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Catalytic Degradation of Phenol Using Different Chelating Agent at Near Neutral pH in Modified-Fenton Process

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$\mathbf{F}$ ENTON'S reagent is a mixture of ferrous iron catalyst and hydrogen peroxide, used for oxidation of organic compounds in acidic medium. As the pH increases, the iron ions precipitate and diminish the oxidative efficiency of Fenton reaction. We selected different chelating agents [glutamic acid (Glu), citric acid (CIT) and sodium citrate (SC)] that form Fe-chelates soluble in neutral pH (Modified-Fenton) for studying its effect on phenol degradation. The results revealed that the rate of degradation by Glu, CIT and SC iron chelates were 73, 60 and 77%, respectively, in short term experiments (3hr). In the long term experiments (24hr), the degradation was increased to 82, 72 and 86%, respectively.

Keywords: Phenol, Modified Fenton (MF), Hydrogen peroxide, Degradation, Glutamic acid (Glu), Advanced oxidation processes (AOPs), Citric acid (CIT) and Sodium citrate (SC).

Treatment of wastewater containing phenolic compounds has been of great concern all over the world due to their toxicity[1]. The high usage/production of phenol in industry and its stability in the environment make it an important target for water treatment. Due to the stability of phenol, its removal with traditional methods is difficult. Various alternative treatment technologies have been developed over the last two decades in order to cost-effectively meet environmental regulatory requirements, some of which are advanced oxidation processes (AOPs).

Advanced oxidation processes (AOPs) have already been used for the treatment of wastewater containing hazardous and recalcitrant organic compounds such as pesticides, surfactants, pharmaceuticals and endocrine disrupting chemicals. They have also been successfully used as pretreatment methods to reduce the concentrations of toxic organic compounds that inhibit biological wastewater treatment processes[2]. A great number of methods are classified under the broad definition of AOPs based on the oxidizing agents applied. Most of them use a combination of strong oxidizing agents (*e.g.* H_2O_2, O_3) with catalysts (*e.g.* transition metal ions) and irradiation

(*e.g.* ultraviolet, visible). Among these methods, the Fenton process has been one of the most popular technologies for wastewater treatment[3-8]. However, the Fenton process produces a large amount of ferric hydroxide sludge at higher pH, which requires additional separation and disposal[9]. The disadvantages limit the further application of the Fenton process in treating wastewater. Therefore, a number of ligands as (amino acids and carboxylic acid) can be used to form ferric chelates that are soluble at near neutral pH, were used for mediating the transformation and mineralization of organic contaminants in polluted water under neutral conditions[10]. However, active chelators must be active and stable in such strong oxidizing media[11]. This adaption of conventional oxidation is known as the modified-Fenton[12]. Paciolla *et al*[13] confirmed that iron-sorbed humic acid produces OH through the reaction with H_2O_2. Complexes of Fe^{2+} fulvic acid increase the Fenton's reaction rate at pH 5, consuming more H_2O_2 than without fulvic acid[14]. Among the chelating agents studied, ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) were effectively activating hydrogen peroxide at near neutral pH. However, the hazardous effects of these two chelating agents were highlighted and their applicability for environmental applications has been gradually reduced. Therefore, there is a need for development of environmentally safe and highly effective chelating agents.

Organic acids can be applied as chelating agents because these acids contain a high density of functional groups, which can conjugate metal ions to form ion complexes. The acids can enhance the effectiveness of Fenton's reaction by providing an iron source and by creating proximity between the catalytic iron and organic contaminants for the reaction[15]. The focus of this study is to investigate using of different chelating agents (CIT, SC and Glu) to improve the Fenton reagent for making the degradation reaction of phenol at neutral pH.

Materials and Methods

Reagents

Phenol was provided from Aldrich (99.9%), citric acid (CIT), sodium citrate (SC), Hydrogen peroxide (30%W/V) from ADWIC (99%), Glutamic Acid (Glu) from Fluka (99 %).

Methods

Modified-Fenton experiments

Glu, CIT and SC solutions were prepared by dissolving the appropriate amount of the acid in deionized water that was adjusted to pH 11 by adding 0.1M NaOH. Hydrogen peroxide (H_2O_2) Concentration (30%) was justified iodometrically by titration with 0.1M $Na_2S_2O_3$, ($Na_2S_2O_3.5H_2O$).

Analysis

Monitoring of phenol degradation was performed with a high performance liquid chromatography instrument (HPLC) equipped with a pump Waters 515, a

sample injector and an UV/Visible Waters 2489. System was controlled by Milleniumv®32 Chromatography Manager (version 3.20).

XBridge C18 (0.5 μm, 6.4m×250 mm) Column was used. The mobile phase was constituted by acetonitrile/water in the volumetric proportion of 30:70 with a flow rate equal to 1ml/min. Detection wavelength for each product was fixed after examination of 3D plot (time, intensity, wavelength). HPLC chromatograms are visualized and integrated on Millenium software (version 3.2).

Oxidant quantification

In selected experiments, Hydrogen peroxide (H_2O_2) concentration (30%w/v) was justified iodometrically by titration with 0.1M $Na_2S_2O_3$, ($Na_2S_2O_3.5H_2O$).

pH control and measurement

Solution pH was recorded using a pH meter (MP120, Mettler-Toledo Gmbh; Schwerzenbach, Switzerland).

Results and Discussion

Fenton reaction

Effect of Fe^{2+} concentration

To inspect the effect of Fe^{2+} concentration on phenol (1.06 mM) degradation we conducted the experiments in presence of 1, 2.5 and 5mM of Fe^{2+} with 30 mM H_2O_2, at room temperature and pH 2.9. The results showed that increasing the Fe^{2+} concentration has a negative effect on the rate of phenol degradation, *i.e.* the rate decreases as the Fe^{2+} concentration increases (Fig. 1). The results of phenol degradation via Fenton reaction, furthermore, appear to show dependence on reaction conditions.

The reaction between Fe^{2+} and H_2O_2 produces a sufficiently $^{\bullet}OH$ within a short period (k=63M^{-1} s^{-1}). The lifetime of the hydroxyl radical is determined by its reactions with phenol (k = 1.8×10$^{10}M^{-1}$ s^{-1}) and other present $^{\bullet}OH$ scavengers: Fe^{2+} (k = 4.3×10$^8M^{-1}$ s^{-1}) and H_2O_2 (k = 2.7×10$^7M^{-1}$ s^{-1})[16].The fraction of OH that reacts with phenol ($f_{^{\bullet}OH,ph}$) can be expressed by Eq. (1), similar to that proposed by Lee and Sedlak [17].

$$f^{\bullet}_{OH,ph} = \frac{k^{\bullet}_{OH,\,ph}[ph]}{k^{\bullet}_{OH,\,ph}[ph] + k^{\bullet}_{OH,\,H2O2}[H_2O_2] + k^{\bullet}_{OH,\,Fe}[Fe^{2+}]} \qquad (1)$$

Considering that [ph] is constant, then the major variables are [H_2O_2] and [Fe^{2+}] which may control the change in $f_{^{\bullet}OH,ph}$. However, despite [H_2O_2] will change with change in Fe^{2+} concentration, yet its lower rate constant of reaction with $^{\bullet}OH$ than that of Fe^{2+} makes the change in [Fe^{2+}] more effective in $f_{^{\bullet}OH,ph}$ specially in case of higher Fe content. Therefore, since the available Fe^{2+} ions to

act as $^{\bullet}$OH scavenger will increase with the increase in $[Fe^{2+}]_o$ we can expect, according to Eq. (1), the decrease in $f_{\bullet OH,ph}$ with the increase in $[Fe^{2+}]_o$, and consequently a decrease in phenol degradation rate which explains the trend shown in Fig. 1. Yoon *et al.* [18] reported that when the Fenton reaction were initiated by a high concentration of Fe^{2+} (usually more than 1mM) a sufficiently $^{\bullet}$OH was produced with a short time. They indicated that under these conditions, the scavenging of $^{\bullet}$OH by Fe^{2+} becomes important at high $[Fe^{2+}]_o/[H_2O_2]$ ratio. Furthermore, at higher Fe^{2+} concentration, the formed Fe^{3+} could be expected to increase so that, due to very low reaction rate constant with H_2O_2 (reaction 3), the recycling of Fenton reaction is greatly slowed down resulting in a slower rate of phenol decomposition upon increasing Fe^{2+} concentration. Generally, the latter effect appears of lower significance than the scavenging effect, unless precipitation is clearly detected.
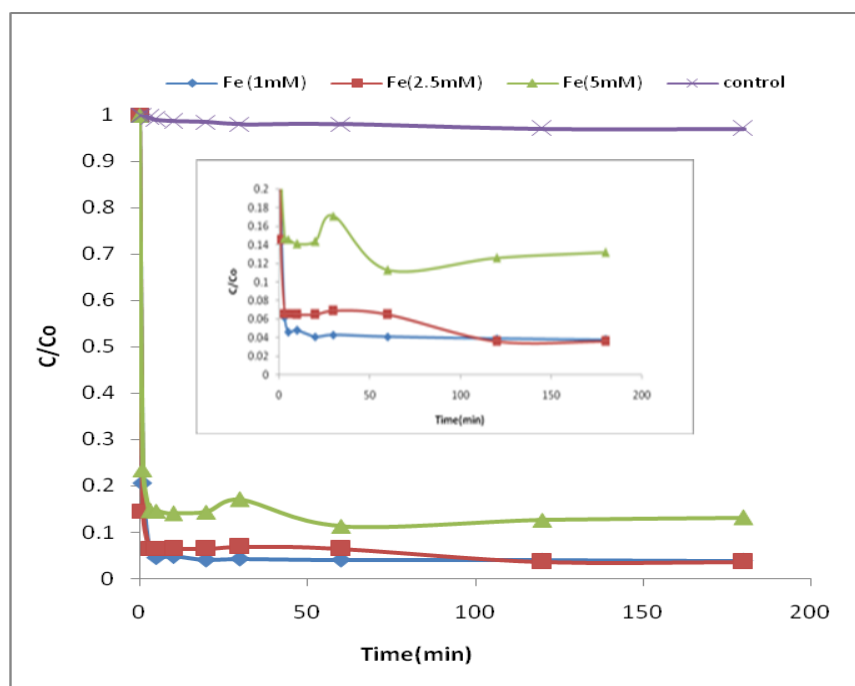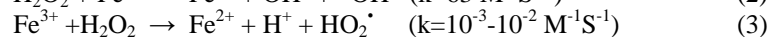
$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (k=63 \text{ M}^{-1}\text{S}^{-1}) \quad (2)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \quad (k=10^{-3}\text{-}10^{-2} \text{ M}^{-1}\text{S}^{-1}) \quad (3)$$
$${}^{\bullet}OH + H_2O_2 \rightarrow HOO^{\bullet} + H_2O \quad (4)$$
$${}^{\bullet}OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad (5)$$

Fig. 1. Effect of iron conc. in acidic medium 2.9, 30 mM H$_2$O$_2$.

Effect of pH

The result of phenol degradation, 1.06 mM, by Fenton reagent at different pH values in presence of 30mM of H_2O_2 and 1mM Fe^{2+} is shown in Fig. 2. It can be seen that both the degradation rate and efficiency have decreased with the increase in the working pH. Rapid degradation occurs initially because of an abundance of $^{\bullet}OH$ generated from H_2O_2 decomposition via reaction (2)[16]. The formed $^{\bullet}OH$ radicals from reaction (2) could rapidly degrade phenol through a reaction of rate constant 1.8×10^{10} M^{-1} s^{-1} [16]. Furthermore, the rate of the reaction between Fe^{2+} and H_2O_2 increases with increasing pH[19] and the formed Fe^{3+} in reaction (2) continues the cycle of Fenton reaction through further decomposition of H_2O_2 and regenerating Fe^{2+} (reaction 3)[16]. However, the lower rate constant of reaction (3) than reaction (2) makes the former the rate determining step. The decrease of phenol decomposition at pH value greater than 3 can be attributed to the controlling role of the formed Fe^{3+}. Furthermore, at pH value above 4 the dissolved fraction of iron species decreases as colloidal ferric species that form insoluble precipitates of amorphous Fe^{3+}-oxyhydroxides, which produce very low yields of oxidants from reaction with H_2O_2[20]. In addition, at neutral pH values, the reaction of Fe^{2+} with H_2O_2 does not always produce $^{\bullet}OH$. The oxidant formed at neutral pH value, the ferryl ion (Fe^{4+}) is capable of oxidizing short chain aliphatic alcohols and arsenite, but cannot oxidize aromatic compounds and other recalcitrant contaminants[17].
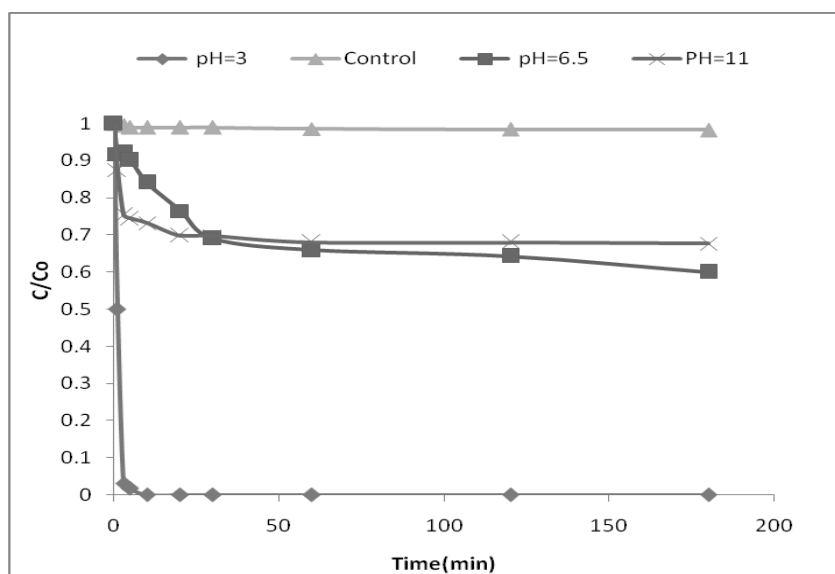

Fig. 2. Effect of pH on phenol degradation, phenol=100ppm, 30mM H_2O_2, Fe^{2+} =1mM.

Modified Fenton reaction

   To circumvent the drawback of working under acidic conditions, a number of ligands as (amino acids and carboxylic acid) can be used to form ferric chelates that are soluble at pH 6, were used for mediating the transformation and mineralization of organic contaminants in polluted water[10] under neutral conditions. The ligands (CIT, SC and Glu) were added as such to the reaction solutions with catalytic systems.

Catalytic degradation on phenol using Fe (II)/ Amino Acid / H_2O_2 systems

   Glutamic acid is used as ligands in the catalytic systems for the degradation of phenol as water pollutants with different concentration (0.5, 1 and 2 mM) as shown in Fig. 3. The result revealed that using 2mM of Glu is capable of more degradation of phenol than 0.5mM and 1mM. 70% degradation was obtained when using 2mM of Glu and this is due to the ability of Glu to form cyclic chelates with iron at neutral pH values or more. In case of iron, the formation of such chelate prevents the precipitation of Fe (III), produced in the course of Fenton's reaction.

   The marked increase in the degradation rate in presence of Glu may be explained as follows: Fe^{3+} ion produced from Fenton reaction (Eq. 2). The Fe^{3+} ion, when produced in solutions at pH 5-7, precipitates presumably as hydrous oxyhydroxide $Fe_2O_3.nH_2O$ [20]. However, in presence of glutamic the Fe^{3+}-amino acid complexes may be formed and then undergo dissociation via ligand to metal charge-transfer excitation[22, 23].

$$L - Fe^{3+} \rightarrow Fe^{2+} + L^{\bullet} \qquad (6)$$
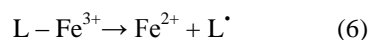
Or the following reaction:

$$L - Fe^{3+} \rightarrow Fe^{2+} + {}^{\bullet}OH \qquad (7)$$
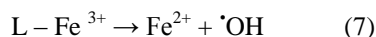
Thus, this dissociation may generate $^{\bullet}OH$ directly (Eq.7) or Fe^{2+} ion (Eq.6) which in turn reacts with H_2O_2 in the Fenton's reaction (Eq.5). In this concern reactions (Eq. 6, and Eq. 7) are known for a variety of carboxyl and hydroxyl containing ligands [23].

   Yehia *et al.* and Elshafei *et al.*[24, 25] reported that, the activity observed in case of glutamic acid may be attributed to the amino group (NH_2) which leads to the ease of formation and stability of its ferryl complexes in comparison with ascorbic acid. Thus, the formation of Fe^{3+}-amino acid chelates followed by dissociation to Fe^{2+} and $^{\bullet}OH$, may be considered as a rapid pathway for the reduction of Fe^{3+} to Fe^{2+}. However, without such ligands, Fe^{3+} is reduced in very slow step to Fe^{2+} (Eq. 3) as mentioned before.
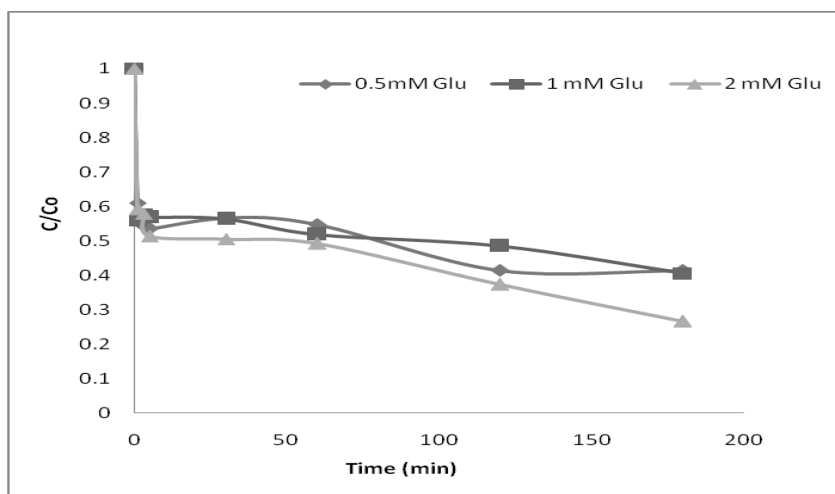
(Conditions: phenol=100PPM, pH= 6-7, H_2O_2=30mM, Fe^{2+} =1mM, Glu=0.5,1,2mM).

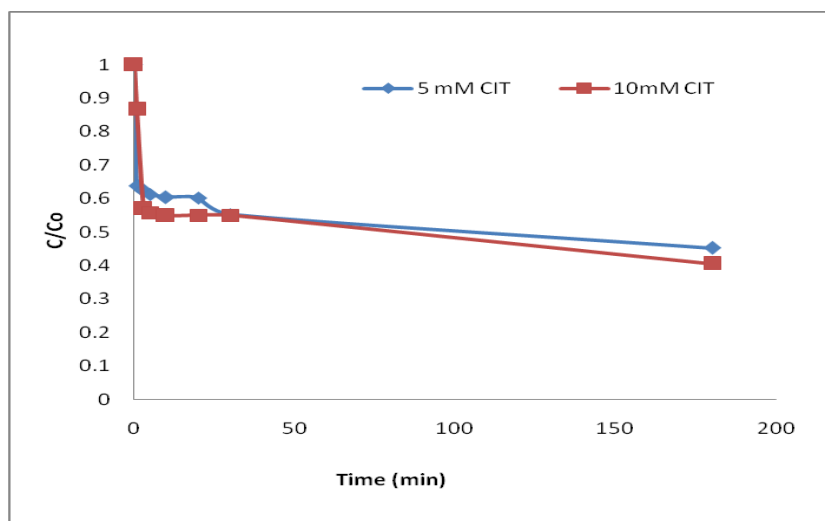**Fig. 3. Effect of different concentrations of Glu on degradation of phenol.**

Catalytic degradation on phenol using Fe (II)/Aliphatic Acid / H_2O_2 systems

Two ligands were used (CIT and SC) as in the catalytic systems for the degradation of phenol as water pollutants. These ligands can readily form cyclic chelates with iron at neutral pH values[26]. (CIT) is biodegradable, when injected to subsurface systems, it could be nutrient for microbes participating in biodegradation of contaminants, as well as an acidifying agent for the chemical oxidation[27]. (SC) was selected as a representative natural occurring organic chelating agent for this study mainly because of its environmentally friendly and readily biodegradable characteristics[26]. The results of degradation of phenol using two concentration of CIT (5 and 10 mM) are summarized in Fig. 4 and degradation by using SC (25 mM) is summarized in Fig. 5. The result revealed that 10 mM of CIT is capable of more degradation of phenol about 60% than 5mM degradation and SC 25mM of SC is capable of degradation of phenol; about 77% of phenol and that is due to the ability of CIT and SC to chelate metal ions and keep them in solution at neutral value of pH where the metals would otherwise precipitate[28].

Comparison between modified Fenton process using different chelating agents

Sodium citrate modified Fenton (SC-MF) treatment resulted in the highest phenol removal efficiency compared with CIT and Glu and that is shown in Fig. 6 and the results also are indicated by rate constant of three legends as shown in Fig. 7 and Table 1.

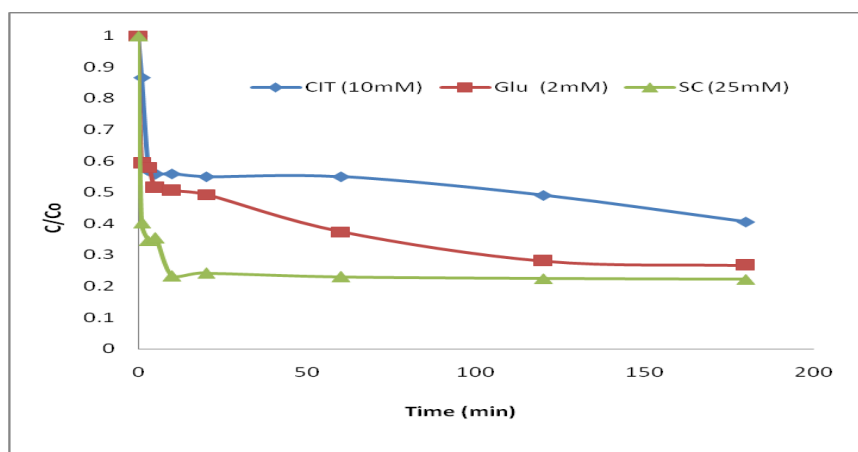(Conditions: phenol=100PPM, pH= 6-7, H_2O_2=30mM, Fe^{2+} =1mM, CIT=5,10mM)

Fig. 4. Effect of different concentration of CIT on degradation of phenol.
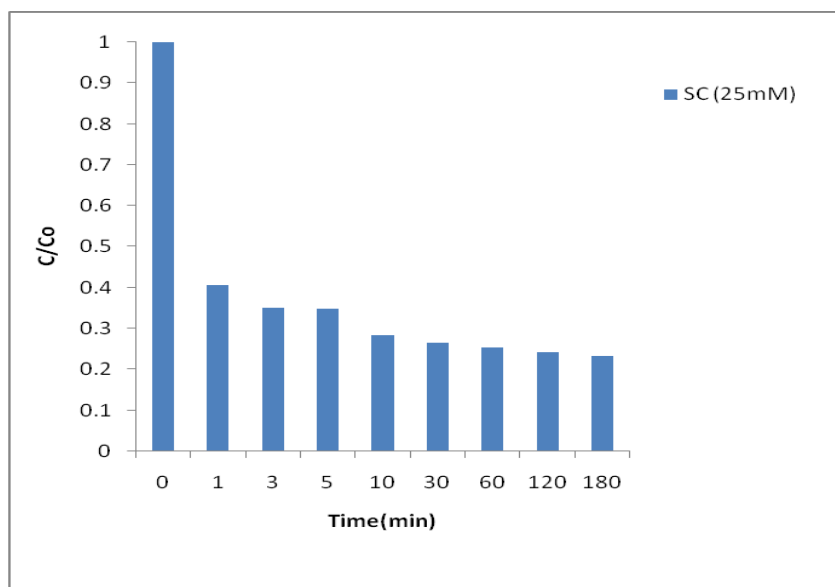
(Conditions: phenol=100PPM, pH= 6-7, H_2O_2=30mM, Fe^{2+} =1mM, SC =25mM)

Fig. 5. Effect of SC on degradation of phenol.

In long term experiment, the SC showed the highest degradation of phenol than Glu and CIT (86, 82, and 72%), respectively, as shown in Fig. 8. This is attributed to the slow H_2O_2 dissociation in case of SC[29]. This was presumably due to high reaction rate between this organic acid and ˙OH radicals (kSC/ ˙OH = $3.2 \times 10^8 M^{-1} s^{-1}$) at pH 6.6[29]. The rate of phenol degradation was increased gradually and continuously in case of SC more than Glu and CIT when the reaction was allowed to proceed to 24 hr which suggested that the application of SC-Fe^{3+} chelates is feasible for slow activation of H_2O_2 in removing recalcitrant pollutants such as phenol which needs a prolonged reaction time[30].
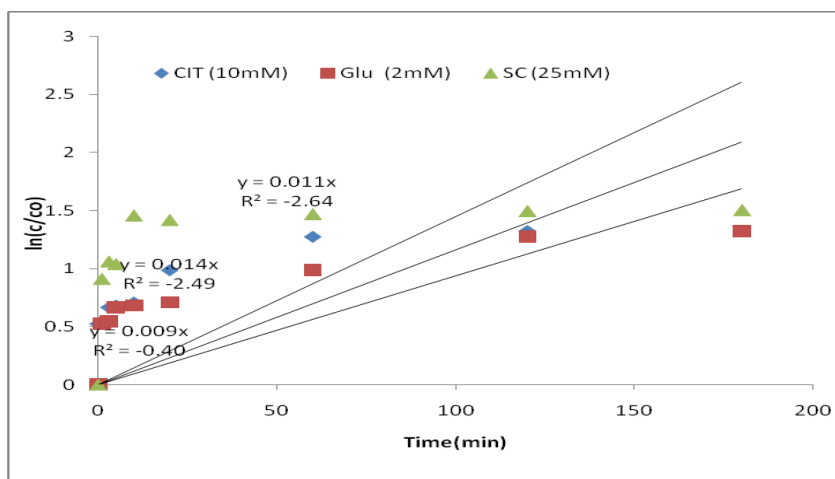

(Conditions: phenol=100PPM, pH= 6-7, H_2O_2=30mM, Fe^{2+} =1mM, Glu= 2mM, SC=25mM, CIT=10mM).

Fig. 6. Effect of different chelating agents on degradation of phenol.

TABLE 1. First order rate constant different chelating agent on degradation of phenol.

Concentration of Chelating agent	CIT=10 mM	Glu acid= 2 mM	SC= 25 mM
Rate constant (min^{-1})	0.006	0.009	0.011
Correlation factor (R^2)	-2.49	-0.4	-2.64

(Conditions: phenol=100PPM, pH= 6-7, H_2O_2=30mM, Fe^{2+} =1mM, Glu acid= 2mM, SC=25mM, CIT=10mM).

(Conditions: phenol=100PPM, pH= 6-7, H_2O_2=30mM, Fe^{2+} =1mM, Glu= 2mM, SC=25mM, CIT=10mM).

Fig. 7. Plot of Ln C/Co vs. time for phenol degradation by different chelating agents.
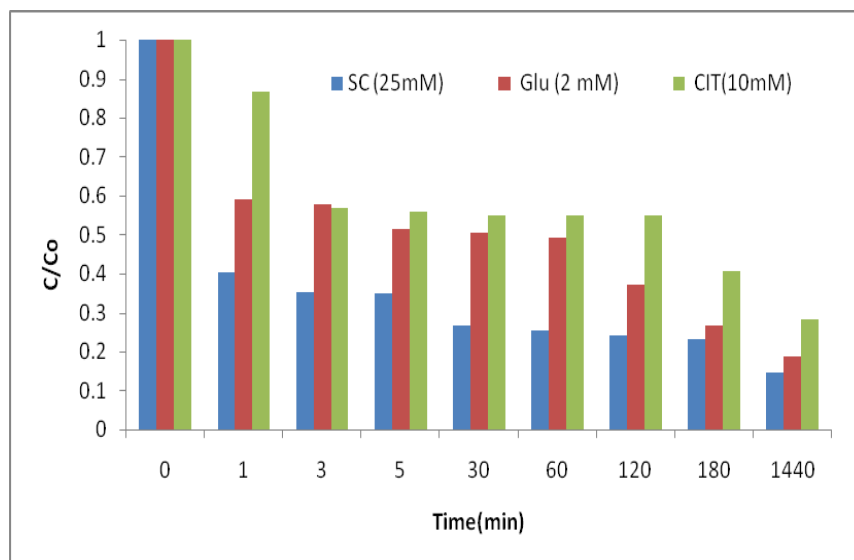
(Conditions: phenol=100PPM, pH= 6-7, H_2O_2=30mM, Fe^{2+} =1mM, Glu acid= 2mM, SC=25mM, CIT=10mM).

Fig. 8. Effect of different chelating agents on degradation of phenol in long term experiment.

Conclusion

In Fenton reaction, different concentrations of ferrous iron catalyst (1, 2.5 and 5 mM) were examined at acidic medium which revealed that 1mM of ferrous iron at 30 mM H_2O_2 gave the highest rate of phenol degradation without any chelating agent. By increasing pH value the rate of degradation was decreased due to the precipitation of Fe ion.

In modified Fenton, the effectiveness of the representative chelating agent Glu, CIT and SC in stabilizing ferrous iron at neutral pH was evaluated. The experiments were performed at 1mM Fe^{+2} and 30 mM H_2O_2 in presence of 2 mM Glu, 10 mM CIT and 25mM SC. The results revealed that the rate of degradation of phenol was 73, 60 and 77%, respectively, that is in short term experiments 3hr, but in the long term 24hr more degradation was obtained about (82,72 and 86%), respectively.

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تحلـل حفــاز للفينـول باسـتخدام عوامـل مخلبيــة مختلفـة عنـد رقـم هيدروجينى قرب التعادل في عملية فنتون معدلة

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يستخدم كاشف فنتون الذى هو عبارة عن خليط الحديد كعامل حفاز مع بيروكسيد الهيدروجين لأكسدة المركبات العضوية فى الوسط الحامضى. ولكن بزيادة الرقم الهيدروجيني تترسب أيونات الحديد وتقلل من كفاءة تفاعل فنتون. تم اختيار عوامل مخلبية مختلفة [حمض الجلوتاميك (Glu)، وحامض الستريك (CIT) وسترات الصوديوم (SC)] ، والتى تكون مخلبيات الحديد القابلة للذوبان عند رقم هيدروجيني متعادل (فنتون المعدل) لدراسة تأثيرها على تحلل الفينول. أظهرت النتائج أن معدل التحلل باستخدام مخلبيات الحديد مع (Glu، CIT و SC) كان حوالي 73، 60 و 77٪ على التوالي وذلك فى تجارب المدى القصير (3 ساعات)، ولكن على المدى الطويل (24 ساعة) كان التحلل أكبر وكان حوالي 82 و 72 و86٪ على التوالي.