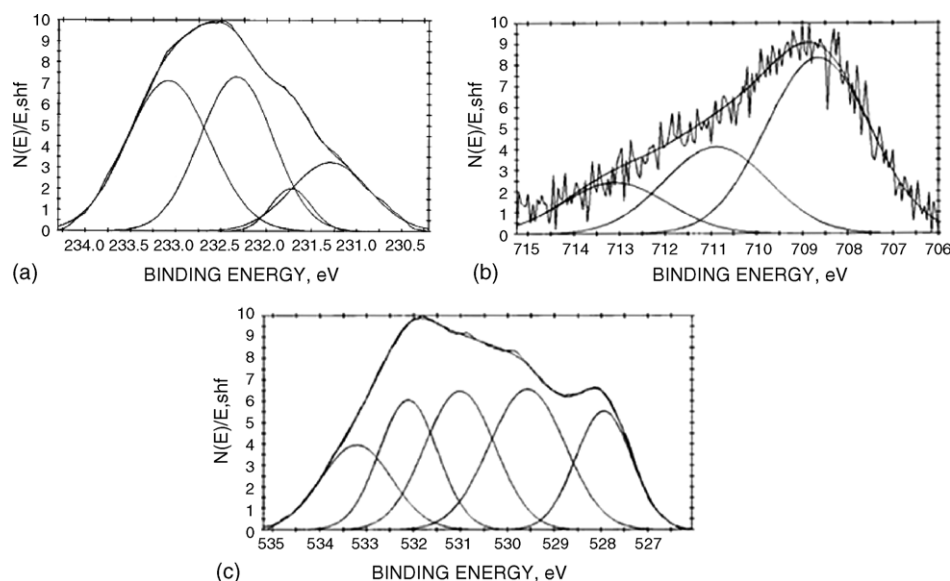Fig. 2. Solid morphology by SEM of (a) kaolin and (b) Mo–P modified kaolin.

Fig. 3. XPS spectra of Mo 3d (a), Fe 2p (b) and O 1s (c).

that there were minor differences in COD removal at the higher different current densities. Furthermore, higher current density causes high electrical energy consumption and operating cost. Therefore current density at $30\,\text{mA cm}^{-2}$ was chosen for the next experiment.

3.2.2. Effect of phosphate on COD removal

Fig. 4 shows the effect of phosphate in the Mo modified kaolin on the COD removal during the electrochemical degradation process with change in time at pH 7. The results were compared in terms of time required for COD changes. Within 40 min about 35% and 51% COD removal was achieved, when mill wastewater was catalyzed by Mo modified kaolin, and Mo–P modified kaolin respectively. This indicates that the Mo–P modified kaolin has higher catalytic activity in the electrochemical degradation of the mill wastewater. The probable reason for this is when P was introduced as catalyst, PO_4^{3-} replaced OH^-, and PO_4^{3-}

Fig. 4. Effects of phosphate and Fe ion on COD removal at pH 7 with time.

being a dispersing agent it highly changed the structure of kaolin [24].

3.2.3. Effect of Fe^{3+} ions on COD removal

Fig. 4 shows the effect of Mo–P modified kaolin loaded with Fe^{3+} on COD removal with time in electrochemical degradation of the mill wastewater at pH 7. The results were compared in terms of the time required for COD changes. A significant difference in COD removal was noted between the catalyst loaded (76%) and unloaded (51%) with Fe^{3+} within 40 min of the reaction. This phenomenon indicated that Fe^{3+} played a great role in the electrochemical degradation of mill wastewater. High COD removal efficiency of electrochemical process may be attributed to two factors: firstly, the reduction of Fe^{3+} to Fe^{2+}, explained by Fenton theory [26] as shown in the following equation:

$$H_2O_2 + Fe^{2+} \rightarrow Fe(OH)^{2+} + {}^{\bullet}OH \tag{1}$$
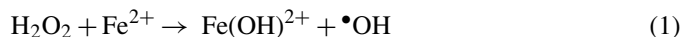
Secondly, during wastewater treatment process Fe^{3+} has a considerable advantages as a flocculation agent, which may be explained by its high oxidation ability of organic compounds [27]; moreover Fe^{3+} oxidizes directly intermediate compounds during electrochemical wastewater treatment process [20].

3.2.4. Effect of initial pH on COD removal

Fig. 5 shows the effect of initial pH on COD removal catalyzed by Mo–P modified kaolin loaded with Fe^{3+} within 40 min of the reaction. It was noted that initial pH strongly affected electrochemical degradation efficiency: the COD removal reached 96% in pH 4 within 40 min, while lower COD removal was observed at high pH value, which could be due to the Fenton's type reaction rate. This indicates that electrochemical degradation strongly depends on pH. In acidic conditions, oxidation ability of OH^- is fairly stronger [20] and its free radicals are easily formed, therefore organic materials are easily oxidized [21]. Consequently, oxidation performance increased rapidly
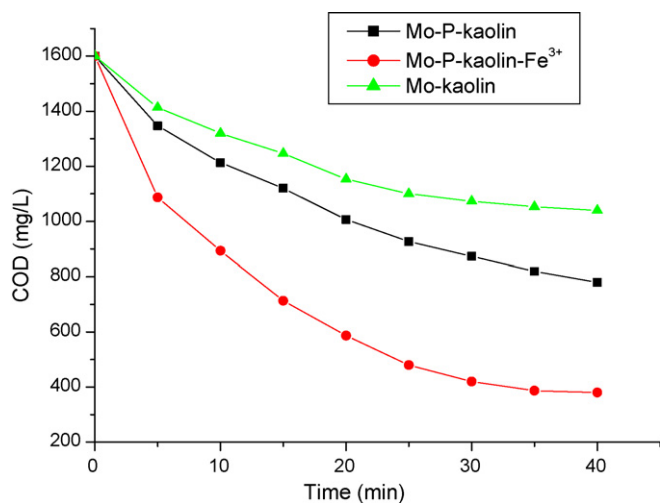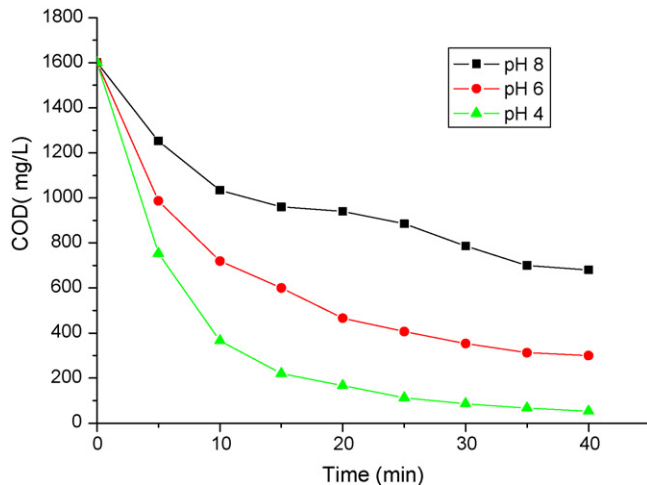
Fig. 5. Effect of pH on COD removal with time.

and thoroughly in acidic conditions. While in basic media, hydrogen peroxide derived from the surface of electrodes, which is considered to be an oxidant in the Fenton reaction, it was unstable and decomposed into oxygen and water, therefore losing some of its oxidation ability, so the oxidation proceeded slowly in basic condition.

3.2.5. Effect of NaCl on COD removal

Fig. 6 shows the effect of NaCl on COD removal with time during oxidation of the wastewater catalyzed by modified kaolin loaded with Fe^{3+} at pH 7. The results were compared in terms of the time required for COD changes. A considerable increase in COD removal at a shorter time was noted in the presence of chloride ions that reached 93%, while its absence COD removal reached 76%, within 40 min. The introduction of NaCl might have led to the formation of such species as $ClOH^-$, Cl_2, ClO_3^- near the surface through oxidation of chloride [28].

3.2.6. Effect of different metal ions on COD removal

Fig. 7 shows the effect of different metal ions loaded on Mo–P modified kaolin with time on electrochemical treatment
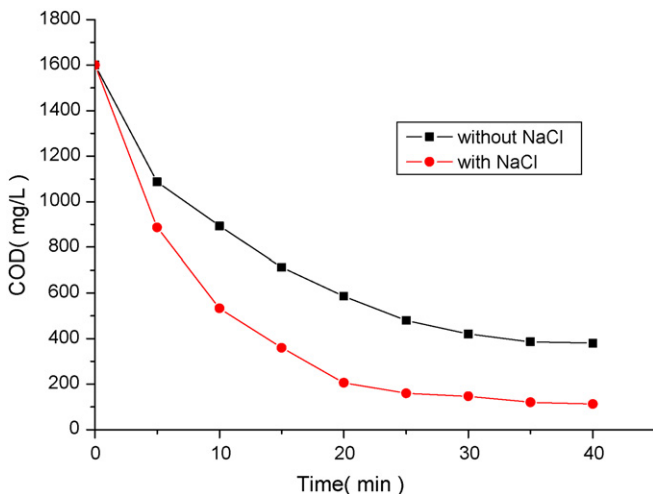
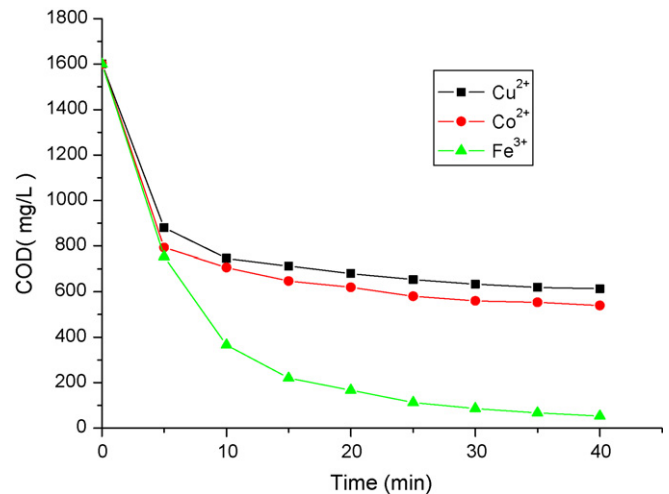

Fig. 6. Effect of NaCl on COD removal with time.

Fig. 7. Effect of different metal ions on COD removal at pH 4 with time.

of the mill wastewater at pH 4. COD removal of over 96% was obtained when modified kaolin was loaded with Fe^{3+}, while around 66% COD removal was obtained, when the modified kaolin was loaded with Co^{2+}, within 40 min of the reaction. Cu^{2+} and Co^{2+} could not yield the same COD removal within 40 min even though they possess equal oxidation states. Therefore, modified kaolin loaded with Fe^{3+} is more suitable than that of Cu^{2+} or Co^{2+} in electrochemical degradation of the mill wastewater at this condition. High COD removal with Fe^{3+} may be attributed to the Fenton reaction that takes place during electrochemical process. Ferrous ions reduced from ferric ions initiated and catalyzed up the decomposition of H_2O_2 produced from the surface of electrodes, resulting in the generation of hydroxyl radicals according to the following equation:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \tag{2}$$
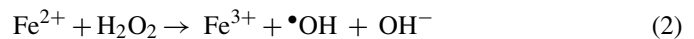
This equation shows the generation of radicals involved in the process of degradation in an aqueous solution. Therefore, modified kaolin loaded with Fe^{3+} showed the highest electrochemical catalytic activity for electrochemical degradation of the mill wastewater.

3.3. Theoretical approach [29,30]

Multi-phase electrochemical degradation with Mo–P modified kaolin loaded with Fe^{3+} takes place via the mechanism of either electro-coagulation or electrochemical oxidation.

During electrochemical process also electro-coagulation takes place: the OH^- produced from cathode react with iron ion and formed a number of iron species, such as: $Fe(OH)^{2+}$, $Fe(OH)_2^+$, $Fe_2(OH)_2^{4+}$, $Fe(OH)_4^-$, $Fe(H_2O)_2^+$, $Fe(H_2O)_5OH^{2+}$, $Fe(H_2O)_4(OH)_2^+$, $Fe(H_2O)_8(OH)_2^{4+}$, $Fe_2(H_2O)_6(OH)_4^+$, $FeO(OH)$, $Fe(OH)_2$ and $Fe(OH)_3$, depending on the pH of the mixture during electrochemical degradation. Flocculation occurring in the low pH ranges can be explained by precipitation mechanism, while at higher pH ranges by adsorption mechanism. At high pH values, the flocs had large surface area that is beneficial for rapid adsorption of soluble organic compounds and trapping of colloidal particles.

During electrochemical oxidation process, pollutants were destroyed by either direct or indirect oxidation process. In the direct electrode oxidation process, both electrode oxidation and metal ion oxidation occurred simultaneously. First pollutants were adsorbed on the surface of electrodes and later destroyed by electron transfer process. Oxidation rate of organic pollutants depended on catalytic activity of the anode, the diffusion rate of organic compounds in the active parts of the anode and the applied current density. Metal ions played an important role in the electrochemical degradation too. Fe^{3+} ions could oxidize some organics directly, likewise to Mo^{6+} ions, which was still an active reagent in the solution. Mo^{6+} ions, were, reduced to Mo^{5+} or $Mo^{\delta+}$ ($5 < \delta < 6$), which is in agreement with the XPS result.

During indirect oxidation process, all strong oxidants such as hydroxyl radicals, hydrogen peroxide, hypochlorite, chlorate, ozone were electrochemically, generated. Thereafter, the generated oxidants destroyed the pollutants through oxidation reaction.

The hydroxyl radical is an important oxidant in electrochemical process. It can be obtained, from three pathways: (i) from the electrode reaction. Anodic discharge of the water takes place forming hydroxyl radicals:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{3}$$

(ii) from the Fenton reaction. When Fe^{3+} was loaded on the modified kaolin catalyst, Fe^{2+} reduced from Fe^{3+}, which react with the hydrogen peroxide produced from the surface of electrodes:
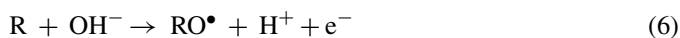
$$O_2 + 2e + 2H_2O \rightarrow H_2O_2 + 2^\bullet OH \tag{4}$$
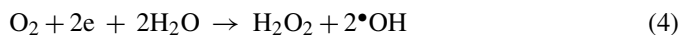
and Fenton reaction occurs thereafter:

$$H_2O_2 + Fe^{2+} \rightarrow Fe(OH)^{2+} + {}^\bullet OH \tag{5}$$
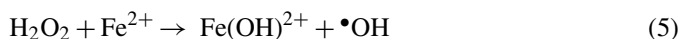
(iii) from the decomposition of H_2O_2 on the surface of the Mo–P modified kaolin catalyst.

After the formation of the hydroxyl radicals, the adsorbed hydroxyl radicals oxidized the organics:

$$R + OH^- \rightarrow RO^\bullet + H^+ + e^- \tag{6}$$

$RO^\bullet$ representing the oxidized organics that may be produced from the hydroxyl radicals that are formed continuously.
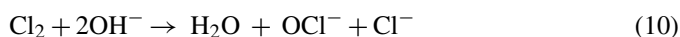
While for high Cl^- content conditions, the anodic discharge of chlorides takes place simultaneously, forming possible chlorine hydroxyl radicals:
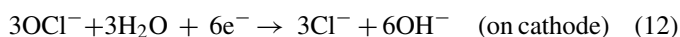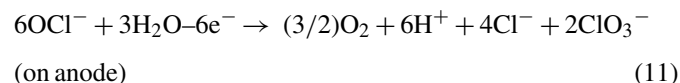
$$H_2O + Cl^- \rightarrow ClOH^- + H^+ + 2e^- \tag{7}$$
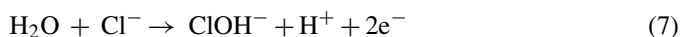
and the free chlorine and chlorides are formed according to the reactions:

$$H_2O + ClOH^- + Cl^- \rightarrow Cl_2 + O_2 + 3H^+ + 4e^- \tag{8}$$

$$R + ClOH^- \rightarrow RO^\bullet + H^+ + Cl^- + e^- \tag{9}$$
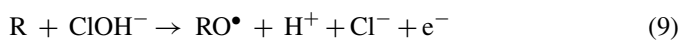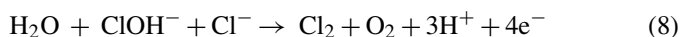
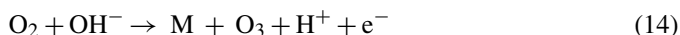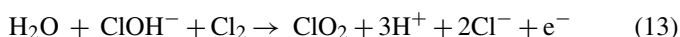The free chlorine produced is in equilibrium with OCl^- ion:

$$Cl_2 + 2OH^- \rightarrow H_2O + OCl^- + Cl^- \tag{10}$$

Hence the products from the primary electrochemical reactions are Cl_2, O_2, OCl^- and $RO^\bullet$. As concentrations of the above oxidants increased in the electrolyzed solution, several other secondary electrochemical reactions take place. At high OCl^- concentrations, the mass transport reactions that were created are:

$$6OCl^- + 3H_2O-6e^- \rightarrow (3/2)O_2 + 6H^+ + 4Cl^- + 2ClO_3^-$$

$$\text{(on anode)} \tag{11}$$

$$3OCl^- + 3H_2O + 6e^- \rightarrow 3Cl^- + 6OH^- \quad \text{(on cathode)} \tag{12}$$

At the same time, ozone, hydrogen peroxide and chlorine dioxide were found among the electrolysis of chlorine solutions. On the anode, the oxidants were produced according to the following hypothetically electrochemical reactions:

$$H_2O + ClOH^- + Cl_2 \rightarrow ClO_2 + 3H^+ + 2Cl^- + e^- \tag{13}$$

$$O_2 + OH^- \rightarrow M + O_3 + H^+ + e^- \tag{14}$$

$$H_2O + M[OH^-] \rightarrow M + H_2O_2 + H^+ + e^- \tag{15}$$
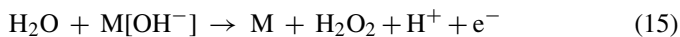
The radicals have an extremely short life due to their high oxidation potential, and either they decompose to other oxidants (Cl_2, O_2, ClO_2, O_3 and H_2O_2) or oxidize organic compounds (direct oxidation). The primary (Cl_2, O_2) and secondary (ClO_2, O_3 and H_2O_2) oxidants that are produced from the destruction of radicals have quite a long life and are diffused into the area away from the electrodes continuing the oxidation process (indirect oxidation or by catalytic). The catalyst introduced can consolidate the secondary oxidants to remove the pollutant in wastewater.

4. Conclusion

A Fenton-like process, involving electro-coagulation or electrochemical oxidation, was evaluated for treating pulp and paper wastewater. The main parameters that govern the complex reactive system (pH, different metal ions and introduction of NaCl) were studied. The COD removal efficiency was greatly affected by the pH of the reaction. The most effective reaction was observed at pH 4 with Mo–P modified kaolin loaded with Fe^{3+} as catalyst at current density $30\,mA\,cm^{-2}$. The results showed that COD removal could reach up to 96% in 40 min. The possible mechanism was also proposed and discussed.

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