

## SPECTROSCOPIC AND PETROGRAPHIC CHARACTERIZATION OF SHALE FROM KUBANG PASU FORMATION, MALAYSIA

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### **Abstract**

Shale samples from Kubang Pasu (KP) Formation has been taken from two small hills in the Beseri area of Perlis: Bukit Chondong and Kampung Guar Jentik, Kedah, and accounted for spectroscopic and petrographic characterization during this study to provide an opportunity to explore the organic matter quality and quantity, hydrocarbon bonds distribution and texture and structure characteristics present in these shale. Determining these properties of KP will help establish relationships between the total organic carbon (TOC) with humic acid. This is achieved by determining the organic carbon content and humic spectroscopic UV-visible ratio (E4/E6). The calculated UV-visible ratios of E4/E6 for both outcrops indicate the dominance of humic acids over fulvic acids indicating a strong possibility of terrestrial origin. The attenuated total reflectance (ATR) fourier transform infrared spectroscopy (FTIR) was used in the assessment of hydrocarbon present in rocks. Analysis with the ATR-FTIR shows that the aromatic OPCH stretching (690-900  $\text{cm}^{-1}$ ) hydrocarbon and aromatic IPCH stretching (600-700  $\text{cm}^{-1}$ ) hydrocarbon groups (both occur in the finger print region) absorbance are more in KP Formation as compare to other hydrocarbon bands. OH groups stretching vibration, alkyne C-H bending bands and alkane C-H bending band in aliphatic hydrocarbons and absorption spectrum of aromatic C=C stretching and aromatic OPCH are found in the FTIR spectra of KP shales. The petrographic analysis results show that KP shale samples consist mainly of dark to light grey, silty, micaceous, massive, discontinuous wavy parallel laminated, brownish massive, parallel laminated and non-calcareous mudstone.

**Keywords:** Aromatic Hydrocarbons; Total organic carbon; Spectroscopy; Shale; Humic spectroscopic ratio (E4/E6).

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### **1. Introduction**

Spectroscopy techniques such as Ultraviolet-Visible Spectroscopy (UV-Vis) and Attenuated total reflectance (ATR) Fourier transform infrared spectroscopy (FTIR) have been well used for the identification of hydrocarbon functional groups and type of humic substance in shale [1-2]. For the organic chemist UV-Vis is mostly concerned in conjugated systems with electronic transitions; the intensities and positions of the absorption band largely depend to a greater extent on the specific system under consideration. The electronic transitions are mostly sensitive to changes in structure and reveal the strains executed on the system by electronic and steric interactions. Unlike infrared spectroscopy functional group absorptions cannot be assigned to fixed and specific regions of the ultraviolet visible wavelength scale, and considerable experience is required in the interpretation of the spectra [3]. Like UV-Vis, FTIR is certainly one of the most important analytical techniques available to today's scientists. One of the great advantages of infrared spectroscopy is that virtually any sample in virtually any state may be studied. Chemical characterization from FTIR can deliver important information on the molecular structure of inorganic and organic components. From the past few decades FTIR has been used extensively for the assessment of hydrocarbon bond distribution of geological samples such as shale, coal, silicate glass, microfossils, fluid and melt inclusions and minerals [4]. Mostly, its use in the characterization of geochemistry and thermal matu-

ration of organic matter in coal and shale is well known. In FTIR analysis, when a photon collides to a molecule and excites it to a higher energy state, absorption of IR radiation takes place. The excited states consequence in the vibrations of molecular bonds (i.e., twisting, stretching, rocking bending, out-of-plane deformation, in-plane deformation and wagging) taking place at variable frequencies (or wavenumbers) in the IR region of the light spectrum [5].

Macroscopic sedimentary characteristics such as shale texture and structure characteristics can interpret by the petrographical characterization. Shale is a fine-grained sedimentary rock that forms from the compaction of silt and clay-size mineral particles. In this study shale has been taken from Kubang Pasu (KP) formation, as this formation comprises very thick sequences of shale which might be a potential energy source ( $\pm 3400\text{m}$  thickness). Although, there is no available literature present, that focused on the spectroscopic and petrographic characterization of the shales in the KP formation. Therefore, this study was designed to address, for the first time, the hydrocarbon bonds distribution, organic matter quality and texture and structure characteristics present in these shale. Furthermore, the processes controlling the level of humic substance in the shale are complex. One of the most important factors is the concentration of TOC in shale [6]. However, no study is also focused on the relationship between humic acid and organic carbon in shale, and its needs to be established.

## 2. Study area

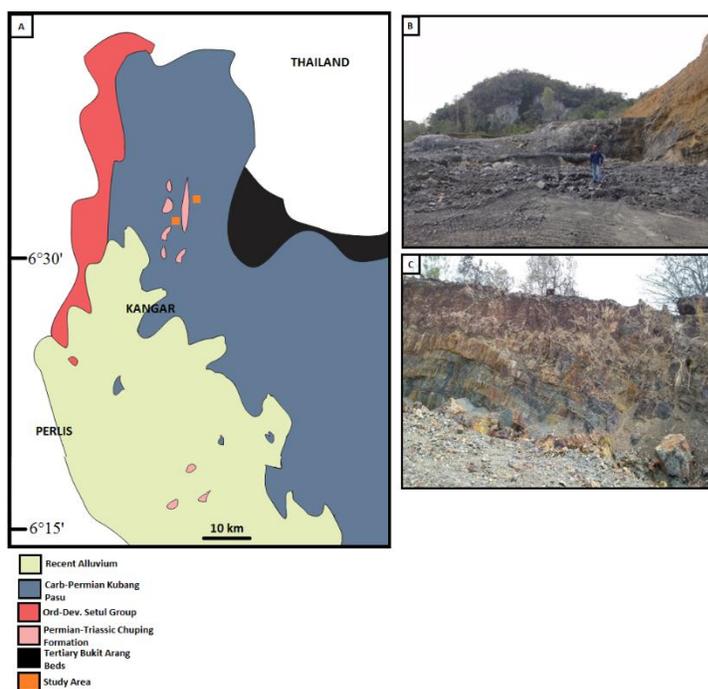


Figure 1. Study area. (A) General Geological Map. (B) Bukit Chondong outcrop. (C) Kampung Guar Jentik outcrop

Shale samples have been taken from two small hills in the Beseri area of Perlis: Bukit Chondong ( $6^{\circ}33'18.2''\text{N}$   $100^{\circ}12'20.5''\text{E}$ ) and Kampung Guar Jentik ( $6^{\circ}33'08.7''\text{N}$   $100^{\circ}14'10.4''\text{E}$ ) (Fig. 1-2). The uppermost Kubang Pasu Formation is exposed at both hills, where they are conformably overlain by the Chuping Formation. Bukit Chondong hill is located in Kampung Padang Malau and in Kampung Guar Jentik, the best exposure has been found in hilly ridge known as Sanai Hill. The age of the basal unit of the Kubang Pasu Formation is Early Carboniferous (Tournaisian--Visean) [6]. The basal unit of the Kubang Pasu Formation is represented by a thick unit of blackish grey-red shale interbedded with sandstone.

In this study shale sample has been collected from the basal unit of Kubang Pasu formation.

## 3. Samples and methods

In Kubang Pasu formation, ten shale samples were collected by using method mentioned in [7]. Two shale samples (KP-1&2) have been taken from Kampung Guar Jentik and eight samples (KP-3 to 10) from Bukit Chondong. All samples were ensured that weathered exposures are removed by eliminating the surface material. The rock samples were all air dried to remove any moisture present in the sample. In Kampung Guar Jentik, the colors of shale are varying from medium light gray to dark. While in Bukit Chondong shales are mostly medium gray. All of the ten samples were crushed into fine grains (2mm). Coning and

quartering sub-sampling method were used to homogenize all of the sample following the procedure outlined by Gerlach and Dobb [8]. Sub-sampling method reduces biased result and increase the accuracy of the data [9]. Furthermore, duplication of all analysis is done and less than 3% percentage of error has been achieved.

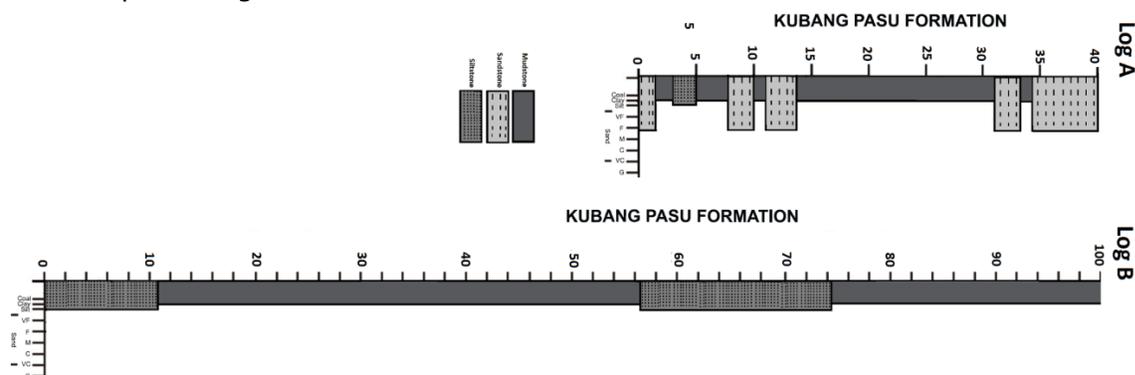


Figure 2. Logged stratigraphic sections of the Kubang Pasu Formation. Log A: Kampung Guar Jentik outcrop. Log B: Bukit Chondong outcrop

### 3.1. Fourier transform infrared spectroscopy (FTIR)

Infrared measurements were made using a Cary 660 Series FTIR Spectrometer equipped with PIKE MIRACLE diamond attenuated total reflectance spectroscopy (ATR). Data collection was done using the Resolutions Pro software package which was also used for background and automatic baseline correction of all spectra. Spectra were acquired and converted to absorbance mode from 16 coded scans between 4000 and 400  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ , then area normalized prior to further analysis. The limit of detection of the instrument is 0.08%. Background scans were collected using the same settings as the sample analyses. Replicate spectra collected on selected samples showed consistent peak positions and absorbance intensities. The area percentage of hydrocarbon functional groups was calculated by summing the absorbance intensities between the respected wavelength [10-11].

### 3.2. Total Organic Carbon Analysis

The total carbon test was used to measure the total organic carbon content in the samples. It is the relative dry weight percentage of organic carbon in the sediments [12]. In this study, 1.0g of each powdered samples were measured and placed in beakers. The samples were acidified with 10ml of hydrochloric acid of 37% concentration to remove inorganic carbon fraction from the samples. They were then left for 12 hours in the fume chamber before being rinsed with reverse osmosis water for 3 times and dried in the oven at 60°C for 24 hours. After drying, 60mg of each sample were being weight and placed on ceramic boats. Percentage of organic carbon was measured using multi n/c 3100. The measurements were run in duplicate, and the results were averaged.

### 3.3. Ultraviolet-visible (UV-Vis) spectroscopy

In this study E4 (465nm) and E6 (665nm) were the primary focus to determine the aromaticity of the samples based on E4/E6 ratio. For extraction of humic substance the U.S. EPA method 3550 was optimized using ultrasonic extraction with Methanol as solvent. In a glass flask with cap, 2 g was weighed of each shale sample. The samples were then submitted to three consecutive extractions with 8mL of Methanol each time, by 3 minutes of ultrasonic stirring (Thornton Unique 1450USC ultrasonic cleaner) and 5 minutes of centrifugation at 2500 rpm (Janetzki T23 centrifuge). The UV-VIS technique analysis of the Methanol extract solution was performed using Perkinelmer lambda 750 UV Vis Spectrophotometer with the liquid samples placed in quartz cells. The scanning wavelength range was 200–800 nm.

### 3.4. Petrography

Petrographic analysis of the samples were obtained from thin sections prepared in Quality thin sections (QTS), USA. Plane and cross transmitted light optical photomicrographs with a spatial resolution of 500  $\mu\text{m}$  were taken of all thin sections using a LEICA DM 750P attached with a LEICA MC170 HD camera at Universiti Teknologi PETRONAS.

## 4. Results

### 4.1. Fourier transform infrared spectroscopy (FTIR)

The FTIR analysis was conducted to characterize the functional groups in the shale. The FTIR spectra of different shale exhibited similar absorption bands and characteristic absorption peaks, based on the vibration of the atoms in a molecule and the spectrum obtained depends on what fraction of the incident radiation is absorbed at a particular energy as shown in Table 1 and Figure 3 [13-14]. Compared to the FTIR spectrum of coal, shale's spectrum normally shows much weaker vibrational bands of aliphatic C-H at 3000–2800  $\text{cm}^{-1}$ , but features strong IR absorbance from aromatics at 600-1250  $\text{cm}^{-1}$  (Fig. 3).

Table 1. Functional groups identified through FTIR spectra of the shale in the Kubang Pasu formation.

Samples	Aromatic C=C stretching 1430-1650 Absorbance	Alkane APH 720 C-H bending Absorbance	Aromatic bending 1275-1000 In-plane C-H bending Absorbance	Aromatic bending 900-690 Out-of-plane C-H bending Absorbance	Alkyne APH 700-600 =C-H bending Absorbance	-OH Stretching 3600-3000 Absorbance
KP-1	0.03	0.05	0.58	0.17		0.05
KP-2	0.03		0.67	0.18		0.01
KP-3			0.55	0.13	0.10	0.01
KP-4			0.52	0.13	0.10	0.02
KP-5			0.55	0.22	0.06	0.01
KP-6			0.52	0.19	0.07	0.01
KP-7			0.44	0.20	0.09	0.02
KP-8	0.01	0.06	0.41	0.09	0.05	0.02
KP-9	0.01	0.07	0.46	0.74	0.06	0.05
KP-10	0.01	0.11	0.58	0.13	0.09	0.05

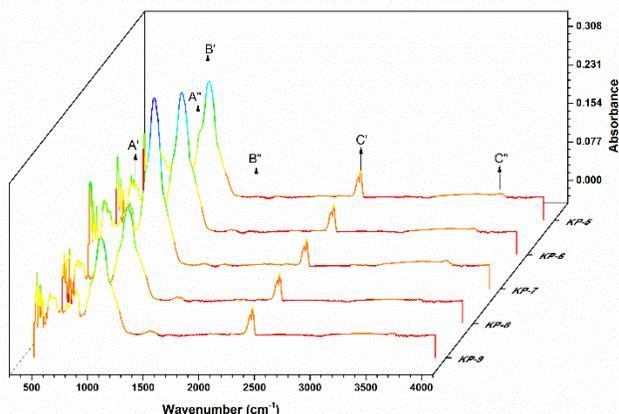


Figure 3. FTIR spectra of few shale samples (from the KP formations) in the frequency interval 4000-400  $\text{cm}^{-1}$  showing the Aromatic bending OPCH (represented by the arrows A' and A'' at approximately 694 and 827  $\text{cm}^{-1}$  respectively), Aromatic bending OPCH (represented by the arrows B' and B'' at approximately 1001 and 1429  $\text{cm}^{-1}$  respectively), ATR Diamond (represented by the arrows C') and -OH Stretching bands (represented by the arrows C'' at approximately 3623)

The FTIR spectra of the shale samples can be divided into three zones, -OH groups stretching vibration, Alkyne C-H bending bands and Alkane C-H bending band in Aliphatic hydrocarbons and absorption spectrum of Aromatic C=C stretching and Aromatic out of plane

C–H bending. Strong intensity peak of free OH-compounds are detected in the region of 3700–3200  $\text{cm}^{-1}$  [12,15-16] and seen in all the samples of the KP formation.

#### 4.2. Total Organic Carbon (TOC)

From the Table 2, it is shown that all shale from the KP formation has low total organic carbon. The measured concentration of total organic carbon content in the shale ranged from 0.36% to 1.42%. KP-4 and KP-5 have the highest TOC content compare to other sample. Moreover, shale sample which has been taken from Bukit Chondong outcrop hill have higher total organic carbon content as compared to Kampung Guar Jentik outcrop.

Table 2. TOC results of shale from Kubang Pasu formation

Sample	A	B	Average	Error %
KP-1	0.365	0.354	0.3595	1.529903
KP-2	0.36	0.34	0.35	2.857143
KP-3	0.856	0.811	0.8335	2.69946
KP-4	0.893	0.878	0.8855	0.846979
KP-5	1.62	1.59	1.605	0.934579
KP-6	0.475	0.45	0.4625	2.702703
KP-7	0.869	0.838	0.8535	1.816052
KP-8	0.544	0.537	0.5405	0.647549
KP-9	0.49	0.46	0.475	3.157895
KP-10	0.54	0.51	0.525	2.857143

#### 4.3 Ultraviolet-Visible spectroscopy

Ultraviolet-Visible spectroscopy, already used to quantify and to evaluate the quality of humic substances [11]. Ultraviolet-visible spectroscopy is a rapid and well known used method for the estimation of humic substance in shale. The light absorption of humic substances seems to rise with an increase of degree of condensation of the aromatic rings that these substances contain, total C content, molecular weight and in the ratio of C in aromatic ring to C in aliphatic side chains.

The value of E4 and E6 that are treated with methanol are range from 0.014 to 1.56 and 0.013-1.447 respectively (Table 3). Almost equal values of E4 and E6 also indicate the presence of humic acid in Kubang Pasu formation which indicates that shale have a strong possibility of terrestrial origin (Table 4).

Table 3. UV-Vis results of nine samples of shale from Kubang Pasu formation treated with methanol

Sample	Absorbance At (Methanol) $\lambda = 465 \text{ nm}$ (E4)				Absorbance At (Methanol) $\lambda = 665 \text{ nm}$ (E6)			
	E4(A)	E4(B)	Average	Percentage Error (%)	E6(A)	E6(B)	Average	Percentage Error (%)
KPP-1	1.5766	1.5450	1.5608	1.0123	1.4745	1.4200	1.4473	1.8829
KPP-2	0.1195	0.1168	0.1182	1.1426	0.1163	0.1139	0.1151	1.0426
KPP-3	0.3398	0.3273	0.3336	1.8738	0.2506	0.2449	0.2478	1.1504
KPP-4	0.8604	0.8329	0.8467	1.6240	0.7338	0.7100	0.7219	1.6484
KPP-5	0.0260	0.0250	0.0255	1.9608	0.0149	0.0145	0.0147	1.3605
KPP-6	0.0251	0.0246	0.0249	1.0060	0.0236	0.0229	0.0233	1.5054
KPP-7	0.4682	0.4584	0.4633	1.0576	0.4170	0.4070	0.4120	1.2136
KPP-8	0.0175	0.0169	0.0172	1.7442	0.0159	0.0159	0.0159	0.0943
KPP-9	0.0143	0.0139	0.0141	1.4184	0.0132	0.0131	0.0132	0.2659
KPP-10	0.0159	0.0153	0.0156	1.9231	0.0149	0.0147	0.0148	0.7417

Table 4. E4/E6 ratio of UV-Vis results based on ten samples of shale from Kubang Pasu formation treated with methanol

Sample	E4:E6 (A)	E4:E6 (B)	E4:E6 (Average)
KPP-1	1.0692	1.0880	1.0786
KPP-2	1.0275	1.0255	1.0265
KPP-3	1.3559	1.3365	1.3462
KPP-4	1.1725	1.1731	1.1728
KPP-5	1.7450	1.7241	1.7346
KPP-6	1.0636	1.0742	1.0689
KPP-7	1.1228	1.1263	1.1245
KPP-8	1.0992	1.0636	1.0814
KPP-9	1.0833	1.0586	1.0710
KPP-10	1.0643	1.0394	1.0518

#### 4.4. Petrography

Lithological and sedimentological features of the rock such as stratification, texture, color, grain size and components can be identified by petrography analysis [17]. The petrographic analysis results show that KP shale samples consist mainly of dark to light grey, silty (Fig .4 A-F), micaceous (Fig .4 C, E), Massive (Fig .4 A, F), discontinuous wavy parallel laminated (Fig .4 C, E), brownish massive (Fig .4 A), parallel laminated (Fig. 4 B) and non-calcareous mudstone.

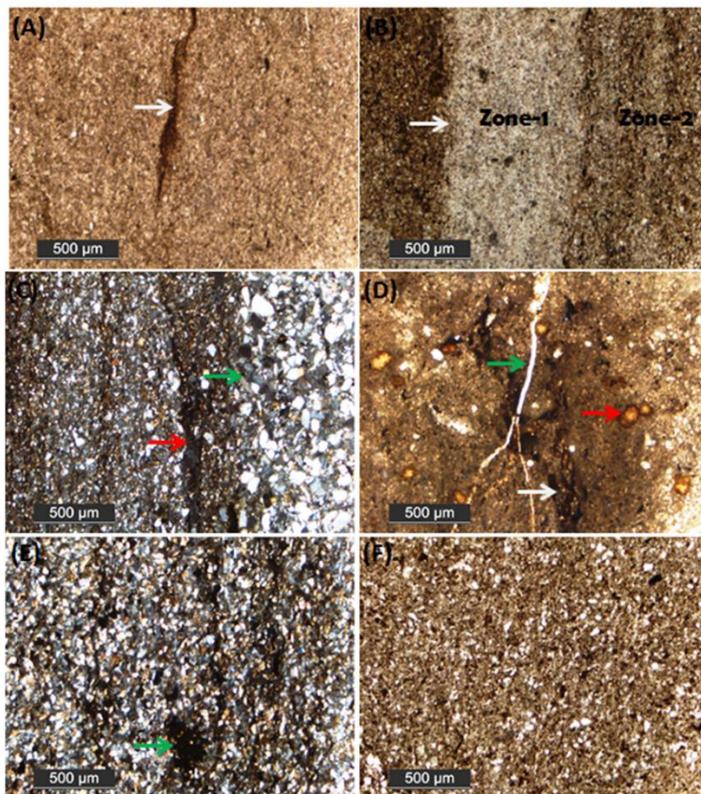


Figure 4. Sedimentologi characteristic of Kubang Pasu shale samples. (A) Brownish, structureless, massive and non-laminated fabric with dominating clay particles. Fissures filled with organic material (white arrow), (B) Thin section of the contact between zones 1 and 2 (white arrow). Zone 1 is dominated by coarser silt particles and zone 2 is dominated by silt and organic rich clay layers, (C) Sharp contact between coarse silt particles and organic rich clay layer (green arrow). Organic material filled in fissures (red arrow) and preferential alignment of mica flakes detected by cross polarized light (D) Abundant fossils fragments (red arrow) and carbonaceous fragment with frayed edge (white arrows). Quartz vein also present (green arrow), (E) Carbonaceous lump in silty shale (green arrow). Wavy-crinkly laminae that contrast with the more planar laminae. Mica flakes also observes parallel to bedding detected by cross polarized light (F) Massive brownish shale with abundant fine to medium size silt particles are present which is surrounded by clay cement

## 5. Discussions

### 5.1. Saturated and unsaturated aliphatic hydrocarbon

The C-H stretch vibrations for methyl and methylene are the most characteristic in terms of recognizing the compound as an organic compound. The bending vibrations help to tell more about the basic structure. For example, a band at 725–720  $\text{cm}^{-1}$  (methylene rocking vibration) is indicative of a long-chain linear aliphatic structure. Samples 1, 7, 8 and 9 of KP formation contains a band at 720  $\text{cm}^{-1}$  which indicates a long-chain compound, and is attributed to crystallinity and a high degree of regularity for the linear backbone structure. The critical region of the infrared spectrum for assessing Alkyne C-H bending bands (unsaturated) in aliphatic hydrocarbon is 600–700  $\text{cm}^{-1}$ . Absence of Alkyne C-H bending bands has been observed in shale samples collected from Kampung Guar Jentik.

### 5.2. Aromatic hydrocarbon

The Aromatic In-plane C–H bending and Aromatic out of plane C–H bending appear in the regions 1275–1000  $\text{cm}^{-1}$  and 900–690  $\text{cm}^{-1}$ . Aromatic C=C stretching can be observed in 1430–1600  $\text{cm}^{-1}$ . Five samples comprises Aromatic C=C stretching. All samples of shale from KP formation contain Aromatic out of plane C–H bending and Aromatic In-plane C–H bending (Table 1).

### 5.3. TOC and humic acid relationship

Biodegradation of organic matter causes humic substances which are the major components of the natural organic matter in soil and water as well as in geological organic deposits such as lake sediments, peats, brown coals and shales. Humic substances can be subdivided into three major fractions (1) Humin, (2) Humic acid, and (3) Fulvic acids. Humic acids (HAs) comprise a mixture of weak aliphatic (carbon chains) and aromatic (carbon rings). On average 35% of the humic acid (HA) molecules are aromatic (carbon rings), while the remaining components are in the form of aliphatic (carbon chains) molecules. It is suggested that values of the relationship E4/E6 for humic acid is smaller than 5.0 and between 6.0 and 8.0 for fulvic acids [18]. Higher degree of aromaticity of humic acid in shale was evidenced by lower E4/E6 ratio value (1.05–1.73) in Kubang Pasu formation extracted by methanol.

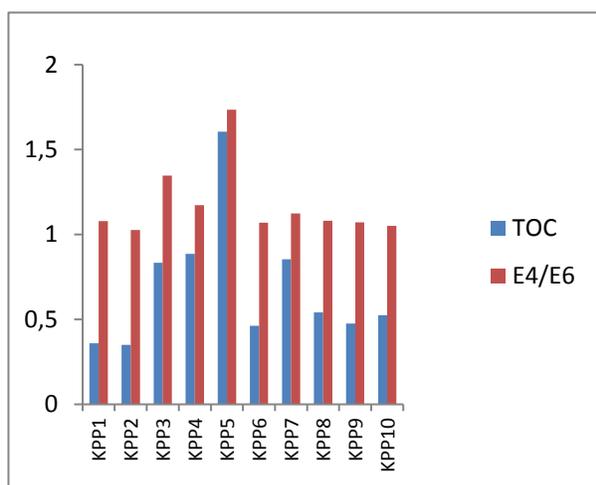


Figure 5. TOC and E4/E6 values in studied shale sample

Preservation and accumulation of organic carbon is different in shale as compared to soil organic carbon. In soils, absorbance of organic carbon increases with increase in the structure of humic substances [19]. However, this phenomenon is not clearly understood in shale. In this study, we proposed that same phenomenon has been observed in studied shale sample of KP formation as by evidence of increase in TOC values with humic substance (Figure 5). This association led us to speculate that, humic substances and organic carbon relationship in is not effected by the grey shale specially with low organic carbon preservation and accumulation conditions.

The performed investigations allowed the formulation of the linear relationship between the humic spectroscopic UV-visible ratio (E4/E6) and total organic carbon concentration. The correlation coefficient calculated for this linear relationship of TOC and E4/E6 is equal to

$R^2=0.873$  (Figure 6). It can be observed that as concentration of organic carbon increases E4/E6 ratio also increases which shows that in the distribution of humic acid in shale, organic carbon may be one of the most important factors.

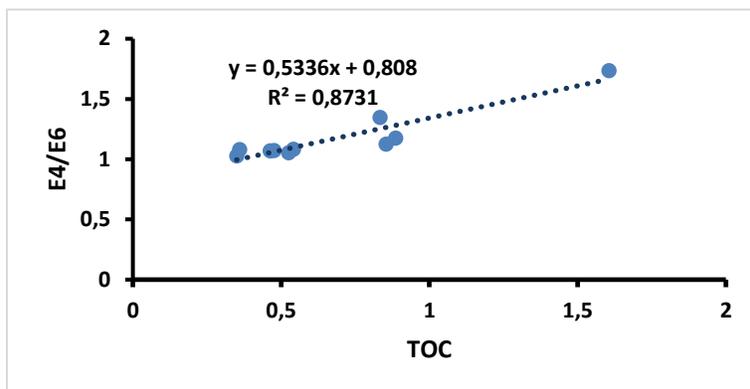


Figure 6. TOC and E4/E6 relationship

## 6. Conclusion

Three division has been made in FTIR spectra of the shale samples from KP Formation: - OH groups stretching vibration, Alkyne C-H bending bands and Alkane C-H bending band in Aliphatic hydrocarbons and absorption spectrum of Aromatic C=C stretching and Aromatic out of plane C-H bending. Dominance of humic acid and aromatic hydrocarbon by UV-Vis and ATR-FTIR analysis in shale samples indicates possibility the terrestrial origin of deposition. This study also explore that the obtained concentration of TOC in the shale of Kubang Pasu formations shows low values indicating the oxidation of organic matter in both outcrops. Petrographic studies reveal that the studied samples consist mainly of dark to light grey, silty, micaceous, massive, discontinuous wavy parallel laminated, brownish massive, parallel laminated and non-calcareous mudstone. This study also shows the significance of spectroscopic techniques to determine the type of humic substance and their relationship with the total organic carbon in shale. Positive correlation ( $r^2=0.873$ ) between total organic carbons with humic acid suggested that if shale enriched in organic carbon had the more powerful absorption of humic acid and it also indicates that TOC plays an important role in controlling the humic acid level in shale.

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