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PEI-M [M:Cu(II) and Co(II)] Hydrogel Catalyst For Methyl Orange Degradation And Epinephrine Oxidation

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Abstract

Here, we report the catalytic activity of catalyst derived from polyethylene imine-M (II) (PEI-M: Cu(II), and Co(II)) hydrogel composite in the presence of H_2O_2 as an oxidant. The PEI-Cu(II)/H_2O_2 heterogeneous composite was used in the degradation of an azo-dye, methyl orange (MO) in aqueous solution. In the presence of 63 mM H_2O_2, 100% of MO was removed in 80 min. The kinetics investigation of the processes demonstrated a pseudo-first-order kinetic model was applicable. Additionally, a pharmaceutical product, epinephrine (EP) was partially oxidized to adrenochrome by PEI-Co(II)/H_2O_2 hydrogel composite system. About 50% of conversion to adrenochrome was reached in less than 55 min again comply with the pseudo-first-order

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kinetic model. Both MO and EP oxidation reaction provided mild activation energies, 44.09, and 58.02 kj.mol^{-1}, respectively. Various parameters effecting MO and EP oxidation were investigated.

Keywords: Hydrogel-metal ion composite; azo compound degradation; epinephrine oxidation; drug oxidation; hydrogel catalyst.

Metil Oranj Bozunması ve Epinefrin Oksidasyonu için PEI-M [M:Cu(II) ve Co(II)] Hidrojel Katalizör

Özet

Bu çalışmada, Polietilenimin-M(II) (PEI-M: Cu(II) ve Co(II)) hidrojel kompozitlerinin H2O2 indirgeyici olarak kullanılıdığı reaksiyonlarda katalitik aktiviteleri incelendi. Buna göre, PEI-Cu/H2O2 heterojen kompozitleri metil oranjın sulu çözeltisinde (MO) bozunma reaksiyonunda katalizör olarak kullanıldı. Metil oranj, 63 mM H2O2 varlığında %100 olarak 80 dakikada ortamdan uzaklaştırıldı. Metil oranj bozunma reaksiyonunun kinetik çalışmalarında pseudo birinci dereceden kinetik modele uygulanabilir olduğu gösterildi. Bunlara ek olarak, bir ilaç olan epinefrin (adrenalin), PEI-Co(II)/H2O2 hidrojel kompozit sistemi varlığında adrenokrom'a yükseltgendi. Epinefrin'in yaklaşık %50'si 55 dakikadan daha az bir sürede adrenokroma dönüştürüldü ve pseudo birinci dereceden kinetik modele uygulanabilir olduğu gösterildi. MO ve EP yükseltgenmesi reaksiyonlarının aktivasyon enerjileri sırasıyla 44,09 ve 58,02 kj.mol-1 olarak hesaplandı. MO ve EP oksidasyonuna etki eden çeşitli parametreler çalışıldı.

Anahtar Sözcükler: Hidrojel-metal iyon kompozit, azo bileşiklerinin bozunması, epinefrin yükseltgenmesi, ilaç yükseltgenmesi, hidrojel kompozit.

1. Introduction

So far, heterogeneous catalysis for degradation of synthetic dyes or other organic compounds by use of hydrogen peroxide has been described with silica-supported complexes of Cu, Ni and Co (Gemeay et al. 2003), zeolite-immobilized metals ions (Centi et al. 2002), metal pillared clays (Guo and Al Dahhan 2003) or metals bound to a polymeric support (Jose et al. 2003). However, the use of these processes for industrial effluents is limit, due to the requirements of visible light for photo–catalysis, unsuitable pH–dependence for better activity (Tang and Chen 1996) or the need to perform the catalysis in two steps such as sorption and degradation (Baldrian et al. 2006) that prevent the application these processes for industrial effluents. (Wu and Qu 2004). Nevertheless, here we used a simple method for degradation of methyl orange (MO), in comparison to the other means by studying the efficiency of catalyst system on the decolorization of dyes such as methyl orange that is another way of elimination of toxic materials in the industrial wastewater. As MO is a water-soluble azo dye that is extensively used in textile, printing, paper, pharmaceutical and food industries (Mittal et al. 2007), it generates great deal of environmental concerns. Herein, the degradation of MO by PEI-Co(II) complex were investigated in details. Various parameters such as the effect of the MO concentration, H_2O_2 concentration, and the catalyst amount on MO degradation rate were examined. It is the aim of this investigation to better understand the PEI-Co(II)/H_2O_2 process and optimizing its parameters which can facilitate scaling up such processes for industrial applications.

Epinephrine (EP) is a significant catecholamine neurotransmitter in the central nervous system and biological body fluids (Ni et al. 1999). Many life phenomena are related to the concentration of EP in blood. Medically, EP has been used as a common emergency healthcare medicine. The decrease of catecholamine level leads to diseases such as Alzheimer's, Parkinson's and inflammation. Hence, an easy, fast and sensitive method is essential for its determination (Taei and Jamshidi 2014), and the catalytic oxidation methods are faster, cheaper, safer analysis and high sensitivity in comparison with other choices. Recently, new kinds of catalysts have been developed for oxidation of EP, and the great number of studies in recent years have focused on the development of catalytic oxidation materials using manganese complex $[Mn_2(HL)_2](BPh_4)_2$ (Szigyártó et al. 2013), mesoporous silica nanoparticles (Tao et al. 2009), metal porphyrin-immobilized anion-exchange resins (Kitamura et al. 2008) and so on. For example, phosphotungstates ($[P_2W_{17}O_{61}M']^{n-}$), iron, copper and vanadium substituted compounds (Dempsey et al. 2003), cationic hydrogels containing cobalt(II) ions (Victoria et al. 2014), silica nanoparticles (Tao et al. 2009), μ-dioxytetrakis(histidinato)-dicobalt(II) (Refiquee et al. 2014) and cobalt complex based on a polyampholyte, Co(II)–Poly(EGDE-MAA-2MI) were widely used as heterogeneous catalyst sytem (Lupanoa et al. 2013). However, amongst these compounds, modifiable polymeric particles with tunable functional groups and sizes such as PEI particles attract great attention due to their superior properties e.g., preferred functionality, high surface area, facile reusability and tunable sizes and charges (Demirci and Sahiner 2014a). In fact, these abilities make PEI particles as an important tool for applications in the biomedical fields and for catalysis (Keresztessy et al. 2014).

Earlier PEI particle synthesis (Sahiner 2013) and PEI-M (M : Co, Cu) composite preparation and their successful use in hydrolysis of $NaBH_4$ and AB (Demirci and Sahiner 2014b) were ported. Here, we report PEI-Co(II) and PEI-Cu(II) hydrogel complexes for the use in degradation of MO, and in the oxidation of EP to adrenochrome, respectively, in the presence of hydrogen peroxide, as an oxidant. The effects of various parameters such as catalyst and substrate amount, hydrogen peroxide concentration and temperature were investigated.

2. Experimental

2.1. Materials

The polyethyleneimine (PEI, 50 wt% in water Mn:1800) were purchased from Aldrich, and glycerol diglycidyl ether (GDE, technical grade) was used as a cross linker. Methyl orange (MO, Reagent European Pharmacopoeia) was used as azo dye, and epinephrine (EP, adrenaline bitartarate, 99%, DROGSAN) procured from local vender, and hydrogen peroxide (H_2O_2, 30%, Merck) were used as an oxidizing agents. Cobalt sulfate heptahydrate ($CoSO_4.7H_2O$, 99%, Merck) and copper sulfate pentahydrate ($CuSO_4.5H_2O$, 99%, Sigma Aldrich) were used sources of metal ions and sodium borohydrate ($NaBH_4$, 98%, Merck) was used reduction agent. Distilled water (DI) was used for washing of hydrogels, and in the preparation of all aqueous solutions such as Co(II), Cu(II), and MO and EP.

UV–Vis spectrophotometer is employed for the MO and EP absorption studies using T80+ UV–Vis model spectrophotometer.

2.2. Synthesis of PEI hydrogel and in its Cu(II) and Co(II) containing composites

PEI hydrogels were synthesized by using epoxy-amine reactions with mole ratio of amine to epoxy 100:6. Glycerol diglycidyl ether were used such as a cross linker, sources of epoxy. In brief, 2 ml PEI solution and 4 ml water was added in a vial and vortexed about 2 minutes. Then, the certain amount of glycerol diglycidyl ether (6% mole ratio for repeating unit of PEI were added to this solution and vortexed again. Following, the prepared mixture was placed in a 12 x 100 mm glass test tubes and placed in autoclave (WiseStir) at 90 °C for 2.5 h. Then, the prepared PEI hydrogels were washed with plenty of DI water for 5 times; every washing period took 2 hours then the wash water was replaced, and PEI hydrogels were dried in freeze dryer, and stored in a closed bags.

The prepared PEI hydrogels were complexed with Co(II) and Cu(II) ions as PEI-Co(II)/Cu(II), and used as catalyst. Certain amount of prepared PEI hydrogels (0.5 g) were placed in 50 ml 1000 ppm metal ion solutions (Co(II) and Cu(II)) from their sulfate salts, in DI water at 750 rpm mixing rate for 12 h. Then, the PEI-Co(II)/Cu(II) hydrogels were used as a catalyst on degradation of MO and oxidation of EP.

2.3. Methyl orange (MO) degradation by PEI-Cu(II) hydrogel complex

The MO degradation studies were carried out by using 100 mg of PEI-Cu(II) complex that was suspended in 100 mL 42 μM MO with 63 mM H_2O_2 solution in DI water. The absorbance of the solution was monitored as a function of time at 464 nm, and the degrading amounts were determined from the previously constructed calibration curve at this wavelength. The control reaction of MO adsorption on the catalyst was made in the absence of H_2O_2 and catalyst. All the experiments throughout this research were done at least three times, and the average values were reported with standard deviations.

2.4 Epinephrine (EP) oxidation by PEI-Co(II) hydrogel complex

The oxidation of EP was carried using 40 mg of PEI-Co(II) hydrogel complex which was suspended in 20 mL of 2 mM epinephrine and 46 mM H_2O_2 solution. Then the change in the absorbance of the solution was monitored as a function of time at 502 nm. The oxidized amounts were determined from the previously constructed calibration curve at this wavelength. A control experiment for EP oxidation in the heterogeneous system was done with a solution of 2 mM EP and 46 mM H_2O_2. Another control experiment was carried using 40 mg of PEI-Co(II) hydrogel complex suspension in 20 mL of 2 mM EP in absence of H_2O_2 keeping all the parameters same.

3. Results and Discussion

3.1. Methyl orange degradation

Methyl Orange (MO) is an azo compound and one of the most commonly used coloring agents in several applications. Therefore, the discharge of this coloring agent present in wastewater cause serious environmental concerns. So, the prepared PEI-M complexes were studied for their potential use in MO degradation. The preparation of PEI hydrogel and PEI-M (Co(II) and Cu(II)) complexes were given in Fig. 1. As can be seen, upon complex formation of amine groups within PEI hydrogels and metal ions, there is a color change, dark maroon for Co(II) and dark blue/navy for Cu(II) ions. These PEI-M hydrogel complexes were used as heterogeneous catalysts and the progress of the degradation reactions e.g., MO degradation in the presence of PEI-Cu(II) hydrogel composite was followed by UV–Vis spectrophotometer.

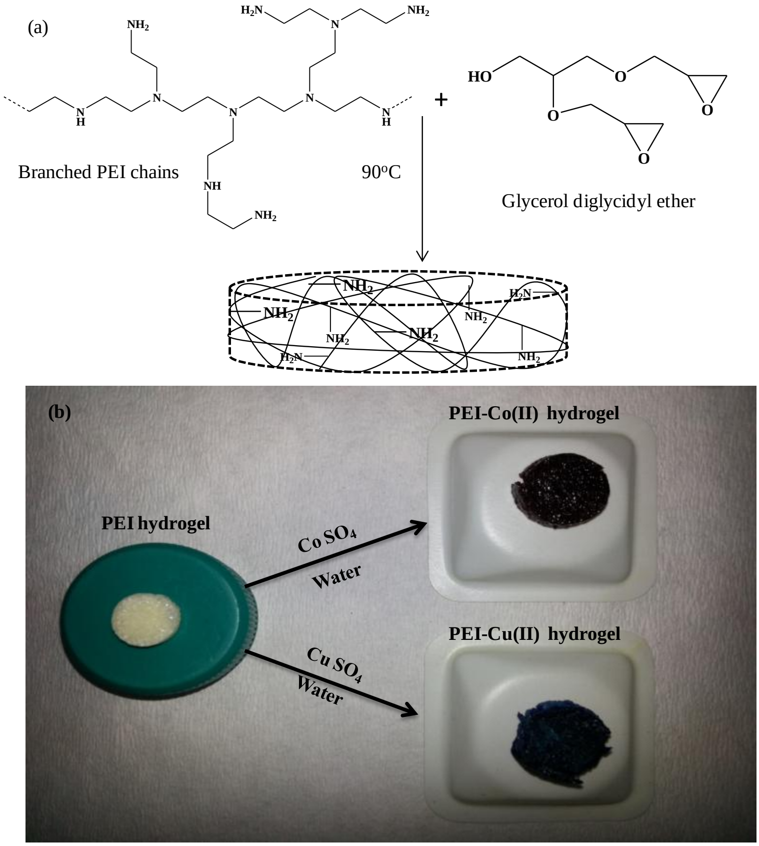


Fig. 1. (a) PEI hydrogel preparation, and (b) PEI hydrogels's complex formation with Co(II) and Cu(II) ions.

The degradation reaction kinetics of MO was investigated with the decrease of peak intensity at 462 nm. As illustrated in Fig. 2, the UV–Vis spectra for the degradation of MO measured at every 10 min after the addition of PEI-Cu(II) hydrogel composite catalyst to reaction medium in order to follow the progress of the degradation reaction. It is noteworthy to mention that the degradation reaction does not take place in the absence of catalysts and this peak at 462 nm remained unaltered without the addition of PEI-Cu(II) hydrogel composite.

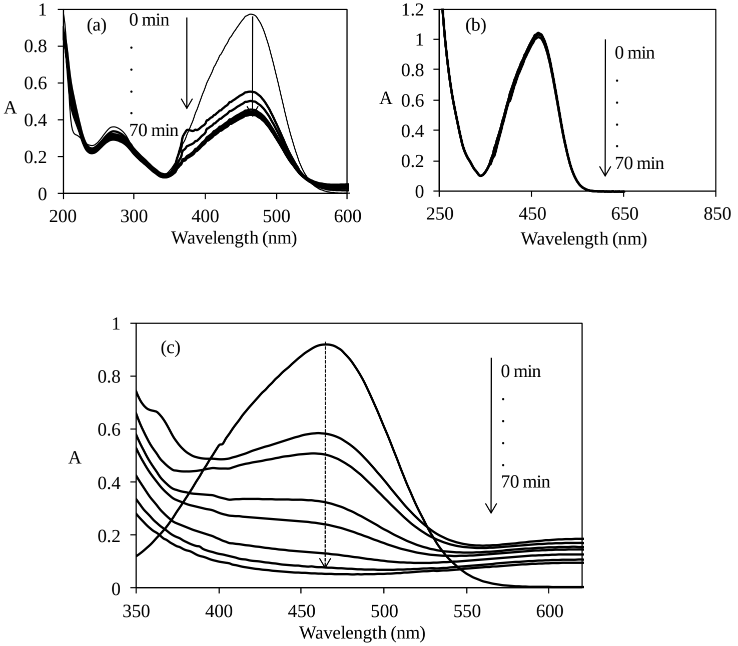
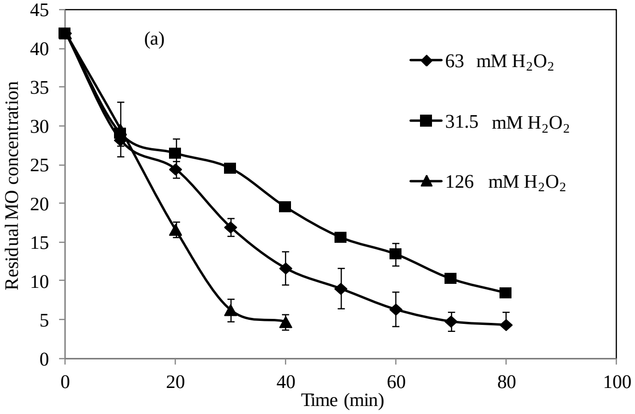
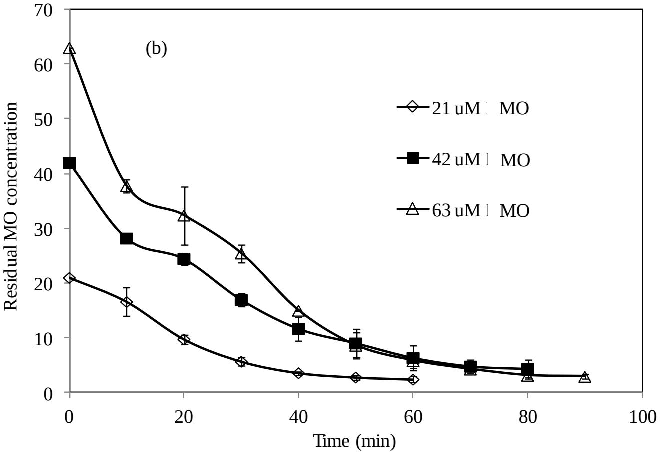


Fig. 2. UV–Vis spectra of degradation of methyl orange with a) PEI-Cu(II) hydrogel composite as a catalyst without H_2O_2, b) H_2O_2 without catalyst, c) PEI-Cu(II) hydrogel composite as catalyst and H_2O_2 as an oxidant.

To determine the effect of the concentration of $H_2O_{2,}$ three different concentration of H_2O_2, 31.5, 63, and 126 mM was used in MO degradation under the same reaction conditions. As can be seen from Fig.3-a, the MO degradation rate was increased by the increase of H_2O_2 concentration from 31.5 to 126 mM. The increase in the H_2O_2 concentration resulted in an increase in the reaction activity, as expected, due to an increase of $^{\bullet}OH$ that place active role in the degradation of MO (Idel-aouad et al. 2011). The effect of MO concentration was also investigated. The initial concentration of MO has significant effect on the MO adsorption. When the amount of MO increased from 21 to 63 μM as shown in Fig. 3-b, the degradation time is increased. In general, the reaction proceeded rapidly within the first 10 min and then slowed down. The higher uptake at low concentration can be explained as follow: at higher initial concentration, the ratio of initial mole numbers of MO to the available surface area is high; as a result, the fractional adsorption is dependent on the initial concentration. For a given adsorbent dosage, the total numbers of available adsorption sites are fixed thereby adsorbing almost the same amount of catalyst. Thus, the percentage degradation of the adsorbate decreases corresponding to an increase in initial MO concentration (Yuan et al. 2009; Zaghouane-Boudiaf et al. 2012).





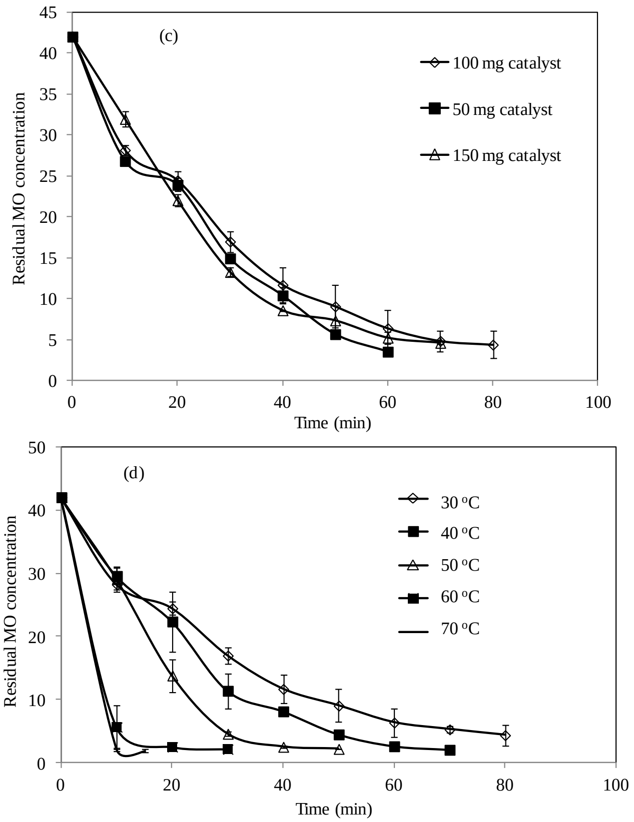


Fig. 3. Residual MO concentration versus time for the degradation of MO catalyzed by PEI-Cu(II) hydrogel composite with a) various H_2O_2 concentration, b) various concentration of MO, c) various amount of catalyst, d) at different temperatures.

The effect of the amounts of catalyst on the degradation of MO was also investigated. As shown in Fig. 3-c, the activity of this heterogeneous catalysts system for MO degradation was independent from catalysts amounts, as the increase in the amounts of catalyst from 50 mg to 150 mg did not change the amounts of MO residue in solution. This behavior could be attributed to the fact that 50 mg of catalyst is enough to provide catalytic sites for the available amount of reactants. If the amount of catalyst is increased by keeping amount of reactant concentration constant, there is no doubt that the number of catalytic sites are increased, but due to small amount of reactants for the current study (Fig. 3-c.), all the catalytic sites may not be used for the catalytic degradation of MO

To determine the effect of temperature, the degradation reactions of MO were carried out at five different temperatures; 30, 40, 50, 60 and 70 °C, respectively, and the degradation rate constants were calculated for each temperature. As shown in Fig. 3-d, it was observed that the degradation rate is increased with increasing reaction temperature. It is obvious as expected, the higher the reaction temperature the lower the time for MO degradation under same reaction condition of increasing reaction temperature. Since temperature of the discharged wastewater containing dye is depend on the location, environments, and the season, it is of concern to investigate the temperature effect of dye degradation. As higher temperatures provide more energy for the reactant molecules to overcome the reaction activation energy barrier; faster dye degradation with higher reaction temperatures is reasonable (Feng et al. 2004). Another interpretation, might be that increasing the reaction temperature accelerated the rate of $^{\bullet}OH$ formation in the heterogeneous catalytic system (Idel-aouad et al. 2011).

To investigate the reaction kinetics, as illustrated in Fig. 4-a, ln (C_t/C_0) versus time at different reaction temperatures were constructed. As can be seen, the linear correlation of ln (C_t/C_0) versus time plot is the proof for the pseudo-first-order rate kinetics.

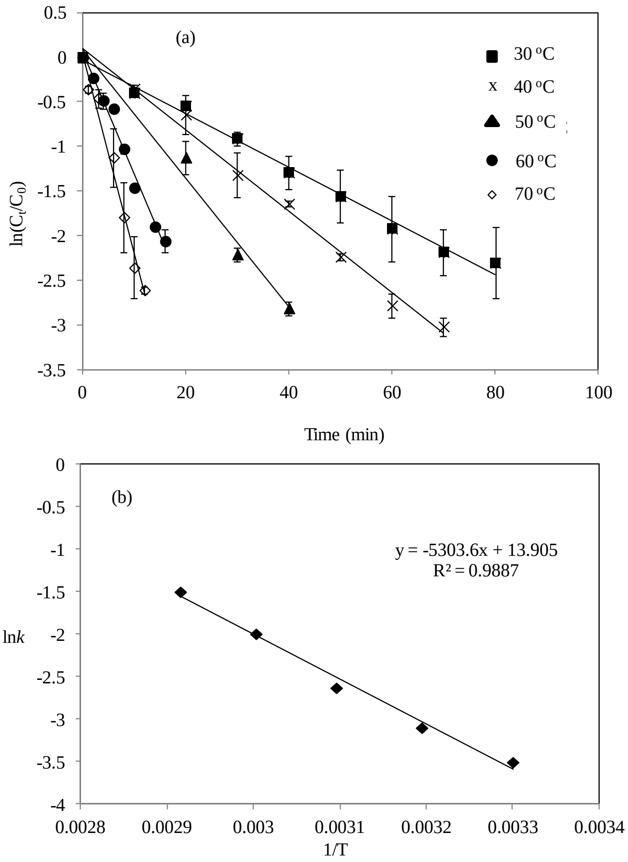


Fig. 4. a) The relationship between ln(C_t/C_0) with time at different temperature, b) Arrhenius plot of ln*k* versus 1/T for the degradation of MO catalyzed by PEI-Cu(II).

The pseudo-first-order rate constants (*k*) and correlation coefficients (R^2) for MO degradation are given in Table 1. As expected, the *k* values increased as the reaction temperatures were increased.

Table 1. The change in rate constants and the correlation coefficient with temperature for the degradation of MO in aqueous environments catalyzed by PEI-Cu(II) obtained from ln (C_t/C_0) versus t plots.

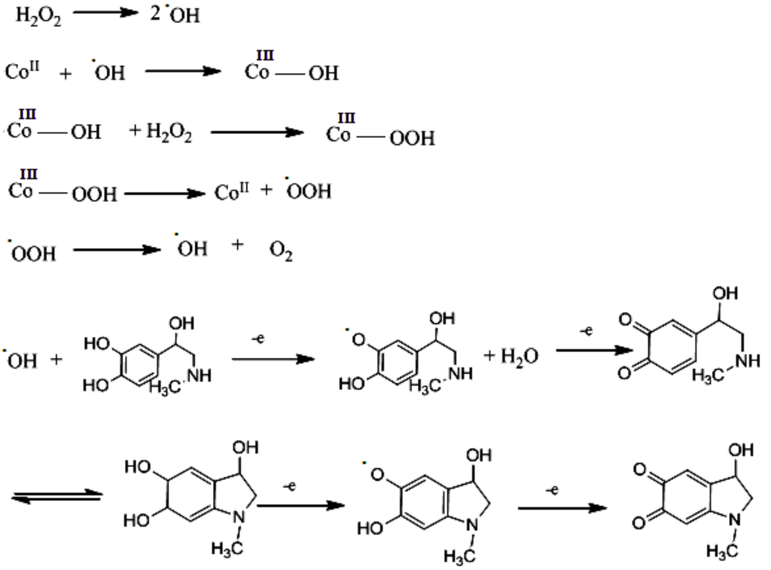
Temperature (°C)	k (min $^{-1}$)	R^2
30	0.03	0.991
40	0.045	0.991
50	0.066	0.98
60	0.136	0.983
70	0.223	0.988

Additionally, the activation parameters at different temperatures for MO degradation reaction catalyzed by P(EI)-Cu(II) were calculated by applying well-known Arrhenius equation and constructing the graph of ln$k$–1/T as shown in Fig. 4-b. The activation energy for degradation of MO was found as 44.09 kJ mol^{-1}. This result is similar to some catalysts from the literatures such as TiO_2/UV light (Akbal 2005) and CdS QTs/chitosan (Jiang et al. 2012). On the other hand, nanoscale zero valent iron (NZVI) particles (Fan et al. 2009) has activation energy was reported lower, 35 kJ mol^{-1} and CTMAB/10SSTA–MMT (Chen et al. 2011) as 4.5 kJ mol^{-1} that are than by PEI-Cu(II) system.

There are also reports that some reaction has higher activation energies, e.g., Fenton-like reaction catalyzed by natural schorl ($NaFe^{2+}{}_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$) (Xu et al. 2014) has higher activation energies, 51.3 kJ mol^{-1}. Also, in comparison of rate constant of MO degradation, the kinetic constant of by PEI-Cu(II) is higher than CNTs/TiO_2 under sono–photo–catalysis, P25 powder (Wang et al. 2009), hetereopolyacid ($H_{14}[NaP_5W_{30}O_{110}]$)/$SiO_2$ nano particles (Bamoharram et al. 2009), CuS incorporated into an Iranian clinoptilolite (CuS–Cp) (Nezamzadeh-Ejhieh and Moazzeni 2013), CdS/CNTs/UV light, and S-TiO_2/solar light (Jiang et al. 2012). Therefore, the simplicity of the procedure, and the ease of catalyst preparation and versatility and practicality make PEI-Cu(II) based catalyst system very attractive in comparison to the other techniques.

3.2. Epinephrine Oxidation to Adrenochrome using PEI-Cu(II)/H_2O_2

Epinephrine is a catecholamine, susceptible to peroxide attack, and can be partially oxidized to the industrial pink product, adrenochrome as illustrated in Scheme 1.



Scheme 1. Schematic representation of epinephrine oxidation with H_2O_2 over Co^{II}–P(EI) catalyst

As Co(II)–based heterogeneous catalysts are oxidized by H_2O_2, they can eventually form cobalt intermediate species ([(HOO)–Co(III)]) possessing catalytic properties. There are several reports with spectroscopic evidence about this intermediate formation (Jiang et al. 2012). The progress of the oxidation reaction in the presence of hydrogel containing cobalt ions was followed by UV–Vis spectrophotometer. The oxidation reaction kinetics of EP was investigated accordingly as an increase of peak intensity at 502 nm. As illustrated in Fig. 5, the UV–Vis spectra for the oxidation of EP measured at every 2 min after the addition of PEI-Co(II) hydrogel composite catalyst to reaction medium in order to follow the progress of the oxidation reaction. In the absence of a catalyst, the oxidation of epinephrine by H_2O_2 was practically negligible. Another control experiment was performed with epinephrine and PEI-Co(II) hydrogel in the absence of H_2O_2 that exhibited some extent of catecholamine oxidation, being less efficient than the oxidation by H_2O_2.

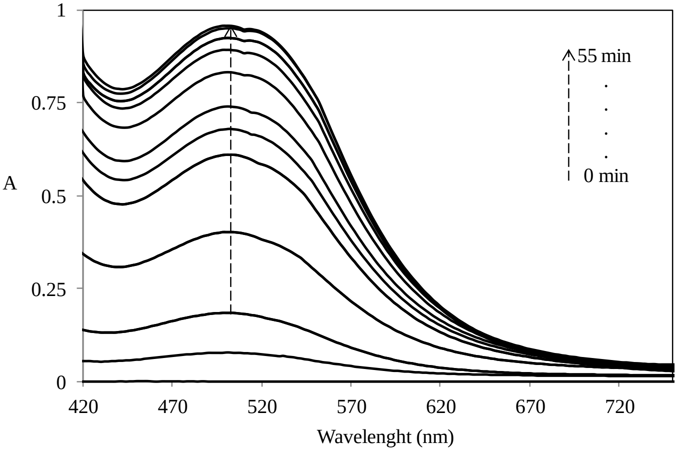


Fig. 5. The change in the absorbance of Epinephrine (EP) with time catalyzed by PEI-Co(II). [PEI-Co(II) = 60 mg), and EP =2 mM, and H_2O_2 = 46 mM at 30 ºC].

The effect of the amounts of catalyst on the oxidation of EP was investigated and the results were demonstrated in Fig. 6-a. It is obvious that the activity of PEI-Co(II) heterogeneous catalyst system for EP oxidation increases with increasing catalyst amount from 20 mg to 40 mg, but further increase in the amount of catalyst, the conversion of EP oxidation was decreased. This behavior could be attributed to the fact that with increasing amount of catalyst may be due to decreased concentrations of the reactant absorbed on the catalyst particles under these conditions (Farzaneh et al. 1999; Maury et al. 2012).

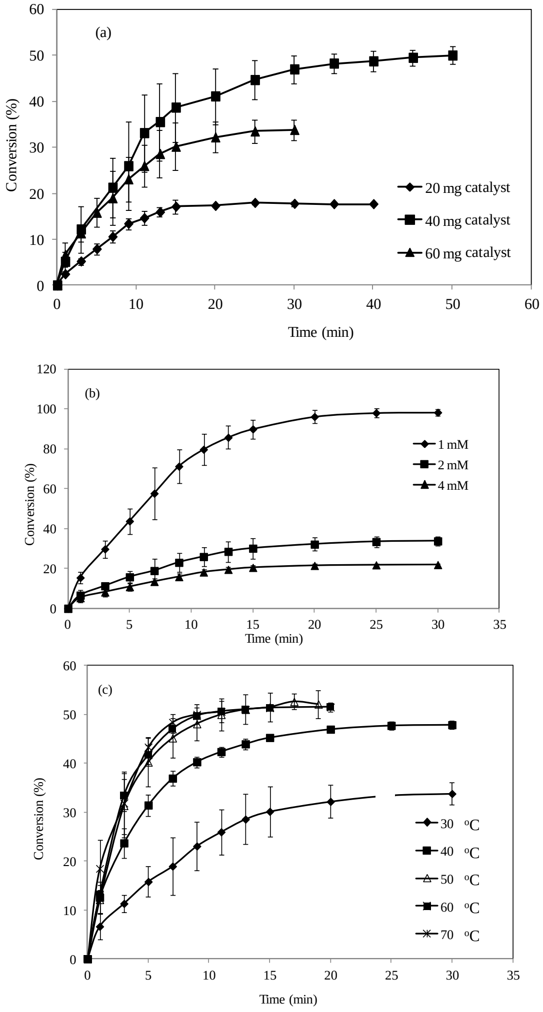


Fig. 6. Epinephrine conversion in the presence a) different amount of PEI-Co(II) catalyst, b) different concentration of epinephrine (EP), c) at different temperatures.

The effect of EP concentration in the oxidation reaction catalyzed by PEI-Co(II)/H_2O_2 catalyst system was also investigated. The amount of EP increased from 1 to 4 mM as shown in Fig. 6-b, and the calculated percentage of EP conversion decreased from 98 to 22% under the same reaction conditions. This phenomenon can be explained as same as initial concentration effect in EP degradation. There reports that the EP conversion in Co(II)–poly(EGDE-DA) (Victoria et al. 2014) and 46 mM H_2O_2, Co(II)–Poly(EGDE–MAA–2MI) complex (Lupanoa et al. 2013) are lower than PEI-Co(II)/H_2O_2 catalyst systems (60 mg catalyst, 42 mM H_2O_2 and 1 mmol EP) catalyst.

A temperature range of 30-70 °C for EP oxidation catalyzed by PEI-Co(II) catalyst system was studied to investigate the effect temperature. As illustrated in Fig. 6-c, the oxidation of EP is increased with increasing reaction temperature from 30 to 50 °C, and at higher temperatures the oxidation rate constants were also increased as given in Table 2, and this increase is slowed at higher temperatures as the rate constants changed less at the reaction temperatures of 50, 60 and 70 °C.

Again, to determine the reaction kinetics for EP oxidation by PEI-Co(II), the $\ln(C_t/C_0)$ versus time plot was constructed as shown in Fig. 7, and good linear correlation of $\ln(C_t/C_0)$ versus time plot confirmed the pseudo-first-order rate kinetics.

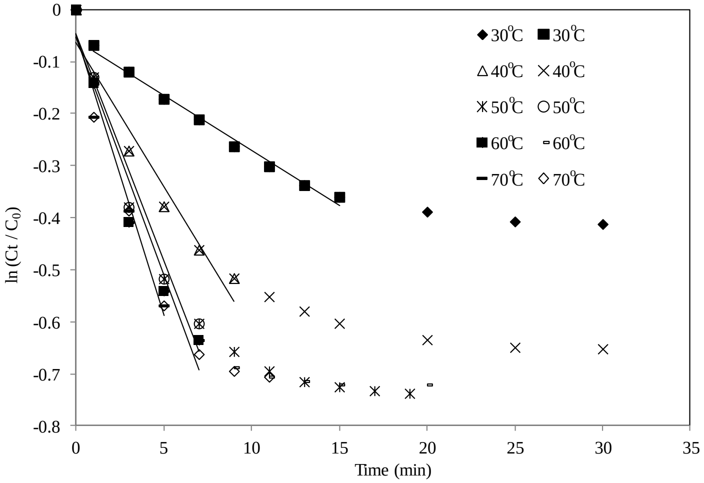


Fig. 7. The effect of temperature on ln(Ct/C0) with time.

The pseudo-first-order rate constants (*k*) and correlation coefficients (R^2) for EP are given in Table 2. As expected, the *k* values were increased as the reaction temperatures were increased. The kinetic measurements have revealed that EP oxidation catalyzed by PEI-Co(II) catalyst systems the pseudo-first-order kinetics. Also, it can be assumed that EP oxidation catalyzed by PEI-Co(II) catalyst system is temperature dependent between 30-50, but it is independent from the temperature about 60 ^{o}C.

Table 2. The change in rate constants with temperature for the oxidation of EP in aqueous solution catalyzed by PEI-Co, and the correlation coefficient for lnC−t plots.

Temperature (°C)	*k* (min $^{-1}$)	R^2
30	0.021	0.99
40	0.055	0.951
50	0.086	0.956
60	0.091	0.952
70	0.108	0.969

Additionally, the activation parameters for EP oxidation from the reaction carried out at different temperatures were calculated from ln*k*– 1/T graph (data is not shown) using well-known Arrhenius equation. The activation energy for oxidation of EP catalyzed by PEI-Co(II) was found as 58.02 kJ mol^{-1}. In the literature, a catalyst that is used for oxidation of EP provide lower activation energy for EP oxidation that is l-dioxytetrakis(histidinato)dicobalt(II) complex (Rafiquee et al. 2014) with 40.92 kJ mol^{-1} which lower than activation energy of the reported catalyst system here; however; because of simplicity of PEI-Co(II) catalyst preparation, and versatility for different applications e.g., applicability for the other catalytic reactions, the presented catalyst system here possesses many advantages.

Conclusion

A chemically stable PEI-M (II) (M = Co, Cu) were synthesized and used in the catalytic treatment of MO and EP from aqueous environments. As most of the organic aromatic dyes such as MO are known to be toxic for the plants and living organism, here it was demonstrated that MO can be treated by decolorization using PEI-M (II) (M = Co, Cu) in wastewaters. The degradation of aqueous MO solution by PEI-Cu(II) hydrogel system is a rapid process, and can almost be completed in about 60 min. The PEI-

Cu(II) hydrogel complex can play two roles simultaneously: adsorption and catalysis as MO is negatively charges and PEI hydrogels are positively charged due to the quaternized amine groups (Victoria et al. 2014; Ozay et al. 2010) during the degradation process. Kinetic studies suggest that the degradation process of MO can be described by the pseudo-first-order kinetic model. Additionally, the it was demonstrated that PEI-Co(II) can be used as catalyst in oxidation of EP. Kinetic studies of EP catalyzed by PEI-Co(II) suggest that the degradation process can be described by the pseudo-first-order kinetic model. The activation energy for both MO and EP oxidation found to comparable with literature, and because of the simplicity of preparation of PEI-M (Cu(II), Co(II) here) and many more catalysts as M could be (Ni(II), Fe(II), Rh(II), Pb(II), and Cd(II) etc) other chemical reaction can be readily catalyzed. Therefore, PEI-M (II or III)) hydrogel composite catalyst system posses great potentials for the catalytic reactions of many different reactions.

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