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Insight Observation into Rapid Discoloration of Batik Textile Effluent by *in situ* Formations of Zero Valent Iron

(Pemerhatian Celik Akal pada Penyahwarnaan Pesat Efluen Tekstil Batik
dengan Pembentukan *in situ* Ferum Bervalensi Sifar)

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ABSTRACT

This study aimed to investigate the discoloration of textile effluent from batik industrial wastewater by Fenton oxidation process using Fe(II), Fe(III) and in situ formation of zero valent iron (Fe(0)). The controlled parameters indicate the Fenton oxidation reaction is ideal on effluent at pH5, concentration colour of 4005 mg/L Pt-Co units using 0.5 mg/mL of catalyst dosage to meet the regulation for Malaysian quality water standard. The optimization of Fe(0) precursors, Fe(II) shows a higher discoloration efficiency in comparison with Fe(III). The synthesized particles of Fe(0) shows a nano spherical structure in the diameter range of 20-70 nm, aggregated and into a chain-like formation. Subsequently, the performance of Fe(0) was improved up to 97% discoloration in comparison with 89% discoloration by Fe(II). Whereas, the in situ formation of Fe(0) in batik effluent shows a complete discoloration ascribable to higher reactivity than partially oxidized of synthesized ex situ Fe(0). On top of that, in situ Fe(0) performed at the expeditious reaction in less than five min. Additionally, the regeneration of Fe(0), Fe(II) and Fe(III) show a potential of catalyst recyclability up to three cycles of Fenton oxidation but with a tolerable reduction to 62.1% of effluent discoloration.

Keywords: Colour removal; Fe(0); Fenton oxidation; in situ nanoparticles; textile effluent; water remediation

ABSTRAK

Kajian ini bermatlamat untuk mengkaji penyahwarnaan efluen tekstil daripada air sisa industri batik melalui proses pengoksidaan Fenton menggunakan Fe(II), Fe(III) dan pembentukan in situ ferum bervalensi sifar (Fe(0)). Parameter terkawal menunjukkan tindak balas pengoksidaan Fenton adalah sesuai ke atas efluen pada pH5, warna berkepekatan 4005 mg/L Pt-Co unit dengan menggunakan 0.5 mg/mL dos pemangkin bagi memenuhi pengawalan piawaian kualiti air Malaysia. Pengoptimuman bagi pelopor Fe(0), menunjukkan Fe(II) memberikan penyahwarnaan yang lebih cekap berbanding Fe(III). Zarah Fe(0) yang tersintesis menunjukkan struktur nano bersfera berdiameter dalam julat 20-70 nm, terkumpul dan membentuk struktur seperti berantai. Kemudian, prestasi Fe(0) telah meningkat sehingga 97% penyahwarnaan berbanding 89% penyahwarnaan menggunakan Fe(II). Sementara itu, pembentukan in situ Fe(0) di dalam efluen batik menunjukkan penyahwarnaan lengkap disebabkan tindak balas yang lebih tinggi berbanding ex situ Fe(0) tersintesis separa teroksida. Malah, in situ Fe(0) terhasil pada tindak balas yang pantas dalam masa kurang lima minit. Tambahan lagi, penjanaan semula Fe(0), Fe(II) dan Fe(III) menunjukkan potensi pengitaran semula pemangkin sehingga tiga pusingan pengoksidaan Fenton dengan penurunan yang boleh diterima kepada 62.1% penyahwarnaan.

Kata kunci: Efluen tekstil; nanopartikel in situ; pengoksidaan Fenton; penyingkiran warna pemulihan air

INTRODUCTION

Batik, the traditional craftsmanship of textile in Malaysia has contributed major parts of the textile industry. Batik producer involves various smallholders mostly located on the west coast of Malaysia. Briefly, the processes of producing batik are categorized into four major stages, which comprise the cloth preparation, waxing, coloring process and dewaxing in boiled water. All these stages required a high amount of water especially during the coloring process (Ahmad et al. 2002). Traditional batik industry is mostly cultivated by small and medium enterprises and done by small-scale industry. This industry usually builds up the factories nearby the river with a

lack of awareness and without proper waste management system (Ramlee et al. 2014). Thus, neglecting proper treatment, the effluent discharges could lead to high release amount of dyes into the aquatic system (Kusic et al. 2006). While the limitation of effluent color as stated by the Malaysian Department of Environment are 100-200 Pt-Co unit (DOE 2011).

Textiles effluent known to have a complex aromatic compound comprises with variety of different structure of dyes chromophore (axo, anthraquinonic, indigoid, xanthene, arylmethane & phthalocyanine) and consequently affect discoloration efficiency especially on conventional biological treatment method (Birgani et al. 2016; Nawaz

et al. 2014; Pereira & Alves 2012). The excess of silicate, sodium and heavy metals especially in the azo dyes which is mostly used during the coloring process has been subsequently increasing the level of Si, Fe, Cu, Zn, Na and Pb in the batik effluent (Ahmad et al. 2002; Birgani et al. 2016; Ong et al. 2017). These aromatic compounds usually withstand under aerobic condition and incurred high maintenance expenses by conventionally wastewater treatments such as membrane filtration, electro-kinetic coagulation and adsorption by activated carbon (Birgani et al. 2016; Pereira & Alves 2012).

Alternatively, the advanced oxidation process (AOP) including ozonation, photocatalytic and Fenton oxidation known to generate active hydroxyl radicals ($\bullet\text{OH}$) for degradation of organic compounds (Ahmad et al. 2002; Khalik et al. 2015; Kusic et al. 2006; Lin & Chen 1997). Whereas, Fenton oxidation process has long been recognized in discoloration of textile effluents due to its feasibility process and low-cost reagents. While the main reaction of Fenton is comprised of the oxidation of iron ions by H_2O_2 in the generation of hydroxyl radical ($\bullet\text{OH}$) for the degradation of organic compounds. However, the generation of sludge after the process is the major drawback especially in the homogeneous phase (Duarte et al. 2013). Therefore, the utilization of heterogeneous Fenton oxidation by impregnated Fenton's reagent on the supported media and the formation of iron nanoparticles are expected to counter this separation obstacle (Pereira et al. 2006; Sun et al. 2006).

Nanoparticles of zero valent iron, Fe(0) has electromagnetic and electrostatic properties which will be useful in the separation and regeneration of the reactant (Chatterjee et al. 2010; Rosická et al. 2011). Fe(0) nanoparticles was reported excelled in various applications on account of large surface area and high reactivity (Santos et al. 2017). However, by considering the nano-sized and the prompt reaction of Fe(0), the oxidation process rates is likewise to be rapid and tend to form into iron oxides during preparation of the material (Feitz et al. 2005). While rapid aggregation of Fe(0) in the formation of the chain-like cluster also limiting its mobility towards the water to saturated porous media (Phenrat et al. 2007).

In this study, the discoloration technique for textile effluent was improvised by Fenton oxidation technology. Initially, the optimization condition of Fenton oxidation on batik effluent was controlled by Fe(II) and Fe(III) as Fenton reagents with different parameter conditions (concentration of reagents, pH effluents and initial concentration of effluent). The optimum precursor of Fe(0) was used as an indicator for *in situ* formations of Fe(0) in the batik effluent. The performance of the Fenton reagents was compared through the discoloration efficiency of batik effluent. The discoloration rates of Fe(II), Fe(III) and Fe(0) were monitored through degradation kinetics and predicted the mechanism of the reactions.

MATERIALS

A sample of batik effluent has been collected from one of batik industry units at Kelantan, Malaysia, nearby the Sungai Pengkalan Chepa. It has been selected as a collection station for this study. Sample effluent has been collected from the final reservoir (after coloring and washing processes) before it discharged into the river.

The color concentration was measured using a UV-Vis spectrophotometer equipped with sipper and peltier (Spectrum SP-UV 300SRB) at a λ_{max} of 200-600 nm. Standard calibration curves for the color concentration of batik effluent was followed from Pt-Co Color Reference Solution (HAZEN 500) (Merck, Darmstadt, Germany) and recorded in mg/L of Pt-Co units.

Stock solutions of Fe(II) and Fe(III) have been prepared from Fe_2SO_4 and FeCl_3 (Merck, Darmstadt, Germany). Fenton oxidation process was assisted by hydrogen peroxide, H_2O_2 (Merck, Darmstadt, Germany) and *in situ* formation of Fe(0) was synthesized by reducing agent of sodium borohydride, NaBH_4 (Merck, Darmstadt, Germany).

METHODS

EFFLUENT PRETREATMENT

In pretreatment study, diluted hydrochloric acid, HCl (Merck, Darmstadt, Germany) has been used to reduce the pH of the effluent. The initial pH of effluent has been changed to 3, 5, 7 and 9. The suspended solid generated in pretreatment stages were separated by centrifugation at 10,000 rpm for 15 min. The stock solution was kept in the refrigerator at 4°C until further use.

FENTON OXIDATION

A preliminary study on Fenton oxidation by Fe(II) and Fe(III) on batik effluent have been carried out as iron precursors for Fe(0) and the optimization condition of Fenton oxidation. Fenton oxidation kinetics study was conducted in a flask of 100 mL batik effluent at different pH solution (3, 5, 7, and 9). The concentration of batik effluent was diluted at 50, 25, and 12.5%. The effluent was treated with a series of Fenton reagents at different concentrations (0.05-0.1 mg/mL) and the assisted of 50 mM of H_2O_2 . The reaction was stirred at a constant speed of 300 rpm with a magnetic stirrer for 2 h at room temperature. Aliquots of solution (~0.2 mL) were withdrawn at identified time intervals and measured the color concentration of Pt-Co by UV-Vis spectrophotometer. Discoloration (%) of effluent is measured by determination of color concentration before and after Fenton oxidation using the following equation:

$$\text{Discoloration} = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of Pt-Co color references (mg/L), respectively.

While the preparation of colloidal Fe(0) as control sample was done by 1:2 weight ratio of iron and a reducing agent, NaBH_4 in 100 mL of ethanol with the addition of ethylenediaminetetraacetic acid (EDTA) for the stabilizer. The formation of Fe(0) was separated by centrifugation at 10,000 rpm for 15 min. The collected sample was washed and sonicated deionized water for 1 h to remove the excess ethanol. The sample was kept dried until further use. Likewise, the *in situ* formation of Fe(0) was done by similar iron to the NaBH_4 ratio of control sample in 100 mL of batik effluent, where the conditions of pH, temperatures and effluent concentration were followed by the previous optimization of Fe(II).

The recyclability of Fenton reagents was conducted by recollecting Fe(II), Fe(III) and Fe(0) after the first cycle of Fenton oxidation. In this study, 100 mL of treated batik effluent was centrifuged at 10,000 rpm for 15 min for the separation of the sludges after the first reaction. The recycle of Fenton reagents were done in batik effluent with a similar condition and assisted with 50 mM of H_2O_2 . Recyclability of Fenton reagents was measured with the comparison of color removal from the first three cycles of Fenton oxidation.

CHARACTERIZATIONS

The morphological structure of synthesized zero valent iron particles have been observed using field emission scanning electron microscopy, FESEM (Merlin Compact, Zeiss Pvt. Ltd., Oberkochen, Germany) and transmission electron microscopy, TEM (CM 12 Philips, Eindhoven, Netherlands).

RESULTS AND DISCUSSION

OPTIMIZATION OF FENTON OXIDATION

The effluent collected shows the typical aspect of textile effluent given the COD, BOD_5 and Pt-Co units color concentration of 6,127, 205 and 8,011 mg/L, respectively. The pH of the effluent showed high alkalinity level (pH10.4) indicates the excessive use of basic dyes during the coloring process. Whereas, due to the high alkalinity of effluent, chromophore groups in the effluent became more complex to decompose. As the effluent pretreatment, the acidification of batik effluent has been carried out by reducing the pH of the effluent from pH 10.4 to pH 3. The pretreated effluents were observed to have agglomeration particles and flocculated wax. While the acidification pretreatment shows a small reduction in the spectrophotometer absorbances with the decrement of pH effluent (Figure 1(a)). The significant peak at 515 nm represents the chromophore components of the color in the effluent (Khalik et al. 2015). Hence, the color concentration has been reduced as well to 7378.7, 6509.3, 6442.7 and 6207.3 mg/L Pt-Co units for pH 9, 7, 5 and 3, respectively. Besides, a preliminary oxidation reaction on the effluent

has been performed as a reference in Fenton oxidation study. The oxidation reaction of the effluent already occurs at 50 mM of H_2O_2 with the discoloration of 14.4%. This owing to the level of Fe in batik effluent was considered significantly high (0.3-3 ppm) which has been reported in the previous study (Birgani et al. 2016; Ong et al. 2017). In general, the generation $\bullet\text{OH}$ of through H_2O_2 decomposition without the existence of catalyst (Fe^{2+} or Fe^{3+}) will slightly occur at a prolonged reaction (Jung et al. 2009). Thus, the small composition of Fe ions in the effluent might incur the Fenton oxidation reaction.

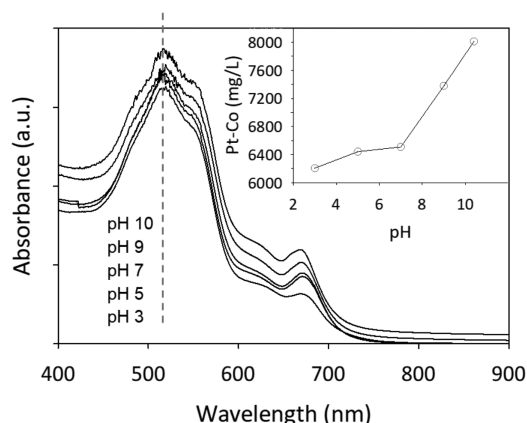
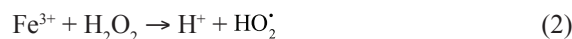


FIGURE 1. Discoloration of batik effluent shows by declining spectrophotometer spectrum and reduction of color concentration at different pH effluent

The effect of Fe(II) and Fe(III) (ferrous and ferric) concentration shows the staggering performance of discoloration with the higher concentration of Fenton reagent (Figure 2(a) and 2(b)). Since the Fenton oxidation is dependable on Fe(III) to Fe(II) formation and closely related to hydroxyl radical $\bullet\text{OH}$ shows in (2) - (7) (Kusic et al. 2009). By the additional Fenton reagents, it has correspondingly increased the Fe^{2+} ions in the effluent, hence enhance the degradation of the color compound in batik effluent (Abou-elela et al. 2016).



The effect of pH effluent shows that the Fenton oxidation reaction is greatly dependent on the acidic condition of effluent (Figure 2(c)). Both Fe(II) and Fe(III) gave the highest efficiency at pH 3 by 83.9 and 76.8%

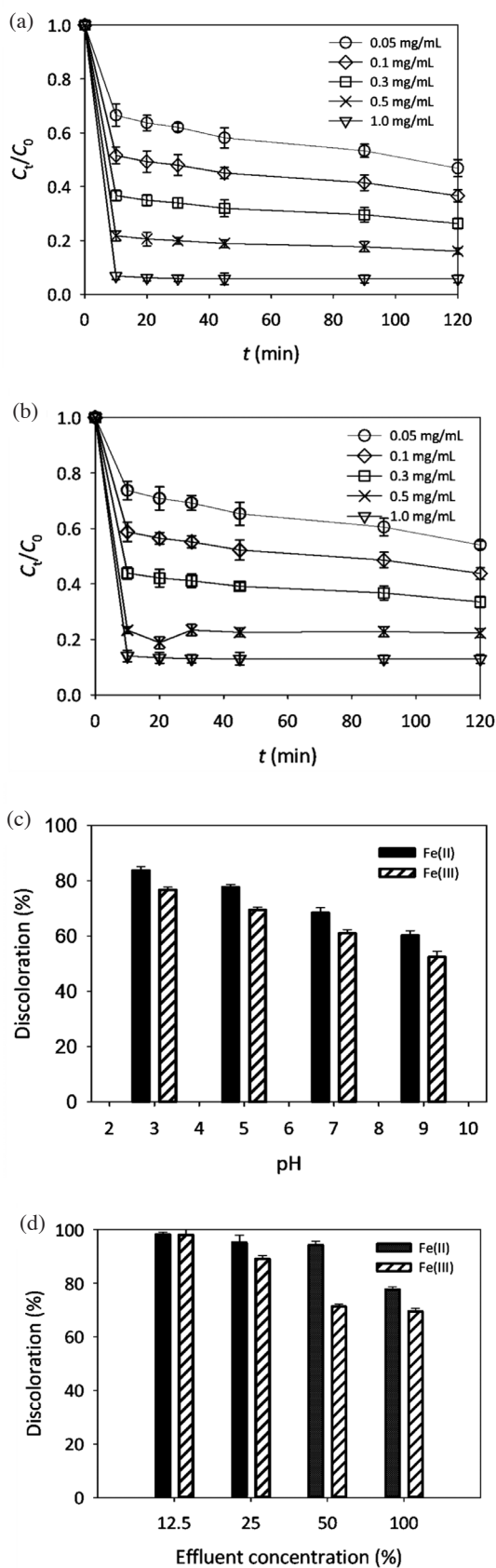


FIGURE 2. Discoloration kinetics of batik effluent at (a) different concentration of Fe(II), (b) different concentration of Fe(III) and the effects of (c) pH effluent and (d) batik effluent concentration for Fe(II) and Fe(III) (Fe(II): 0.05-1 mg/mL; pH: 3-9; fixed H_2O_2 : 50 mM)

discoloration, respectively. Theoretically, the optimum rates of $\bullet OH$ generation by homogeneous Fenton oxidation reaction take place in acidic condition (Duarte et al. 2013). The optimum pH of 3 has been frequently reported for Fenton oxidation activity (Ertugay & Acar 2017; Lin & Chen 1997; Mesquita et al. 2012). On the contrary, the high pH solution inhibited the catalytic reaction of Fe^{2+} as a result of the Fe^{3+} complex molecules formation (Wu et al. 2010). The high alkalinity of batik effluent will contribute to the transformation of iron to $Fe(OH)_3$ and selectively decompose H_2O_2 to oxygen (Pereira & Alves 2012). However, the discharge of treated effluent at pH3 can be harmful to the environment unless the solution is treated to standard pH before discharge. Thus, in the further study, pH5 is selected to be constant variable for other manipulating parameters to meet the regulation for Malaysian standard (DOE 2011).

Furthermore, the effect of color concentration through a series of effluent dilution was tested to evaluate the ability of Fe(II) and Fe(III) at a lower color concentration (Figure 2(d)). As in the previous condition of Fenton oxidation (0.5 mg/mL at pH5), Fe(II) and Fe(III) are capable to remove 77.8 and 69.5% of colour. Subsequently, at the lower color concentration, the removal of color was increased significantly up to 98.2 and 98.1% of discoloration and which is equivalent for 125 and 132 mg/L Pt-Co for Fe(II) and Fe(III), respectively. In this condition, more $\bullet OH$ was available and sufficient to decompose dyes, thus gave higher removal efficiency (Ertugay & Acar 2017).

CHARACTERIZATION OF COLLOIDAL Fe(0)

The morphology of colloidal Fe(0) was examined by FESEM and TEM was shown in Figure 3. In the FESEM micrograph observation, the shapes of colloidal Fe(0) particles are spherical and they were existed in contact with each other and agglomerated. Since the preparation of Fe(0) was synthesized by EDTA as an oxidation inhibitor for decelerated of iron oxide formation, the existence of polymeric structures and the rough surface can be seen distributed around colloidal Fe(0) particles. However, the high reactivity of Fe(0) nanoparticles contributed in size transformation of FeOOH. High distribution of larger particles (~ 300 nm) shows the oxidation of Fe(0) has promptly occurred with the interaction with an aqueous medium (Torrey et al. 2015).

While TEM image of colloidal Fe(0) particles (Figure 3(b)) was measured immediately after being synthesized. The micrograph image shows a nanosphere particle with the diameters is in the range of ~ 20 -70 nm and can be distinguished from each particle (Santos et al. 2017; Sun et al. 2006; Zhang et al. 2013). In the closer inspection of the TEM image, the metallic iron and iron oxide phases can be distinguished from the corresponding color contrast. The lighter regions are mainly on the surface of the particle and the dark regions are concentrated in the center of the particle. The elements with higher atomic numbers seem darker than the ones with lower atomic numbers, where

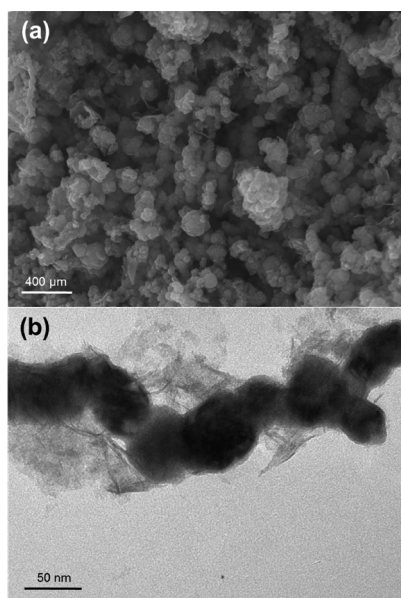


FIGURE 3. Micrograph images of nano-spherical of Fe(0) from (a) FESEM and (b) TEM analyses

the core is formed of metallic iron and the surface (shell) is formed of iron oxides (Yuvakkumar et al. 2011). Moreover, the linear orientation and aggregation of Fe(0) is nearly due to the magnetic properties of iron species (Rosická et al. 2011). These formations are expected to form in a short period of time after the synthesized, which could limit the mobility of the nanoparticles (Phenrat et al. 2007; Sun et al. 2006). Unlike its precursor, Fe(0) also has the potential to generate H_2O_2 and Fe^{2+} when consuming oxygen and hydrogen (Feitz et al. 2005).

EFFLUENT DISCOLORATION BY *In Situ* Fe(0) FORMATION

In theory, the transformation of Fe(0) was promptly oxidized to $FeOOH$ and $Fe(OH)_3$ in a short time exposure to an aqueous medium (Torrey et al. 2015; Zhang et al. 2013). Thus, in order to identify the scavenging reactivity of Fe(0) toward the batik effluent, colloidal Fe(0) were synthesized with different formation times of 5 and 10 min (5-Fe(0) and 10-Fe(0)) and reacted to effluent. As an alternative, *in situ* formations of Fe(0) was synthesized in the batik effluent.

Figure 4(a) shows a significant discoloration efficiency in comparison with different Fenton reagents after 10 min of reaction. The initial retention time on Fenton oxidation for Fe(II), Fe(III), 5Fe(0) and 10Fe(0) are starting to remove the color up to 78.2, 63.3, 82.1, and 75.4%, respectively. While *in situ* formations of Fe(0) shows slightly higher discoloration efficiency at 95.9%. Figure 4(b) shows in the insight discoloration kinetics of effluent for the first 120 s. This is due to the *in situ* formation method which could contribute on higher efficiency and the mobility of Fe(0) for degradation organic substance, hence reducing the preparation cost of stable colloidal Fe(0) (Phenrat et al. 2007). Meanwhile, despite the additional stabilizing

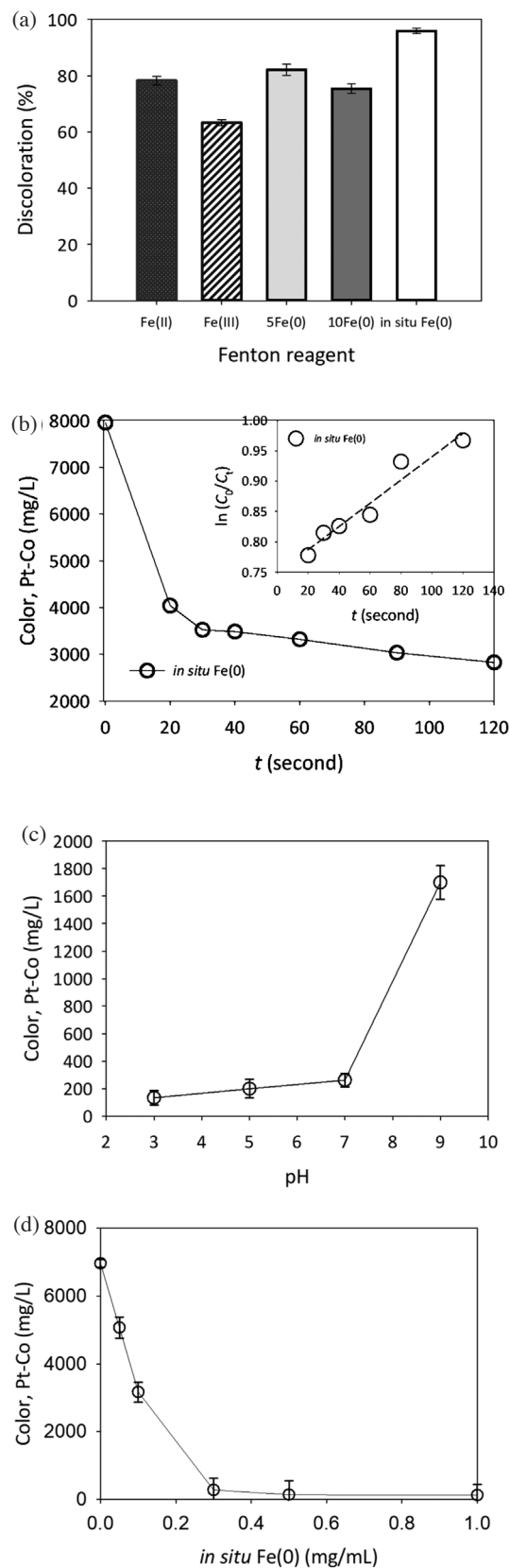


FIGURE 4. The discoloration efficiency (a) after 10 minutes reaction of Fe(II), Fe(III), *ex situ* 5Fe(0) and 10Fe(0) and *in situ* Fe(0), (b) in-depth kinetics reaction of *in situ* Fe(0), the effect of (c) pH and (d) Fe(0) concentration (Fenton reagents: 0.5 mg/mL; Effluent: 100 mL; pH: 3-9)

agent of EDTA during preparation of the colloidal Fe(0), the oxidation of Fe(0) in the generation of iron oxide or hydroxide oxide is still likely to occur due to the nature of Fe(0) (Feitz et al. 2005; Yuvakkumar et al. 2011). The short-life of hydroxyl radical generated by the Fenton oxidation reaction has been a massive limitation on the removal of the target compounds (Jung et al. 2009).

The effect of *in situ* formations of Fe(0) towards effluent discoloration has been observed by different parameters based on the previous condition of Fe(II) and Fe(III). The influence of initial pH towards the effluent discoloration shows a comparable outcome by Fe(II) and Fe(III) (Figure 4(c)). At low initial pH between pH 3 to 5, a higher concentration of H⁺ has led to higher decomposition of dyes (Feitz et al. 2005). However, the interaction between Fe(0) and organic dyes in the effluent is more complex due to the formation of an oxidized layer of Fe(0). Poor discoloration efficiency at higher initial pH could be due to the inefficient reaction of oxidized Fe(0) and the adsorption-repulsion reaction of dyes on the surface of oxidized Fe(0). Since the oxidation of Fe(0) could lead to FeOOH, the alkalinity of the effluent could cause the negative surface charges and reduced the interaction between Fe(0) and dyes (Chatterjee et al. 2010). Moreover, high concentration of Fe(0) shows a distinct improvement of effluent discoloration up to 98.6% (95.1 mg/L Pt-Co) by 1.0 mg/mL of Fe(0) (Figure 4(d)). This can be attributed to the important ratio of dye molecules and Fe(0) towards the equilibrium reaction of Fenton oxidation (Pereira et al. 2006).

REGENERATION OF FENTON REAGENTS

In consideration of the catalyst regeneration, the advantageous of recycling Fenton reagents have been performed by using sludge collected from the first reaction for a few cycles of batik effluent discoloration (Figure 5). As a result, the Fenton oxidation efficiency up to third cycle reaction has been consistently removing the color up to ~87.1 and ~83.9% for Fe(II), respectively. However, the sludge from the first *in situ* formation of Fe(0) could not perform well after the sequences process and reduced drastically on the second and third cycle of the reaction by 96.6 to 62.1% of discoloration. The ferric sludge might incur the generation of ferric-hydroperoxo intermediate (Fe(HO₂)²⁺) which capable to degrade selective organic compound directly (Bolobajev et al. 2014). In contrast to Fe(II) and Fe(III), the Fe(0) sludge after the first cycle of reaction shows a similar condition as oxidized Fe(0), which generate iron oxide or hydroxide oxide and decrease the efficiency after sequence cycle (Feitz et al. 2005; Yuvakkumar et al. 2011).

CONCLUSION

In conclusion, the adaptation of the simultaneously synthesized Fe(0) in textile effluent demonstrated a rapid discoloration in comparison to conventional ferric

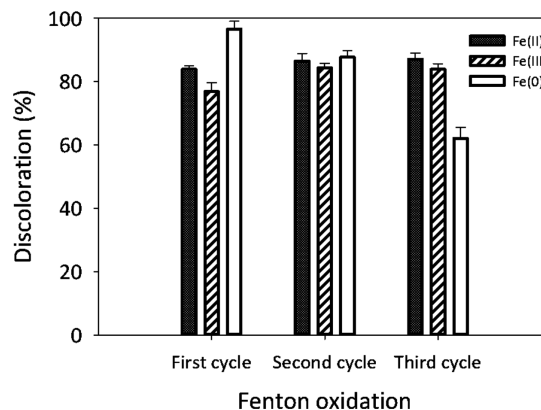


FIGURE 5. Cycles of Fenton oxidation on batik effluent discoloration using sludge formation from Fe(II), Fe(III) and *in situ* Fe(0) from first Fenton oxidation (Fenton reagent: 0.5 mg/mL; Effluent: 100 mL; pH: 5; fixed H₂O₂: 50 mM)

and ferrous in Fenton oxidation system. Meanwhile, the discoloration of the effluent through the synthesized Fe(0) was improved up to 95.9% after 10 min of the reaction, which is significantly higher in comparison with Fe(II) and Fe(III) which presented 78.2 and 63.3% discoloration, respectively. The expeditious transformation of *ex situ* Fe(0) to iron oxide or hydroxide oxide has been resulted in the diminished generation of hydroxyl radical and cut down the full potential of Fe(0). Thus, *in situ* formations of Fe(0) provided better performance without delay. However, due to the oxidation process, the regeneration of Fe(0) decline significantly after the first cycle of discoloration which limits the recyclability of the Fenton reagent.

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