

Enhanced electrochemical oxidation of Acid Red 3R wastewater with iron phosphomolybdate supported catalyst

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ABSTRACT

Electrochemical oxidation of Acid Red 3R (AR3R) was investigated with the new catalyst of iron phosphomolybdate (FePMo_{12}) supported on modified molecular sieves type 4 Å (4A) as packing materials in the reactor. The results of the Fourier transform infrared spectroscopy and X-ray diffraction indicated that the heteropolyanion had a Keggin structure. The optimal conditions for decolorization of simulated AR3R wastewater were as follows: current density 35 mA/cm², initial pH 4.0, airflow 0.08 m³/hour and inter-electrode distance 3.0 cm. With the addition of NaCl to the system, the decolorization efficiency increased. But Na₂SO₄ had a negative effect on the decolorization efficiency, which was attributed to the negative salt effect. The degradation mechanisms of AR3R were also discussed in detail.

Key words | Acid Red 3R, catalyst, decolorization, electrochemical oxidation, iron phosphomolybdate

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INTRODUCTION

With the rapid growth of dye industry, dye pollutants are considered as a significant source of environmental contamination. It has been estimated that 50,000 metric tons of azo dyes are released into the land and natural water each year (Zhou *et al.* 2007). The molecular structure of azo dyes contains azo groups ($-\text{N}=\text{N}-$) and auxochromes, such as $-\text{OH}$ and $-\text{SO}_3\text{Na}$ groups. When azo dyes are discharged into the water body, not only do they bring undesirable colors, but more importantly they are toxic, high oxygen demanding and have rather low biodegradability (Martínez-Huitlea *et al.* 2012). Therefore, proper treatment of azo dyes wastewater has drawn more attention.

Electrochemical oxidation process (EOP) is an environmentally friendly method for wastewater treatment through direct anodic oxidation or indirect oxidation. On the one hand, there is no consumption of chemicals and no production of sludge during the process. On the other hand, the process is carried out at room temperature and atmospheric pressure generally (Maria *et al.* 2011). However, the low removal efficiency of azo dyes has limited the development of traditional electrochemical oxidation technology.

It is strongly believed that the use of catalyst provided a promising way to overcome the limitation. Polyoxometalates (POMs) have gained considerable interest due to their versatility for the oxidation of organic substrates (Omwoma *et al.* 2014). They can be used as dual functional catalysts in both homogeneous and heterogeneous systems. Nevertheless, POMs were limited by small specific surface area and dissolution in polar solvent (Song & Mark 2002). A set of $\text{R}_n\text{PMo}_{12}\text{O}_{40}$ ($\text{R} = \text{H}^+, \text{Ba}^{2+}, \text{Zn}^{2+}, \text{Co}^{2+}$ and Cu^{2+}) with different counter-cations has caused more interest due to their unique structured properties and application in electrochemical oxidation (Song & Mark 2002). Iron ion was introduced as a counter-cation in order to generate the synergistic effect between redox and Fenton-like reactions in this study.

In this paper, molecular sieves type 4 Å (4A) were selected as carrier to support POMs in order to improve the specific surface area of the catalyst. Iron phosphomolybdate ($\text{FePMo}_{12}\text{O}_{40}$, abbreviated as FePMo_{12}) was loaded on the modified 4A with 3-aminopropyltriethoxy silane (APTES) to prepare $\text{FePMo}_{12}/\text{APTES-4A}$. Coupling reagent was

applied to modify 4A so as to improve the chemical stability and resistance of acid or alkali. The optimal parameters of treating (Acid Red 3R (AR3R)) were studied. The degradation mechanisms of AR3R were also investigated.

EXPERIMENTAL

Materials and reagents

AR3R, a typical azo dye, was provided by Hebei Rising Chemical Co., China. Its purity was above 99%. APTES, $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$ (PMo_{12}) and all the chemical reagents were of analytical grade and purchased from Tianjin Bodi Chemical Holding Company, China. All reagents were used without further purification.

Preparation

FePMo₁₂ preparation

FePMo₁₂ was prepared as follows: 2.02 g $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ and 20.0 g CH_3COOK were added into PMo_{12} solution (3%) under stirring at 90 °C. The equivalent volume of methanol was added (under stirring) into the PMo_{12} solution. The solution was stabilized at 5 °C for 24 hours. After that, it was recrystallized three times in 80 °C water and dried at 55 °C.

FePMo₁₂/APTES-4A preparation

At first, 4A was pretreated to remove impurities on the carrier. It was dipped into dilute sulfuric acid for 12 hours and rinsed with distilled water three times. Subsequently, 4A was boiled in distilled water three times and dried at 120 °C. Then the pretreated 4A was modified by 50.0 mL toluene containing 3.0 mL APTES. The mixture was stirred for 12 hours. The modified 4A was added into 15.0 mL FePMo₁₂ aqueous solution and then kept at room temperature for 24 hours. Finally, the produced FePMo₁₂/APTES-4A was rinsed with distilled water and dried at room temperature.

Electrochemical setup

Batch experiments were performed in an open undivided polytetrafluoroethylene plate electrochemical reactor containing AR3R solution. The dimension stable anode (DSA) anode ($\text{Ti}/\text{RuO}_2 - \text{IrO}_2$, 6.0 × 12.0 cm) and graphite cathode

were fixed vertically and aligned parallel to each other. The effective electrode area was 18 cm² and their inter-distance could be adjusted. Compressed air was blown into the reactor through a microporous plate at the bottom. A regular DC power supply was equipped to provide power.

Electrochemical oxidation process and analysis procedures

To eliminate the additional adsorption effect, the catalytic particles were dipped into the AR3R solution until a saturation phase. Fifty grams of this catalyst were then placed between the anode and the cathode. Before each run, a fresh solution of AR3R was prepared with deionized water, and initial concentration was kept at 500 mg/L. A control trial without any catalyst present was also done.

The Fourier transform infrared spectroscopy (FT-IR spectrum) and X-ray diffraction (XRD) pattern were performed by Nicolet6700/FT-Raman modules (500–4,000 cm⁻¹) and Rigaku-D/Max-2500 (Cu target, tube voltage 40 kV, tube current 100 mA, 2θ: 0.5–100°), respectively. Elemental composition of catalyst FePMo₁₂/APTES-4A was determined with a Bruker SRS-3400 sequential X-ray fluorescence (XRF) spectrometer. The absorbance value was measured with double beam UV-vis spectroscopy (UV-2600 spectrophotometer, China) at maximum absorption wavelength 507 nm. Total organic carbon (TOC) concentration was measured with a Shimadzu OCT-1 TOC-V_{CPH} analyzer to quantitatively characterize the mineralization degree.

The decolorization efficiency was examined to evaluate the effect of the oxidation process. It was calculated by Equation (1).

$$\text{DC} = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

where A_0 is the initial absorbance value of the solution, and A_t is the absorbance value at reaction time t (minutes).

RESULTS AND DISCUSSION

Catalyst characterization

The FT-IR spectrum of FePMo₁₂ is shown in Figure S1(a) (available online at <http://www.iwaponline.com/wst/071/027.pdf>). The major peaks belonging to the Keggin structure were located at: 1,030 cm⁻¹ for stretching vibration $\nu(\text{P}-\text{O})$, 896 cm⁻¹ for $\nu(\text{Mo}-\text{O}_b-\text{Mo})$, 842 cm⁻¹ for $\nu(\text{Mo}-\text{O}_c-\text{Mo})$

(Song & Mark 2004). Double bond of Mo = O opened and Mo–O–Fe was formed by iron ion. The results showed that Fe³⁺ worked as counter-cation and PMo₁₂O₄₀³⁻ unit had the Keggin structure.

The XRD pattern of FePMo₁₂/APTES-4A is presented in Figure S1(b) (online at <http://www.iwaponline.com/wst/071/027.pdf>). Three diffraction peaks appeared at 9.0°, 20.0° and 29.0°, which represented that FePMo₁₂ on the carrier had the Keggin structure (Maria *et al.* 2011). Four peaks appeared at 12.0°, 16.0°, 19.0° and 24.0° in the pattern, which belonged to the characteristic peaks of 4A (Wang *et al.* 2010). From the evidence of the XRD pattern and FT-IR spectrum, it was shown that the active ingredient FePMo₁₂ on the modified 4A still possessed the Keggin-type structure. Moreover, the XRD result indicated that FePMo₁₂ was dispersed on the 4A surface.

The XRF analysis showed that a certain amount of Mo and Fe was found in the catalyst, which was loaded with 1.723 wt% MoO₃ and 1.068 wt% Fe₂O₃. Approximately 1.87 wt% FePMo₁₂ was loaded on the carrier.

Decolorization of AR3R under different systems

To evaluate the synergetic effect of FeMo₁₂/APTES-4A with the electrochemical process, the degradation of dye wastewater treated in the same electrochemical conditions without the catalyst was investigated in Figure S2 (available online at <http://www.iwaponline.com/wst/071/027.pdf>). The decolorization efficiency was 48.6% after 90 minutes and 50.3% after 120 minutes in the electrochemical process without the catalyst. Moreover, AR3R decolorization efficiency did not increase obviously after 120 minutes. In contrast, AR3R decolorization efficiency in electrochemical system with FeMo₁₂/APTES-4A was enhanced greatly. Decolorization efficiency with FeMo₁₂/APTES-4A was 77.1% after 90 minutes and 78.4% after 120 minutes. Decolorization efficiency was 28.1% higher than that without the catalyst.

Effect of electrolysis conditions on AR3R decolorization

Effect of current density

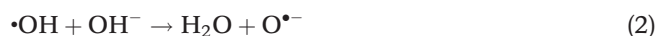
The current density of the electrochemical system had a major role during the EOP. The decolorization efficiency was enhanced from 38.1 to 72.1% when the current density increased from 5 to 35 mA/cm² (Figure 1(a)). The strong oxidants, such as H₂O₂ and •OH, might be electro-generated by water and discharged to oxidize AR3R with increase of the

current density (Liu *et al.* 2012). However, the decolorization efficiency decreased when the current density exceeded 35 mA/cm². The higher current density that would cause more side reactions such as the anode oxygen evolution can consume more power energy (Xiong *et al.* 2002). Therefore, to choose an appropriate current density is most important to favor the decolorization efficiency.

Effect of initial pH

The effect of initial pH on decolorization was investigated (Figure 1(b)). Comparing with the decolorization efficiency at pH 4.0, it was lower when pH was 2.0 or 3.0. The decolorization efficiency decreased with increasing pH from 4.0 to 8.0. It was shown that the decolorization efficiency in acidic conditions was slightly higher than that in alkaline and neutral conditions. The optimal initial pH value was 4.0.

On the cathode, oxygen was converted into stronger oxidizing agent H₂O₂ by the two-electron reduction of oxygen. Fenton-like reaction that H₂O₂ reacted with Fe³⁺ to produce •OH was favored to occur in acidic conditions. But low pH caused the evolution of hydrogen on the surface of cathode, which was negative to produce H₂O₂ (Liu *et al.* 2012). POMs were strong Brønsted acids, and the suitable pH value for POMs was resistant to hydrolytic decomposition (Omwoma *et al.* 2014). In addition, POMs can dissociate completely or stepwise in aqueous solution at different pH. UV spectra of FePMo₁₂ aqueous solutions at different pH are shown in Figure S3 (available online at <http://www.iwaponline.com/wst/071/027.pdf>). Adsorption peaks appeared at pH 2.0, 3.0 and 4.0, which indicated that PMo₁₂O₄₀³⁻ was relatively stable at lower pH conditions. Once pH exceeded 4.0, adsorption peaks disappeared. POMs would decompose partly. As a result of PMo₁₂O₄₀³⁻ protonation, the decolorization efficiency decreased with increasing pH in neutral and alkaline conditions. And PMo₁₂O₄₀³⁻ was subject to alkaline hydrolysis for its low surface negative charge and high dielectric constant of water (Song & Mark 2004). Hydroxyl free radical (•OH) electro-generated in the system was favored to transform into O^{•-} in the alkaline condition, according to Equation (2). But the oxidation capacity of O^{•-} was lower than that of •OH. The electrode surface was passivated more easily in alkaline media than in acidic media (Lv *et al.* 2009). These reasons led to the result that the decolorization efficiency in acidic conditions was higher than that in alkaline and neutral conditions.



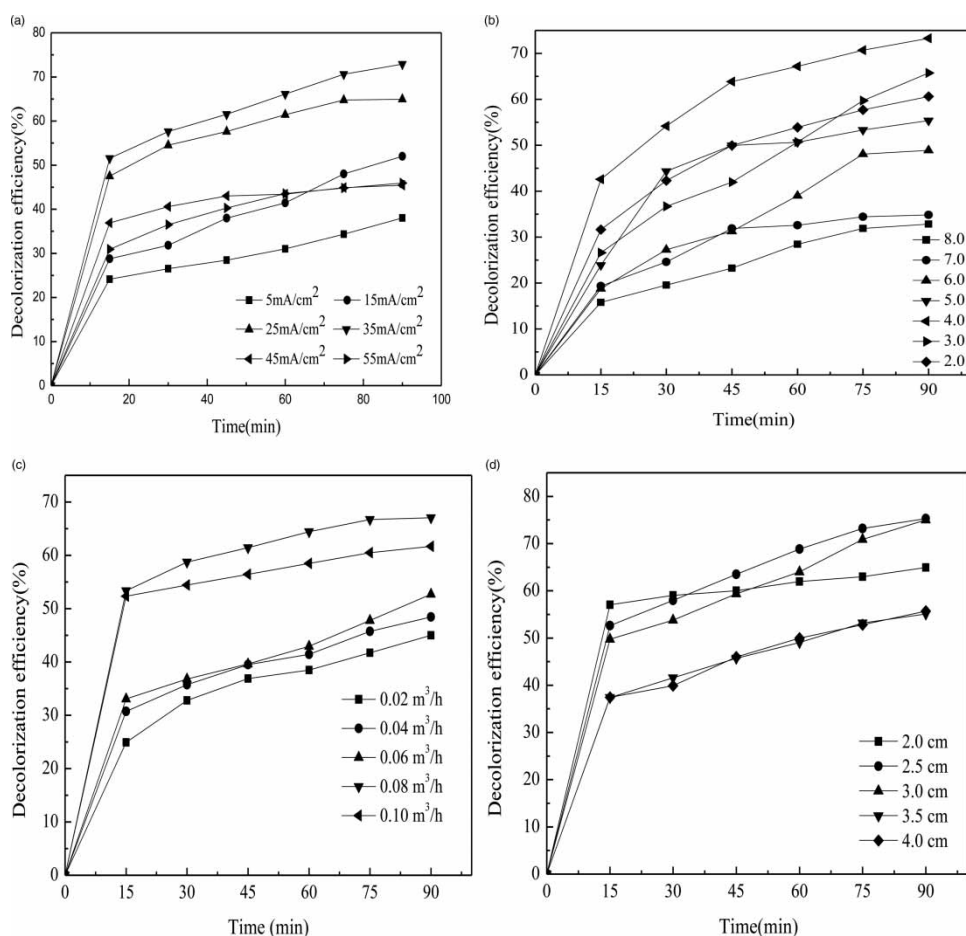


Figure 1 | (a) Effect of current density on decolorization efficiency of AR3R; initial pH 4.0, airflow $0.08 \text{ m}^3/\text{hour}$ and inter-electrode distance 3.0 cm. (b) Effect of initial pH on decolorization efficiency of AR3R; current density $35 \text{ mA}/\text{cm}^2$, airflow $0.08 \text{ m}^3/\text{hour}$ and inter-electrode distance 3.0 cm. (c) Effect of airflow on decolorization efficiency of AR3R; current density $35 \text{ mA}/\text{cm}^2$, initial pH 4.0 and inter-electrode distance 3.0 cm. (d) Effect of inter-electrode distance on decolorization efficiency of AR3R; current density $35 \text{ mA}/\text{cm}^2$, initial pH 4.0 and airflow $0.08 \text{ m}^3/\text{hour}$.

Effect of airflow

Air was blown into the electrochemical system for two purposes: to promote mass transfer and activate the surface of particle electrodes, and to supply the essential oxygen for electrochemical reactions. Oxygen was converted into stronger oxidizing agent H_2O_2 on the cathode by two-electron reduction, according to Equation (3) (Lv *et al.* 2009). To investigate the effect of airflow, electrochemical reactions were performed at different airflow rates (Figure 1(c)). The decolorization efficiency increased when the airflow rate changed from 0.02 to $0.08 \text{ m}^3/\text{hour}$. And at $0.08 \text{ m}^3/\text{hour}$, the decolorization efficiency reached the maximum value.



Meanwhile, Mo was the coordination atom of phosphomolybdate, which had high oxidation state (Antonaraki

et al. 2010). The oxidation state Mo would oxidize the organic molecule, and the reduction state Mo would be oxidized by O_2 . The typical reversible redox process was exhibited.

The decolorization efficiency declined when the airflow rate exceeded $0.10 \text{ m}^3/\text{hour}$. It indicated that aeration at unsuited flow rate had a negative effect on the decolorization efficiency. The aeration may cause severe fluid short-circuiting due to the volume taken up by the air in the cell. It forced AR3R to react with active site of $\text{FePMo}_{12}/\text{APTES-4A}$ at short retention time and led to a decrease in the decolorization efficiency (Saleh 2009).

Effect of inter-electrode distance

Inter-electrode distance was an indispensable factor to optimize the electrochemical system. The effect of inter-electrode distance on the AR3R decolorization was

determined in Figure 1(d). The decolorization efficiency decreased with reducing inter-electrode distance from 3.0 to 2.0 cm. Short inter-electrode distance could cause more side reactions and energy consumption and then a decrease in decolorization efficiency (Yue *et al.* 2013). When the inter-electrode distance exceeded 3.5 cm, the decolorization efficiency decreased. With the distance increasing, the movement of produced ions got slower and ions would have fewer opportunities to aggregate. The decrease of decolorization efficiency was due to less hydroxyl free radical ($\cdot\text{OH}$) (Wang *et al.* 2009).

Effect of electrolyte

Effect of NaCl

Electrolytes could improve the solution conductivity and accelerate the electron transfer, which benefitted the electrochemical oxidation. The decolorization efficiency was investigated by adding different concentrations of supporting electrolytes (Figure 2). The decolorization efficiency increased and then decreased with an increase in the NaCl concentration. By adding a NaCl concentration of 0.05 mol/L, the decolorization efficiency was enhanced from 74.6 to 95.3% because hypochlorous acid or hypochlorite, as strong oxidizing species, which was generated in the system, could oxidize organic compounds (Equations (4) and (5)).



On the one hand, the high decolorization efficiency was attributed to the indirect electrochemical oxidation by the

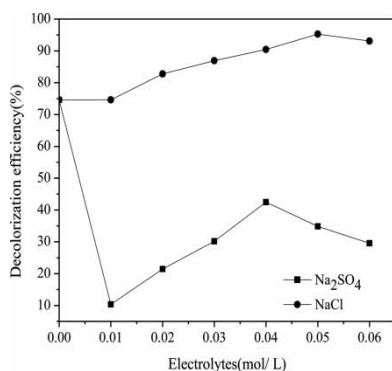


Figure 2 | Effect of electrolyte concentration on the decolorization efficiency; current density 35 mA/cm², initial pH 4.0, airflow 0.08 m³/hour and inter-electrode distance 3.0 cm.

active chlorine (Mijin *et al.* 2012). On the other hand, NaCl increased the ionic strength of $\text{PMo}_{12}\text{O}_{40}^{3-}$ (Song & Mark 2004). It was reported that NaCl in the POMs solution screened out the electrostatic repulsions, which allowed the anions to move more closely (Song & Mark 2004).

Effect of Na₂SO₄

The decolorization efficiency was exhibited to be lower than that of no electrolyte, when Na₂SO₄ was added. When the concentration of Na₂SO₄ was 0.04 mol/L, decolorization efficiency reached the peak value of 42.5%, which was still lower than that without supporting electrolyte (Figure 2). The presence of Na₂SO₄ showed an obvious inhibition effect on the AR3R degradation. It should be mentioned that negative salt effect occurred. The difference between two supporting electrolytes was mostly due to the aggregation or association with ionic dye in wastewater. High concentration of salts and $-\text{SO}_3^-$ group of AR3R molecule were favorable for aggregation or association. Therefore, aggregation was enhanced by the addition of Na₂SO₄ and subsequently gave rise to lose the chance of AR3R reacted with catalysts (Niu *et al.* 2014). But the amount of persulfate electro-generated in a higher concentration of Na₂SO₄ solution was larger than that in a lower concentration of Na₂SO₄ solution. The result that the decolorization efficiency increased gradually with increasing concentration of Na₂SO₄ was attributed to the generation of persulfate ions that can oxidize azo dyes, according to Equation (6). Although persulfate ions were beneficial to the decolorization, the amount was little. Na₂SO₄ cannot play a decisive role in the AR3R decolorization (Martínez-Huitile *et al.* 2012).



Electrochemical mechanism

UV-vis spectra of AR3R at different reaction time were investigated in order to clarify the changes of molecular and structural characteristics (Figure 3). Three absorption peaks appeared in UV-vis spectra. In the visible region, there was a rapid decrease in absorbance at 507 nm due to azo bond ($-\text{N}=\text{N}-$) cleavage in the dye molecules. The azo bond was the most active site for oxidation. It was confirmed that the electrochemical process was able to remove color in a short time. The adsorption peaks at 331 and 215 nm were due to the $\pi-\pi^*$ transition of the benzene and naphthalene rings. The absorbance in the UV region

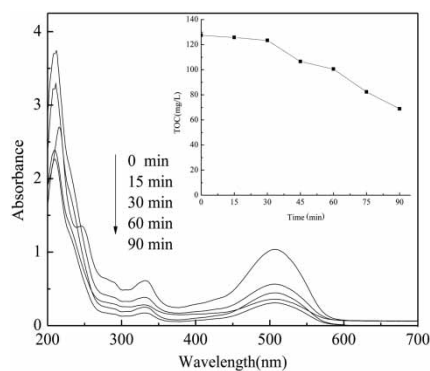


Figure 3 | UV-vis spectra and TOC changes of AR3R sample at different degradation time; current density 35 mA/cm², initial pH 4.0, airflow 0.08 m³/hour and inter-electrode distance 3.0 cm.

increased within 30 minutes and then decreased. This absorbance increase was related to intermediate formation. Aromatic amine compounds were generated at initial reaction process because of the breakage of azo bond. The absorption peaks were weakened after 30 minutes, indicating that the relevant structures were destroyed gradually. On the basis of the results, the removal of TOC was analyzed. After the 30 minutes it was found that the removal of TOC was slow. In this stage, the azo bond was broken. Subsequently, a series of consecutive degradation steps occurred, including desulfonation, denitrogenation, opening loop reaction and mineralization. After 90 minutes, the removal efficiency of TOC reached 46.0%.

Intermediate products were identified by liquid chromatography–mass spectrometry (LC–MS) according to previous research in our team (Yue *et al.* 2015). Briefly, AR3R was degraded to aromatic and organic acids gradually, followed by final mineralization to CO₂ and H₂O. Organic pollutants were oxidized directly on the anode surface by electron transfer. The activity of electrode and the current density determined the rate of electron transfer in the electrochemical process. In addition, H₂O₂ was continuously produced by two-electron reduction of oxygen on the cathode surface. Radicals •OH and HO₂• with strong ability of oxidation were produced, accompanying electron exchange between electrode and pollutants. It is worth mentioning that PMo₁₂O₄₀³⁻ had coordination atom Mo, which had the highest oxidation state. On the catalyst, the transient species would interact rapidly with AR3R to form the Mo-oxygen-organism intermediate. In the subsequent step, the bonds between the oxygen atom and Mo were broken, and quinones as oxydates of intermediate products were produced. Quinones produced in the system

were confirmed by LC–MS (Yue *et al.* 2015). The reduction states of Mo could be oxidized reversibly to the oxidation state by molecular state O₂. The reaction processes were deduced in Figure 4. However, the valence state change of Mo atom has not been measured. Thus, the degradation mechanism for the FePMo₁₂/APTES-4A combined system needed further investigation.

Reusability and leaching properties

To prove the reuse potential of the catalyst, cycle experiments were performed, as shown in Figure S4 (available online at <http://www.iwaponline.com/wst/071/027.pdf>). The decolorization efficiency decreased from 95.3 to 82.1% after five runs. The catalyst was characterized by XRF after five runs, indicating that 16.7% of FePMo₁₂ was lost in total. Reduction of the catalytic effect was mainly due to the loss of catalyst. The decolorization remained at more than 80% even after recycle five times. Therefore, the reusability of the catalyst was possible.

Performance based on TOC and decolorization efficiency was compared with previous studies, as shown in Table S1 (available online at <http://www.iwaponline.com/wst/071/027.pdf>). Conventional particle electrode had good electrical conductivity and large surface area, but the removal of TOC was not high. The catalyst loaded on the supporter was introduced to extend the promotion of mass transfer, which was regarded to improve the electrochemical oxidation. Similar decolorization efficiency was obtained under the conditions of higher wastewater concentration and lower current density in this paper (He *et al.* 2014). FePMo₁₂/APTES-4A showed high efficiency of

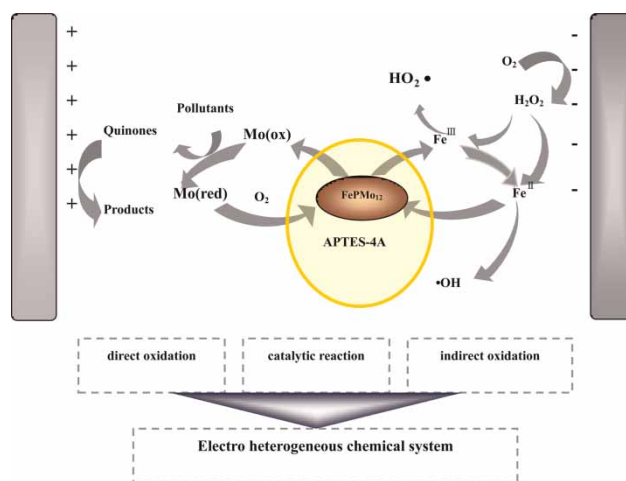


Figure 4 | Illustration of the reaction mechanisms for electrochemical oxidation of AR3R wastewater with FePMo₁₂/APTES-4A.

decolorization and removal of TOC, which can be ascribed to the enhancement of stability and catalytic activity compared to other studies.

CONCLUSIONS

This study demonstrated that employing the Keggin-type FePMo_{12} as catalyst, AR3R wastewater can be effectively decolorized by electrochemical oxidation. Employing the constructed experimental facility, a series of experiments were conducted to examine the effect of the catalyst on the decolorization reaction, and through which the operating parameters were greatly optimized. The decolorization efficiency was increased by 28.1% compared with treatment without any catalyst. Introducing NaCl into the dye solution could improve the decolorization during the electrochemical process and this study found that adding Na_2SO_4 would cause a negative effect. The adsorption peaks were weakened, indicating that azo bond ($-\text{N}=\text{N}-$) and naphthalene rings were destroyed gradually in UV-vis spectra. AR3R degradation reaction contained direct oxidation, catalytic reaction and indirect oxidation in this work. The electrochemical method coupled with POMs catalyst could be considered as an effective and promising technical option for azo dye wastewater treatment.

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