

Chelate Enhanced Modified Fenton Treatment for Polycyclic Aromatic Hydrocarbons Contaminated Soils

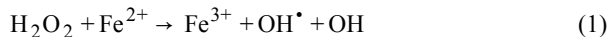
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Abstract—This work focuses on the remediation of polycyclic aromatic hydrocarbons (PAHs)-contaminated soil via Fenton treatment coupled with novel chelating agent (CA). The feasibility of chelated modified Fenton (MF) treatment to promote PAH oxidation in artificially contaminated soils was investigated in laboratory scale batch experiments at natural pH. The effects of adding inorganic and organic CA are discussed. Experiments using different iron catalyst to CA ratios were conducted, resulting in hydrogen peroxide: soil: iron: CA weight ratios that varied from 0.049: 1: 0.072: 0.008 to 0.049: 1: 0.072: 0.067. The results revealed that (1) inorganic CA could provide much higher PAH removal efficiency and (2) most of the proposed CAs were more efficient than commonly utilised CAs even at mild ratio. This work highlights the potential of novel chelating agents in maintaining a suitable environment throughout the Fenton treatment, particularly in soils with high buffer capacity.

Keywords—Chelating agent, Fenton, hydroxyl radicals, polycyclic aromatic hydrocarbon.

I. INTRODUCTION

THE presence of polycyclic aromatic hydrocarbons (PAHs) in contaminated lands possesses environmental concerns due to the hazardous characteristics of PAHs such as high toxicity and carcinogenicity. Conventional Fenton's reagent which is a solution of hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}), invented by Henry John Horstman Fenton in 1890s is widely known for its ability to destroy organic contaminant such as PAHs in soils, as in (1).



Although simple in theory, conventional Fenton processes have maximum catalytic activity at low pH values (pH 2-4) by avoiding the formation of $\text{Fe}(\text{OH})_{3(s)}$ which leads to impractical applications in most geologic materials with high buffering capacity. Many integrated techniques for soil remediation have been studied to overcome the difficulty in applying conventional Fenton process onto soils. Of these, modified Fenton (MF) treatment which involves chelate based-Fenton reactions has gained recognition as a potential treatment for contaminated soils. In the MF process, iron catalyst combined with chelating agent (CA) to minimise non-

specific loss of soluble iron by avoiding its precipitation. Consequently, the MF treatment offers higher contaminant removal efficiency and shorter treatment time even at neutral pH [1]. Catechol and gallic acid have been employed as CAs for the degradation of PAHs in a former manufactured gas plant soil [2]. The combined treatment of MF and biodegradation resulted in 98% degradation of 2- or 3-ring PAHs and 70%-85% degradation of 4- or 5-ring PAHs while maintaining the pH at 6-6.5. The performances of other CAs such as ethylene diamine tetraacetic acid, carboxy methyl cyclodextrin, oxalate, tartrate, sodium citrate and succinate have also been reported for the oxidation of pentachlorophenol in the presence of magnetite. The majority, if not all, of previous works performed with organic CAs has shown limited capability of organic CAs towards high molecular weight PAHs while the application of inorganic CAs such as sodium pyrophosphate has been scarcely reported. The main objectives of this study are (1) to compare the performance of organic and inorganic CAs for remediating soils contaminated with PAHs (2) to experimentally investigate the kinetics of the chelated MF treatment.

II. MATERIALS AND METHODS

A. Chemicals

Phenanthrene (PHE, 90%) and fluoranthene (FLUT, 98%) were procured from Sigma-Aldrich. H_2O_2 was purchased from Merck (30%, synthesis grade), ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99+%, ACS grade) and ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, 97%, ACS grade) from Sigma-Aldrich. Ethylene diamine tetraacetic acid (EDTA, 99%), oxalic acid (OA, 99%), malic acid (MA, 99.5%) and sodium pyrophosphate (SP, $\geq 99\%$) were purchase from Merck and tri-sodium citrate (SC, $\geq 99\%$) from Fisher Scientific. Dichloromethane (DCM, 99.5%, AR analysis), acetone (99.5%, AR analysis), calcium chloride dehydrate (CaCl_2 , 99+%, ACS grade), sulphuric acid (H_2SO_4 , 98%) and mercury chloride (HgCl_2 , >99.5%) were purchased from Merck. Acetonitrile (ACN, 99.8%, HPLC grade) and n-pentane (99%, Labscan, AR grade) were purchased from Rank Synergy. N-hexane ($\geq 96\%$, Merck) for aqueous phase extraction was purchased from Merck. Silica gel 40 (0.063-0.2 mm mesh) and anhydrous sodium sulphate (Na_2SO_4 anhydrous, 99+%, analysis ACS) for removing aliphatic hydrocarbons during silica gel column chromatography cleaning were purchased from Fisher Scientific. To avoid cross-contamination, all glassware and vessels were rinsed with acetone and distilled water before use.

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B. Soil Samples

Surface soil samples (0-10 cm) were collected in January 2010 from Semenyih Malaysia (N 02° 56' 48.8", E 101° 52' 32.7"). Gummy and fibrous materials not amenable for grinding were removed to allow maximum exposure of the sample surface for subsequent treatment. The soil samples were air-dried at ambient temperature (20-25°C) until the moisture content was less than 3%, passed through 2 mm mesh using laboratory test sieve (Endecotts Ltd, England) and stored at ambient temperature (20-25°C) prior to spiking of PAHs onto the soil.

C. Soil Characterisation

The particle size analyses were determined according to the Buoyoucos hydrometer method [3]. A standard procedure was adapted for which 25 g dried soil sample was treated with 100 mL of 5% w/v dispersing agent, i.e. sodium polyphosphate solution, to break down soil aggregates so that the particles act individually in the analysis, by means of a magnetic stirrer for 24 h at ambient temperature (20-25°C). The soil bulk density was determined using an oven-dry (130°C for 20 h) basis per unit volume [3]. The specific surface area of soils, on the other hand, was determined by the BET nitrogen adsorption method with a porosimeter (Micromeritics, ASAP 2020). The degassing vacuum was 10 µm Hg for 3 h and degassing temperatures of 150°C [4].

The measurement of moisture content for the fresh soil was performed using a moisture analyser (MX-50, A & D Company) which operated at 105°C and 0.05% /min. The pH_{H2O} test was conducted according to the US EPA Method 9045D. In the present work, the loss on ignition (LOI) value for determining the soil organic matter is defined as the loss of mass after the soil sample is heated at 550°C for 3 h [5]. Ten grams of soil sample was placed in a crucible and dried at 105°C for 2 h prior to combustion at 550°C. The total iron available in the soil sample was measured by nitric acid digestion. The experimental procedures followed the US EPA Method 3050B for which 2 g of dried soil was digested without boiling at 95°C±5°C. The filtrate was collected and diluted with distilled water up to 100 mL along with final analysis using an atomic absorption spectrometer (Perkin-Elmer AAnalyst 400).

D. Artificially Contaminated Soil

DCM was used as the carrier solvent for PAH mass transfer into the soil. A 30 g soil sample (dried and sieved to 2 mm mesh) was divided into 6 portions. Each portion of 5 g uncontaminated soil was placed in a glass vial and 500 µL of PAHs-DCM stock solution was poured to make up a concentration of 500 mg/kg dry soil each for PHE and FLUT respectively. The stock solution was shaken using a Vortex Mixer (REAX, C/N 541, Heidolph) for 1 min prior to mixing with the fresh soil. After the stock solution was added to the fresh soil, mixing was performed thoroughly using a stainless steel spatula for 1 min. The procedures were repeated for the remaining portions and the solvent was allowed to evaporate

TABLE I
LABORATORY SCALE MODIFIED FENTON TREATMENT FOR PAH-CONTAMINATED SOIL

Test	H ₂ O ₂ : soil: Fe: CA (w: w: w: w)
MFa1	0.049:1:0.072:0.067
MFa2	0.049:1:0.072:0.034
MFa3	0.049:1:0.072:0.022
MFb1	0.049:1:0.072:0.023
MFb2	0.049:1:0.072:0.011
MFb3	0.049:1:0.072:0.008
MFe1	0.049:1:0.072:0.053
MFe2	0.049:1:0.072:0.026
MFe3	0.049:1:0.072:0.017
MFd1	0.049:1:0.072:0.024
MFd2	0.049:1:0.072:0.012
MFd3	0.049:1:0.072:0.008
MFe1	0.049:1:0.072:0.080
MFe2	0.049:1:0.072:0.040
MFe3	0.049:1:0.072:0.027

A: EDTA; B: OA; C: SC; D: MA; E: SP.

for 3 h in a fume hood. Every portion was then mixed and transferred to a clean glass vial. The spiked soils were subsequently stored in a refrigerated environment (4°C) in order to prevent soil microbes to remain active and continue to degrade labile compounds.

E. Modified Fenton Treatment

Following contaminant aging of 15 days, the soil samples were subjected to a slurry phase treatment with Fenton's reagent in 100 mL borosilicate vials with screw caps. For each test, 5 g of spiked soil was slurried in 15 mL of distilled water containing 0.03 g of HgCl₂ (0.2 % w/v) to inhibit potential microbial activity [2], [6] and a specific amount of CA. There was no pH adjustment prior to the addition of the catalyst (0.9 ml of 1M Fe³⁺), which was freshly prepared daily to prevent iron precipitation. A fixed amount of the oxidant (0.735 ml of 30% H₂O₂) was added for all tests resulting in an oxidant (480 mM) to catalyst (60 mM) molar ratio of 8 (Table I). The Fenton oxidation was initiated upon the addition of H₂O₂ and the reaction took place in a horizontal water bath shaker (Mettmert WNB 7-45, Germany) at 30°C and 150 strokes per minute. At the end of the treatment, the soil slurries were treated with five drops of 1 N H₂SO₄ (pH≈1) to terminate the Fenton oxidation and subjected to phase separation process. Control experiments were also carried out under the same conditions without the Fenton's reagent i.e. the volume of the reactants (H₂O₂ and Fe³⁺) were substituted by distilled water. All of the Fenton oxidation experiments were conducted in triplicates (n=3).

F. Automated Soxhlet Extraction (Solid Phase)

After the Fenton treatment in slurry suspensions, PAH extractions were carried out. For PAH extraction from the solid phase, automated Soxhlet extraction (Gerhardt Soxtherm) was selected because it is not as time consuming as other extraction processes. The supernatant was separated from the solid phase by vacuum filtering with filter paper (Sartorius Stedim Biotech, each of Grade 292 and 389).

The separated solid phase was placed in an extraction thimble (Advantec, ID (84) 33x80 mm, Japan) and then mixed with anhydrous sodium sulphate (granular Na_2SO_4 , initially purified by heating at 400°C for 4 h in a furnace) at a ratio of 2:1 w/w (10 g per 5 g of soil sample) to reduce the moisture level. The Soxhlet extraction was performed according to the US EPA Method 3540C. The soil-sodium sulphate mixture was covered with glass wool and extracted with 140 mL of n-pentane for 3 h, i.e. immersed in boiling solvent for 90 min, rinsed for 60 min and evaporated for 30 min. The remaining solvent was cleaned using silica gel column chromatography and evaporated to dryness. All of the Soxhlet extraction experiments were conducted in triplicates ($n=3$).

G. Liquid-liquid Extraction (Aqueous Phase)

The PAHs in the aqueous phase was extracted by means of liquid-liquid extraction using hexane at a ratio of 1:1 v/v. The hexane extracts from the triplicates were combined due to very low concentration of PAHs found in the aqueous phase of each replicate. The final combined eluate was sent for cleaning using silica gel column chromatography.

H. Silica Gel Clean-up

In order to eliminate interfering substances for the subsequent instrumental analysis and detection, the extracts were cleaned up through silica gel column chromatography according to the US EPA Method 3630. Approximately 10 g of silica gel (initially activated in an oven at 130°C for 16 h) was packed in a chromatography column (Favorit, 300 mm effective length and 10 mm ID). Initially, the column was pre-washed with 25 mL of n-pentane at 2 mL/min. The sample extract was then transferred to the column and followed by the addition of 25 mL of n-pentane for removal of aliphatic hydrocarbons. The PAHs fraction was collected from the subsequent elution with 25 mL of DCM: n-pentane (2: 3 v/v). The eluate was further evaporated to dryness in a rotary evaporator (Heidolph) with temperature held at 60°C (extract from Soxhlet extraction) or at 85°C (extract from liquid-liquid extraction) and further dissolved in 1 mL of ACN for gas chromatography (GC) analysis.

I. Gas Chromatography Analysis

The PAHs from both the solid and aqueous extracts were analysed using a GC (Clarus 500 Agilent USA), equipped with a flame ionisation detector (FID) and fused silica capillary column, according to the US EPA Method 8100. Further details on the instrumentation and conditions are summarised in Table II. The concentration of individual PAH in the solvent was quantified using the external standard calibration method. Under this condition, individual PAHs were identified by retention times of 8.2 min and 9.6 min for PHE and FLUT respectively.

III. RESULTS AND DISCUSSIONS

A. Soil Properties

Fig. 1 depicts the particle size distribution of the soil with

TABLE II
GC-FID INSTRUMENTATION AND CONDITIONS

Column	DB-5MS capillary column 30 m x 0.25 mm x 0.25 μm
Sampler	5 μL syringe (SGE, 1 μL splitless)
Injector	290°C
Carrier	Helium gas 16 psi
Oven	100°C for 1 min, $25^\circ\text{C}/\text{min}$ to 310°C , hold for 2 min
Detector	300°C

the majority of the particles present in the following ranges: 0.15-0.3 mm (25.4 wt %), 0.6-1.18 mm (21 wt %) and 0.5-0.6 mm (20.4 wt %). The soil properties are shown in Table III. Under the temperature programme of the GC-FID analysis, the limit of detection (LOD) and limit of quantification (LOQ) for each PAH were determined with triplicates. The LOD was calculated as the blank concentration plus three standard deviations whereas the LOQ was defined as the blank concentration plus ten standard deviations. The LOD were found to be 1.24 and 0.9 mg/kg and the LOQ were 1.97 and 1.30 mg/kg for PHE and FLUT respectively.

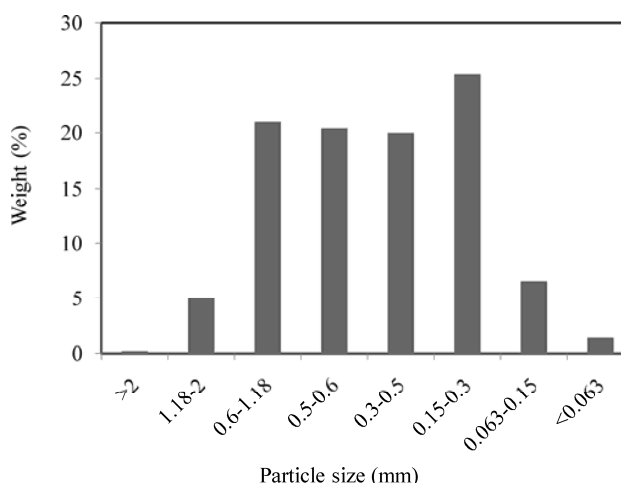


Fig.1 Particle size distribution of the soil sample

B. Effect of Reaction Time and Chelating Agents

The removal of both PHE and FLUT was characterised by a very fast initial rate which occurred mostly in 15 min for all types of CAs. It is not possible to present all data for 15 conditions (3 different Fe^{3+} to CA molar ratios for 5 types of CAs and 8 intervals for each scenario). Hence, only the data at selected intervals (Fe^{3+} to CA molar ratio of 1 after 30 min and 24 h reaction) are presented in Table IV. As expected, the data show an increase in PAH removal as the Fenton treatments continued from 30 min to 24 h.

This observation applied to both organic and inorganic CAs. For example, PHE removal increased from 55.79% to 78.68%, 41.73% to 73.10%, 31.09% to 58.53%, 44.58% to 68.53% and 61.70% to 79.53% for EDTA, OA, SC, MA and SP respectively. Similarly, FLUT removal also increased by

24%, 31.8%, 26.51%, 24.13% and 18.62% for EDTA, OA, SC, MA and SP respectively. Despite the fact that SC is a biodegradable CA, SC-enhanced MF treatment resulted in lower PAH removal efficiency (58.53% and 57.52% for PHE

$$\frac{dC}{dt} = kC^m \quad (2)$$

where C represents PAH concentration in mg/kg and m describes the order of reaction. Kanel et al. [8] reported that heterogeneous oxidation of PHE in sand in the presence of goethite followed pseudo first order kinetics. The rate constants were reported to be varied between 2×10^{-4} and $1.1 \times 10^{-3} \text{ min}^{-1}$. Valderrama et al. [9] described the Fenton oxidation kinetics of PAHs in aged soil samples with creosote oil from a wood preserving site. Values reported for 3-aromatic ring PAH (e.g. PHE) were $6.5 \times 10^{-4} \text{ min}^{-1}$ and $3.83 \times 10^{-8} \text{ kg mg}^{-1} \text{ min}^{-1}$; for 4-aromatic ring PAH (e.g. FLUT) were $3.33 \times 10^{-4} \text{ min}^{-1}$ and $2.0 \times 10^{-9} \text{ kg mg}^{-1} \text{ min}^{-1}$ for pseudo first and second order respectively. Obviously, the values reported in the literature are few orders lower in magnitude compared to those obtained in this work, as shown in Table VI. There are two possible explanations for the higher rate constants in the present study (2.23×10^1 – $4.89 \times 10^1 \text{ mg kg}^{-1} \text{ min}^{-1}$ for zero order; 6.53×10^{-2} – $2.78 \times 10^{-1} \text{ min}^{-1}$ for first order and 2×10^{-4} – $5.7 \times 10^{-3} \text{ kg mg}^{-1} \text{ min}^{-1}$ for second order). Firstly, the experiments conducted by the previous authors did not implement the use of CA to enhance the PAH removal. Secondly, aged or field soils were used in some cases instead of artificially contaminated soils. In addition, data on the kinetic rate constants for chelated MF treatment are limited, especially for MA- and SP-systems since the application of these two CAs are relatively new.

IV. CONCLUSION

Among all types of CAs tested in the present study, applying MFel (Fe^{3+} : SP molar ratio of 1:1) onto the PAHs-contaminated soil resulted in the highest PHE and FLUT removal efficiencies (79.53% and 89.13%), followed by MFal (Fe^{3+} : EDTA molar ratio of 1:1) which were 78.68% and 78.51% respectively. The better performance of SP- enhanced MF treatment can be attributed to its lower likelihood to compete for generated radicals in its oxidised form. Overall, it can be concluded that the oxidation of PAH in the Fenton system occurred in a nonlinear trend.

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TABLE III

SOIL SAMPLE CHARACTERISATION AND PROPERTIES	
Characteristic	Loamy sand
Sand (%)	85.68
Silt (%)	1.44
Clay (%)	12.88
Bulk density (g/mL) ^a	1.33 ± 0.02
Specific surface area (m ² /g soil)	2.23
Porosity (%) ^a	49.76 ± 0.79
Moisture content (%) ^a	0.34 ± 0.03
pH ^a	7.13 ± 0.02
Walkley-Black SOM (%)	0.20
Loss on ignition SOM (%) ^a	0.26 ± 0.07
Total iron (mg/g soil) ^b	29.84 ± 0.01

^aAverage of four replicates determinations.

^b Specific surface area and total iron measurements were conducted with duplicate only

and FLUT respectively) compared to conventional Fenton treatment (65.53% and 69.89% for PHE and FLUT respectively). This is presumably due to slower reaction rate of PAH removal in the SC-enhanced MF system, as previously reported by Xue et al. [7]. Among all the CAs employed in the present study, SP resulted in the highest PAH removal efficiency for both PHE (3-aromatic ring PAH) and FLUT (4-aromatic ring PAH). The efficiency of CAs in removing PAHs followed the following sequence of: SP>EDTA>OA>MA>SC. The better performance of SP-enhanced MF treatment can be attributed to its lower likelihood to compete for generated radicals in its oxidised form. Apart from this, it was found that PHE removal in the MF treatment was higher than that of FLUT except for the cases when MA or SP was used as the CA. The findings suggest that MA and SP are effective CAs in the MF treatment for the removal of higher molecular weight PAHs, which are often more resistant to chemical oxidation treatment.

C. Effect of Fe^{3+} to Chelating Agent Molar Ratio

In most scenarios, the PAH removal efficiencies were not directly proportional to the increase in CA concentration. In other words, there was no clear trend between catalyst-CA ratio and PAH removal and that higher concentration of the CA (i.e. Fe^{3+} : CA = 1: 1) may result in a significant quenching effect of hydroxyl radicals that reduces PAH degradation efficiency. This is particularly true for all tested CAs within 30 min of the MF reaction. Nevertheless, PAH removals with longer reaction time were affected in a different manner. For instance, by extending the reaction to 24 h, Fe^{3+} to CA molar ratio of 1 was the best option for all scenarios (only data for MA and SP are shown in Table V).

D. Degradation Kinetics

A simple m^{th} order reaction kinetic was used in order to compare the experimental results with values reported in the literature, as in (2).

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TABLE IV
EFFECT OF REACTION TIME ON PAH REMOVAL IN MODIFIED FENTON TREATMENT

CA type	Test	30 min						24 h						
		PHE			FLUT			PHE			FLUT			
		Aqueous (mg/kg)	Solid	Removal (%)	Aqueous (mg/kg)	Solid	Removal (%)	Aqueous (mg/kg)	Solid	Removal (%)	Aqueous (mg/kg)	Solid	Removal (%)	
Organic CA	EDTA	MFeI	0.44	91.00	55.79	0.63	141.86	54.45	0.27	25.74	78.68	0.84	95.71	78.51
	OA	MFeI	0.90	160.81	41.73	1.24	209.01	40.90	4.14	49.73	73.10	7.27	118.14	72.74
	SC	MFeI	1.43	213.48	31.09	1.46	259.85	30.69	0.59	126.14	58.53	1.30	201.79	57.20
	MA	MFeI	0.93	146.53	44.58	1.23	153.94	51.91	1.06	75.65	68.53	1.19	107.73	76.04
	Inorganic CA													
	SP	MFeI	1.07	60.81	61.70	1.23	60.98	70.51	0.89	20.83	79.53	1.33	42.12	89.13

TABLE V
EFFECT OF CATALYST TO CHELATING AGENT MOLAR RATIO ON PAH REMOVAL IN MODIFIED FENTON TREATMENT

CA type	Fe ³⁺ : CA (mol: mol)	30 min						24 h					
		PHE			FLUT			PHE			FLUT		
		Removal (%)	RSD (%)	Removal (%)	RSD (%)	Removal (%)	RSD (%)	Removal (%)	RSD (%)	Removal (%)	RSD (%)	Removal (%)	RSD (%)
MA	1:1	44.58	4.82	51.91	12.25	68.53	29.74	76.04	17.34				
	2:1	51.44	13.32	51.81	4.00	66.73	3.90	76.88	10.04				
	3:1	61.51	18.26	60.17	9.46	64.89	10.64	75.29	5.02				
	1:1	61.70	9.89	70.51	19.53	79.53	22.75	89.13	14.88				
	2:1	69.01	15.34	74.60	24.18	76.88	13.48	87.11	25.12				
	3:1	66.34	17.18	64.18	21.98	72.89	15.81	80.74	18.07				

TABLE VI
PSEUDO RATE CONSTANTS FOR PAH OXIDATION VIA MODIFIED FENTON TREATMENT

CA type	Test	Pseudo zero order			Pseudo first order			Pseudo second order		
		k_0 (mg kg ⁻¹ min ⁻¹)			k_1 (min ⁻¹)			k_2 (kg mg ⁻¹ min ⁻¹)		
		R^2			R^2			R^2		
MA	MFe1	PHE	33.3110	0.59	0.1307	0.70	0.0006	0.73		
		FLUT	31.2090	0.63	0.1128	0.78	0.0005	0.92		
	MFe2	PHE	31.8310	0.53	0.1206	0.51	0.0006	0.37		
		FLUT	28.0200	0.55	0.0923	0.57	0.0003	0.53		
	MFe3	PHE	30.3770	0.67	0.1071	0.80	0.0004	0.91		
SP		FLUT	26.6710	0.81	0.0853	0.92	0.0003	0.97		
	MFe1	PHE	39.8890	0.60	0.2462	0.85	0.0032	0.83		
		FLUT	38.9920	0.64	0.2205	0.88	0.0023	0.90		
	MFe2	PHE	40.4180	0.60	0.2771	0.97	0.0057	0.77		
		FLUT	38.2380	0.59	0.1976	0.87	0.0017	0.99		
	MFe3	PHE	33.4070	0.79	0.1371	0.97	0.0007	0.95		
		FLUT	30.0320	0.78	0.1071	0.94	0.0005	0.97		