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Potential of OM of Iranian peat and swamp and characterization of physico-chemical properties of organic soils

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Abstract

The objective of this work was to investigate the potential of three different kinds of Iranian peat and swamp soils as sources of organic matter (OM) in the Golestan Province, Northern Iran. Comparison of the peats was done in terms of the degree of humification on the von Post scale. Moreover, the X-ray fluorescence, X-Ray Diffractometry, and Fourier transform infra-red (FT-IR) techniques were used to investigate their mineralogical and geochemical properties. Also a method was tested for the sequential extraction of OM from Suteh peat, in which the following organic solvents were utilised in sequence: (I) ethyl ether, (II) ethanol, (III) 1,4-dioxane, and (IV) n-hexane; each extract was analysed by FT-IR spectroscopy, and the residue was used in the next phase. The results obtained indicated that OMOM extracted during each step was different; nevertheless, some spectral features such as those attributable to lignin, carbohydrate, phenol, wax, and fats were common to all phases. Major absorbance spectra were related to specific extraction steps, namely polysaccharide, proteins, alkyne, humic acids, esters, aldehydes, and cellulose.

1. Introduction

Peat and organic soils are formed by the accumulation of partially decayed vegetation in areas of poor water drainage [1]. Deposits of peat vary from the small pockets of organic soil that are found along the banks of rivers and around the margins of lakes to much larger areas of peatland, and are known by several names including mire, fen, and swamp [2]. The thickness of a peat deposit ranges from as little as 30 cm (the minimum thickness of organic material that can be considered as peat soil) to 50–70 m [2]. Basin peat swamps are often dome-shaped, with thick ombrogenous peat forming the central portion of the dome [3-5]. Thus peat offers high concentrations of organic matter (OM) in soilOM; yet this is often closely associated with an inorganic fraction. The mineral components are derived from inOM contained in sediments and by adsorption from groundwater [6], and consequently, the source of water significantly influences peat geochemistry [7]. In addition, the inorganic composition of peat varies considerably with respect to its localization [8].

Peat soils are found in most countries and regions except for desert and polar zones [9]. The scarcity of ecological and geochemical data on tropical peat, especially in SE Asian region, has been recognized when assessing its potential role in, and impact on, the global carbon budget [10]. According to the IMCG global peat database [11], the interpreted World Soil Map of Van Engelen & Huting [12] shows 11,510 km^2 of gley soils and no Histosols in Iran, although there are reports of >3 m of sedge peat around Lake Zeribar in the Zagros Mountains [13] and “peatlands” on the Caspian Sea and along rivers [14]. More recently,

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Rahgozar & Saberian (2015) have studied the properties of peat collected from two Ramsar wetlands in central Iran, namely the Chaghakhor Wetland in the Chahar Mahal and Bakhtiari Province and the Gavkhuni Swamp in the Isfahan Province [9]. On the basis of climate, the Golestan Province (North Iran) should be one of the most suitable locations for peat formation within Iran, and although there is no peatland inventory for this area, some peatlands have been found with the help of a consultant and the Gorgan Mountain Climbing Council.

Peat is a concentrated form of soil OM that has environmental, industrial, agricultural, and medical uses that range from sustaining the productive capacity of agricultural land, for example, through its role in the transportation of trace metals in ecosystems [15] to the use of Pentacyclic triterpenoid ketones extracted from soil OM as tools in cancer therapy [16]. Numerous methods have been proposed for the extraction of OM from soil. Almost 200 years ago, Achard (1786) used alkali to extract humic and fulvic acids from peat [17]. More recently, many studies have used ionic liquids to extract and dissolve OM [18], lignin [19], carbohydrates [20], and proteins [21]. Osman & Saim (2012) removed organic contaminants from soil using a pressurised liquid extraction technique [22]. Nowadays, the most common methods used for extracting humic substances from soil are still based on the Achard’s procedure [23]. Recently, several methods have been suggested for extraction using organic and alkaline solvents, aqueous solutions, chelating agents, and sodium hydroxide + sodium pyrophosphate solution [23, 24]. According to Alexandrova (1960), sodium pyrophosphate solution extracts organomineral complexes without removing iron and aluminium from soil. Using glycerol, it is believed that a subsequent release of any humic substances can be obtained [23]. Organic carbon associated with soil OM was sequentially extracted at incremental pH by You et al. (2006) [15]. Preston & Newman (1992) believed that some forms of OM could not be extracted with alkali [25]. Hayes et al. (1975) proposed the sequential extraction and indicated that this method had more treatment than the others [26]. Senesi et al. (1983) examined the chemical and spectroscopic properties of soil OM isolated by the sequential extraction method [27]. Many extraction methods have been explored, especially since the identification of OM from mineral soil components was simplified by the development of techniques such as GC-MS, HPLC, and elemental analysis [28-29].

The aims of this work were to (a) compare the composition of peat soil of the Golestan Province (North Iran) as three different kinds of peat and swamp and differential characteristics with peats of other ecological condition; and (b) to test a sequential extraction method for extraction of organic material from peat soil materials.

2. Methods

2.1. Studied area and field sites

The field sites were three peatlands with different ecological conditions located in the Golestan Province, Iran (Figure 1).

For this work, we chose three peatlands of different types located in different parts of the province, namely a coastal swamp (CS) (Galougah CS), a highland peat swamp (PS) (Ghaleh-ghafeh PS), and a peat swamp forest (PSF) (Suteh PSF) (Table 1).

Galougah CS

Galougah CS lies near the Qareh Sou Basin and Gorgan Gulf (Figure 1, No. 1). It is a coastal swamp (Figure 2a) located on the southern shore of the Caspian Sea (-28 m a.s.l.). The Gorgan Gulf, covering an area of around 400 km^2, is one of the surface water resources of SW Golestan. Its unique ecosystem provides a crucial habitat for cartilaginous fish and many migratory birds. The vegetation of the Gorgan Gulf is dominated by the Phragmites and Potamogeton species.

Ghaleh-ghafeh PS

Ghaleh-ghafeh PS is a highland peat swamp situated near the Minudasht City in SE of the Golestan Province (Figure 1, No. 2). Geologically, the Ghaleh-ghafeh area mainly consists of alternating dark grey to greenish shale and sandstone, thick-bedded sandstone with plant remains and coal seams, thin-to-thick-bedded fossiliferous limestone with grey shale, thick-bedded and unconsolidated sandstone and conglomerate, clay, and silt. The predominant soil texture is silty clay loam and clay loam [30]. The climate of the Minudasht area is a temperate mountain type at altitude, while in the plains, a temperate and semi-humid climate prevails. The mean annual precipitation within the studied area ranges from 138 to 335 mm [31]. Ghaleh-ghafeh PS (Figure 2b) is a seasonal swamp that is used as pasture for livestock, and there is some local irrigation nearby. Its vegetation is dominated by the Carex and Phragmites species.

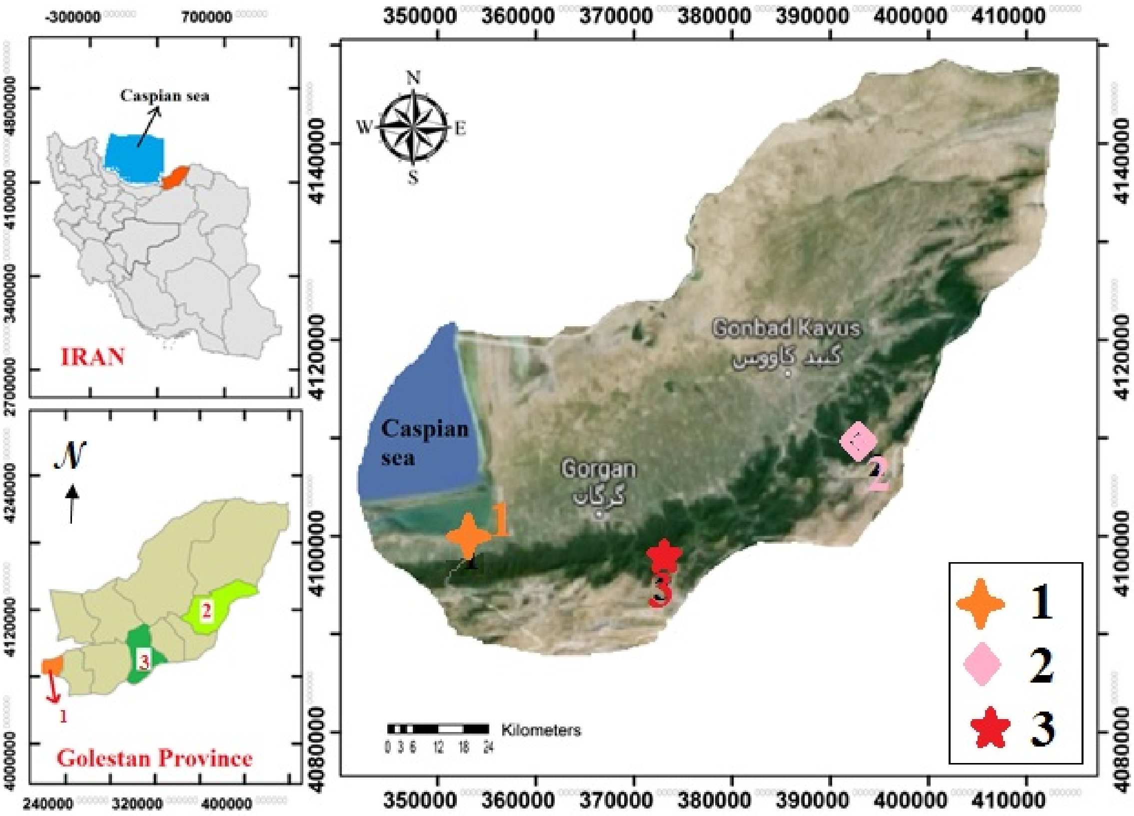


Figure 1. Map of Golestan Province in the north of Iran. The field sites are indicated by the filled red circles: (1) Galougah CS; (2) Ghaleh-ghafeh PS; (3) Suteh PSF.

Table 1. The coordinates of sampling locations.

Site	Latitude	Longitude	Altitude (m a.s.l.)
Galougah CS	36° 47' 13.01" N	53° 47' 47.55" E	-28
Ghaleh-ghafeh PS	37° 0' 46.78" N	55° 27' 28.52" E	1600
Suteh PSF	36° 40' 6.79" N	54° 25' 45.93" E	1500

Figure 2. Studied areas: a) Galougah CS; b) Ghaleh-ghafeh PS; and c) Suteh PSF.

Suteh PSF

Suteh PSF is located in the Ziarat jungle, in the southern part of the Golestan Province (Figure 1, No. 3). The altitude of the region is approximately 950–2000 m a.s.l. Two stratigraphic units, the Precambrian and Mesozoic sediments, play major roles in its lithology. The Precambrian sediments consist mainly of dark green metamorphic schist (mica schist, chlorite schist, quartzite, marble, and slate) and the bright green Gorgan green schist. The Mesozoic sediments are mostly limestone and dolostone with layers of marl in the upper

Jurassic. In some places, there are loose sandy Quaternary sediments. According to the Emberger climate diagram, the climatic conditions are temperate and semi-arid [30]. The annual rainfall is approximately 520 mm, and the annual mean temperature is approximately 18 °C. Figure 2c shows an image of Suteh PSF. The forest canopy is formed by beech, oak, alder, maple, plum, elm, linden, maple, and walnut along with some rare species like cypress and yew. There is an understory of bushes, and the most important ground cover plants around and within the Suteh PSF are Phragmites sp. and mosses. Due to the presence of rare plant species, the site is protected under the natural resource legislation of Iran.

Moreover, some of the hydrological data such as flow velocity, hydraulic radius, and bed slope of the major hydrometric station in the studied area, based on [32], have been presented in Table 2. In terms of permeability of the studied area, most part of this area can be considered as class C (infiltration rate between 12.5 and 25 mm/h) and several part in class B (infiltration rate between 2.5 and 12.5 mm/h) of hydrology of soil.

Table 2. Hydrological information about major hydrometric station of the studied area [30].

Rivers	Qareh-Sou (near Galougah CS)	Narmab (near Ghaleh-ghafeh PS)	Chehel-Chay (near Ghaleh-ghafeh PS)	Khormaloo (near Suteh PSF)	Soosara (near Suteh PSF)
Bed slope (%)	0.14	0.03	1.75	1.09	0.17
Velocity (m s^{-1})	0.32-0.89	0.28-1.32	0.4-1.14	0.7-1.4	0.21-1
Hydraulic radius (m)	0.45-2.4	0.16-0.53	0.15-0.32	0.21-0.34	0.08-0.46

2.2. Collection and preparation of peat samples

The samples were collected in April 2014 (spring season) from various locations within all the three sites. At each sampling station, peat was excavated with a hand trowel from an area 10 cm in diameter, and some cores were obtained from each site to 40 cm deep. The samples were collected from four depths (0–10, 10–20, 20–30, and 30–40 cm). Since the area of the studied peats and swamps was not too much, some samples were randomly selected and collected. The degree of humification was determined in the field according to the von Post scale. In the laboratory, the samples were dried to a constant mass at 110 °C and then pulverised in a swing mill.

2.3. Characterization of peats and OM

The mineralogy of the samples collected from 30-40 cm depth at all sites was characterized using standard powder X-ray diffractometry (XRD) (EQuniox 3000, Inel, France) to study their structure and properties, and X-ray fluorescence (XRF) (Xunique II X-ray diffractometry with Cu Ka radiation) to study their inorganic matter.

FT-IR spectroscopy is one of the most applicable techniques used for determining OM in soil. The spectral properties represent the OM content based on superposition of the absorbance of bands [33]. In this work, the FT-IR technique was used to examine the OM contents of all the three peat types, and to investigate the spectral characteristics of the dried OM extracted from Suteh peat in each phase of the extraction procedure described below. For the FT-IR analysis, sub-samples of soil (0.035 g each) were mixed with 0.35 g of KBr and then pressed into pellets. The spectra were recorded on a Nicolet Nexus 670 (U.S.A) spectrometer within a spectral range of 400-4000 cm^{-1}.

2.4. Extraction of OM

On the basis of characterisation, the Suteh PSF peat was chosen for extraction of OM. The remainder of the dried and pulverised peat collected from all depths at this site was mixed to form a composite sample.

Sequential extraction of OM was carried out on about 500 g of the composite soil sample in four phases in a glass bottle. Each phase involved mixing the soil with 500 mL of the solvent at room temperature, then shaking (IKA, model KS 501 digital) for ten days. At the end of each phase, the remaining soil residue was separated from the liquid phase by centrifugation, then treated with the next solvent. The supernatant solution removed at the end of each phase was dried for the FT-IR analysis.

The sequential extraction scheme is illustrated in Figure 3. In phase 1, the sample was dissolved in ethyl ether, which is an organic compound in the ether class (formula $(C_2H_5)_2O$). The solvent for phase 2 was ethanol (ethyl alcohol) (C_2H_6O). In phase 3, the soil residue was dissolved in dioxane ($C_4H_8O_2$), which is an organic compound that resembles ethyl ether, and is similarly classified as an ether. Finally (phase 4), the soil residue that remained from the other extractions was dissolved in n-hexane (C_6H_{14}), which is an alkane solvent.

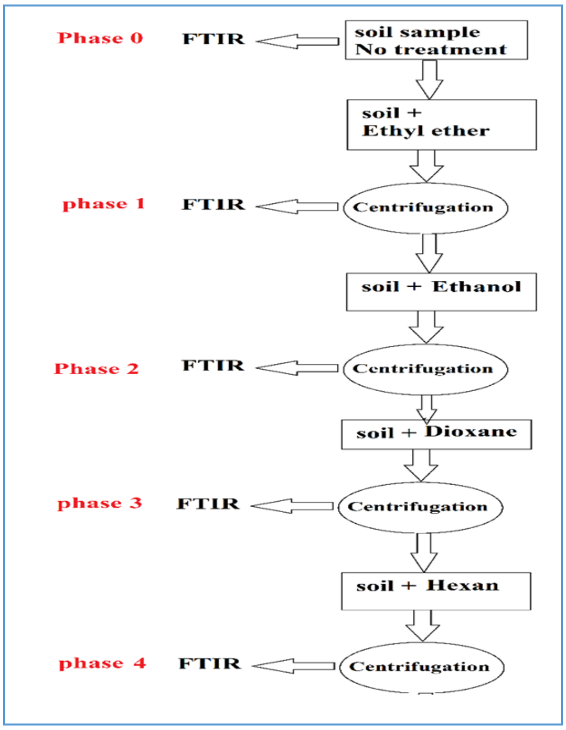


Figure 3. Flowchart of OM extraction.

3. Results

3.1. Characterization of peats

Degree of decomposition

The schematic pictures of the peats from the three sites are compared in Figure 4. At Galougah CS, the peat is almost completely undecomposed and falls in the range of H1 to H2 on the Von Post scale. Ghaleh-ghafeh PS has a very slightly decomposed (H3) peat, which, when squeezed, releases muddy brown water. Suteh PSF peat is composed of moderately decomposed plant material with a degree of humification ranging from H3 to H5 on the von Post scale (muddy brown water, no peat passing between the fingers, and some plant structures remaining).

Inorganic materials

A detailed account of the mineralogy of the samples obtained using XRD (EQuinox 3000 Inel, France) is shown in Figure 5. The XRD analysis of the samples of Galougah CS peat revealed an abundant presence of quartz and magnesium silicate (Figure 5A). Even though XRF of this sample shows a high Ca content (16.5%), this is not reflected in XRD, which may be due to the absence of calcite crystals.

The XRD analysis of the sample from Ghaleh-ghafeh PS revealed mineral characteristics with the presence of quartz mineral, anorthite, and kyanite (Figure 5B). The XRD analysis of the sample (Su-40) from 40 cm depth at Suteh PSF revealed mineral characteristics with the presence of the quartz mineral, anorthite, calcium carbonate (calcite), chloritoid, and montmorilonite (Figure 5C).

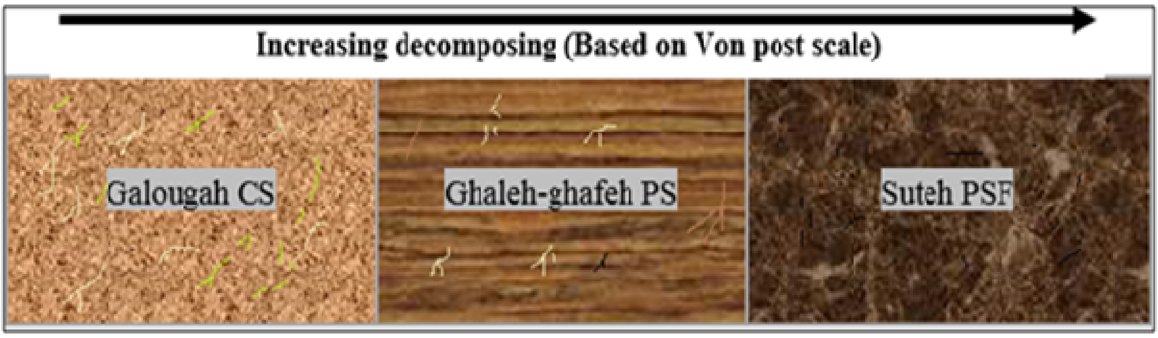


Figure 4. Schematic comparison of the studied area (arranged in order of increasing degree of decomposition according to the von Post scale).

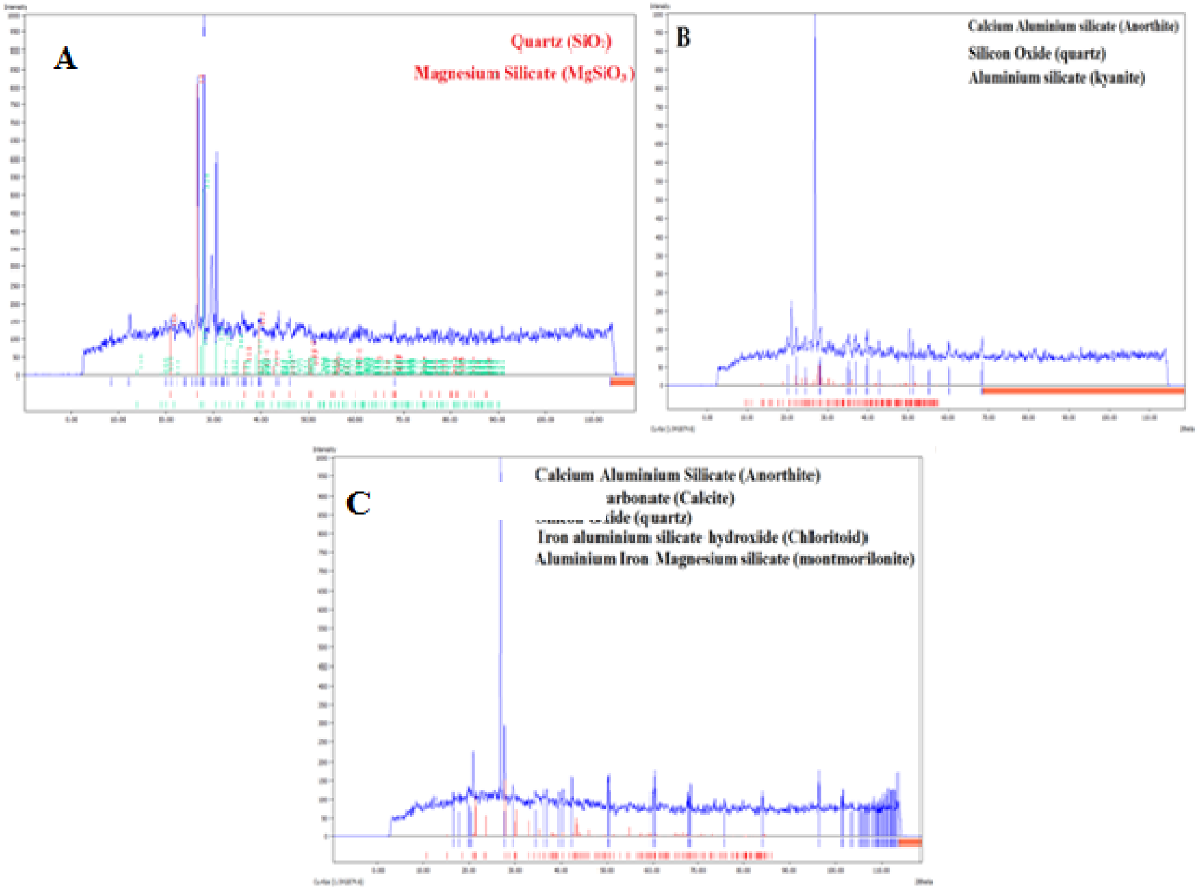


Figure 5. XRD results of samples: a) Galougah CS, b) Ghaleh-ghafeh PS, and c) Suteh PSF.

Table 3 presents the elemental composition, as determined using XRF (Xunique X-ray cu-ka radiation). Concentration of sodium, chlorine, and magnesium in Galougah CS samples among the studied areas is the highest, whereas that from Ghaleh-ghafeh PS shows the greatest abundance of a compound of aluminum, silicate, and carbonate. The sulfur value for Suteh PSF is greater than that for the other sites. In terms of iron, all the three areas are the same. As shown in Table 3, the highest concentration among the sampling areas (comparative among three kinds of studied peat) for each element is indicated by shaded cells.

Table 3. XRF results of the samples.

	Galougah CS (%)	Ghaleh-ghafeh PS (%)	Suteh PSF (%)
Na_2O	1.56	0.31	0.06
MgO	3.03	1.78	1.63
Al_2O_3	7.1	9	5.93
SiO_2	30.2	56.4	41.9
P_2O_5	0.11	0.25	0.29
SO_3	1.15	0.3	1.58
Cl	1.71	0.01	0.05
K_2O	1.47	1.88	1.85
CaO	16.5	1.3	7
TiO_2	0.68	0.9	0.77
V_2O_5	0.02	0.02	0.03
Cr_2O_3	0	0.01	0.01
MnO	0.11	0.05	0.09
Fe_2O_3	5	4.8	5.5
SrO	0.21	0.02	0.03
L.O.I	31.1	22.9	33.23
Sum La-Lu	0.01	0.02	0.05
BaO	0.03	0	0

Organic materials

Figure 6 shows the FT-IR results (Nexus and Thermo Fourier transform infrared spectrometer) of different samples. The FT-IR spectra displayed a number of characteristic absorbance peaks. Samples from all of the sites showed spectral signals indicating the presence of silicate minerals in the form of the diagnostic peaks of clay minerals at 3700 and 467 cm^{-1} [34, 35].

In addition, the 467 cm^{-1} band is also present in the spectrum of quartz. Mineral interference is also apparent in the 1030 cm^{-1} polysaccharide band due to the strong superimposed silicate band near 1000 cm^{-1}.

The FT-IR spectra for Galougah CS (Figure 6A) include spectra with a weak intensity of OH stretch from water, carbohydrates and phenols (3300–3700 cm^{-1}), spectra with a weak intensity of CH stretch of aliphatic compounds (2850–2950 cm^{-1}), and C-H deformations (1450 cm^{-1}) that are related to the phenolic (lignin) and aliphatic structures.

Major absorbance bands in the FT-IR result of Ghaleh-ghafeh PS (Figure 6B) include spectra with a weak intensity of OH stretch from carbohydrates (3300–3700 cm^{-1}), spectra with a weak intensity of CH stretch of aliphatic compounds (2850–2950 cm^{-1}), and spectra with a weak intensity of aromatic C═C stretching (1600-1650 cm^{-1}) that is related to lignin and other aromatics.

Suteh peat was chosen for trial of the sequential extraction method on the basis of:

- Value of loss on ignition (highest for the Suteh PSF peat)
- Degree of humification based on the von Post scale (again highest for the Suteh PSF peat)
- FT-IR results of pristine samples (FT-IR spectra for Suteh PSF peat show a higher absorbance and more peaks than those of peat from the other two sites)
- FT-IR results for some preliminary test extractions using ethanol indicated that more organic components appear to be present than in the other two peats.

For the Suteh PSF peat, FT-IR at phase 0 (pristine soil sample) (Figure 6C) shows evidence of silicate minerals including the diagnostic peaks for kaolinite at 3700 and 467 cm^{-1}. Also the peak of 467 cm^{-1} may be related to the presence of quartz in the sample [34]. Major absorbance bands in the FT-IR spectra include the CH stretch of aliphatic compounds (2850–2950 cm^{-1}), the band at about 1513 cm^{-1} related to an aromatic lignin band, the OH stretch from water [36], carbohydrates and phenols (3300–3700 cm^{-1}), and the O-H deformation and C-O stretching (1030-1080 cm^{-1}) that is related to polysaccharides. In addition, FT-IR analysis of the peat samples showed aromatic C═C stretching or asymmetric C-O stretch (1600–1650 cm^{-1}) that is related to lignin and other aromatics or aromatic or aliphatic carboxylates and C-H deformations (1450 cm^{-1}) that are related to phenolic (lignin) and aliphatic structures, and the CH stretch of aliphatic compounds (2925 cm^{-1}) that is related to waxes and lipids. Also at 533 cm^{-1}, the FT-IR results show disulphide spectra that may be related to proteins. Disulphide bonds play an important role in the stability of proteins [37]. Due to the ability of sulfur to reduce the oxidation number, the presence of disulphide may be due to the presence of minerals such as pyrite (iron sulphide).

3.2. Extracts of organic material

Phase 1 (diethyl ether extract)

The FT-IR result of the first extraction phase (using ethyl ether) is shown in Figure 7. The result of this phase shows some common spectra between phase 0 (soil) and phase 1 (supernatant) like aromatic C═C stretching (1621 cm^{-1}) that is related to lignin, the CH stretch of aliphatic compounds (2925 cm^{-1}) that is related to waxes, carboxylate and fats, the OH stretch from water, carbohydrates, and phenols (3407 cm^{-1}). In addition, the FT-IR spectrum shows some characteristic absorbance peaks at 602 and 673 cm^{-1} and 1117 cm^{-1} assigned to inorganic sulphate, the C–O stretch (1426 cm^{-1}) due to carboxylic structures (humic acids), and the small and weak peak (1707 cm^{-1}) due to the presence of free organic acid that may be generated by a chemical reaction between the ether and the peat sample. In addition, the bands at 1426 and 873 cm^{-1} can be assigned to inorganic carbonate. The spectral characteristics indicating the presence of clays cannot be seen in this phase (phase 1). Also disulphide spectra due to proteins are not present in the bands.

Phase 2 (ethanol extract)

The FT-IR result of the second extraction phase is shown in Figure 8. The major absorbance bands in the FT-IR spectra of ethanol extracts include a very weak peak of C-H compound (649 cm^{-1}), which may be due to an alkyne; ester peaks (743, 1074, 1125 cm^{-1}), which may be derived from ethanol in the presence of a dehydrating agent; a weak polysaccharide peak at 1039 cm^{-1}; humic acids (1462 cm^{-1}) due to reaction between carboxylic structures and ethanol in aerobic conditions (in the presence of oxygen); a small peak for C=C stretch at 1641 cm^{-1} due to lignin (the same as untreated sample); and IR spectrum exhibits a strong carbonyl band at 1728 cm^{-1}, which is typical of an ester. In addition, the CH stretch of aliphatic compounds (2925 and 2854 cm^{-1}) is related to waxes, carboxylate, and fats; and adsorbed water (3407 cm^{-1}) was observed.

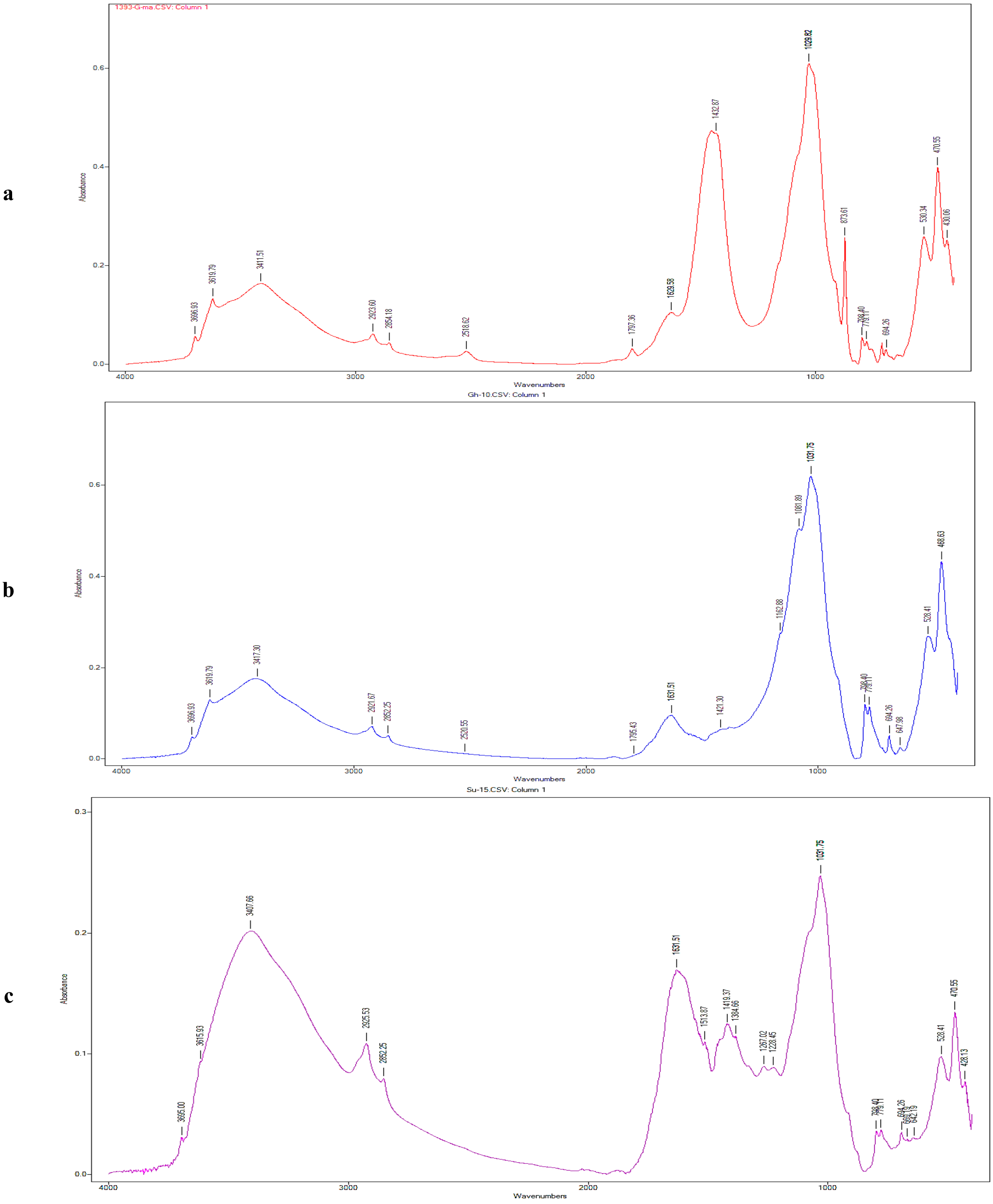


Figure 6. FT-IR results of (untreated) samples: A) Galougah CS, B) Ghaleh-ghafeh PS, and C) Suteh PSF.

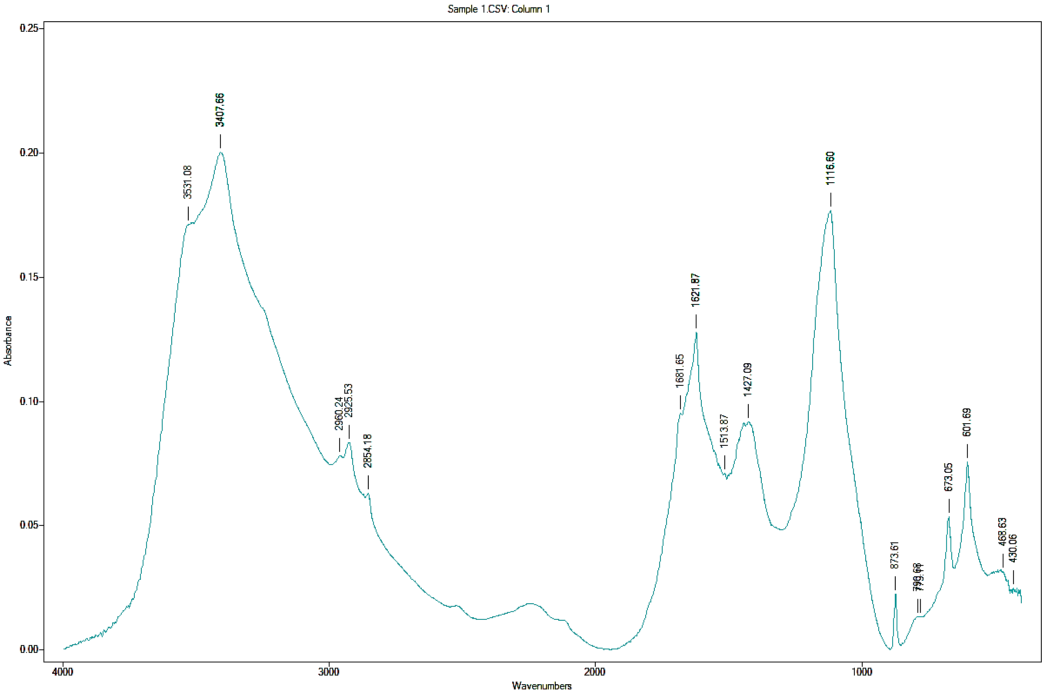


Figure 7. FT-IR result of the Suteh PSF sample after phase 1 (ethyl ether) extraction.

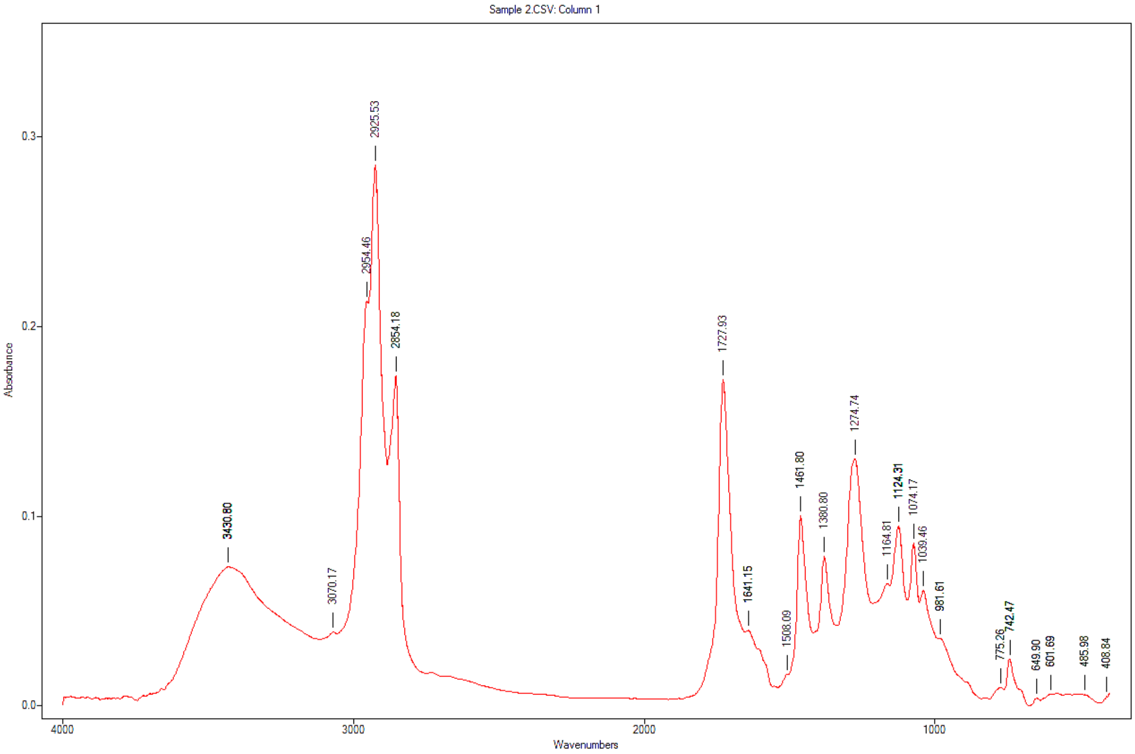


Figure 8. FT-IR spectra of phase 2 (ethanol) extraction.

Phase 3 (dioxane extract)

The FT-IR result of the third (dioxane) extraction phase is shown in Figure 9. The FT-IR spectrum of this phase shows some specific absorbance peaks like ester peaks (879 and 1213 cm^{-1}) that may be generated by dehydration of alcohol; a polysaccharide peak at 1076 cm^{-1}; a small and weak cellulose peak at 914 cm^{-1} that might be due to plants or wood; an ether peak (1139 cm^{-1}) that may be related to similarity of dioxane and ether and the effect of dioxane on the sample; a small peak for C=C stretch at 1455 cm^{-1} due to lignin; C=C stretch at 1646, which is more likely to be due to water associated with the KBR pellet and peak at 1743 cm^{-1} actually suggests the presence of alcohol/glycol hydroxyl and ester-type functional groups or may be the C=O stretch of ketone that might be the result of glucose production from fatty acids. Also like the other previous extractions, the CH stretch of peaks associated with aliphatic compounds (waxes, carboxylate, and fats) and adsorbed water were observed but with a lower intensity.

Phase 4 (hexane extract)

The FT-IR result of the final phase 4 (hexane) extraction is shown in Figure 10. The following peaks are present: ester peaks due to dehydration of alcohol (705 and 742 cm^{-1}); C-O stretch due to ether that may be generated by the impact of hexane on the sample (1123 cm^{-1}); peaks of polysaccharide (1072 and 1040 cm^{-1}); phenols from lignin (1380 cm^{-1}); humic acids (1463 cm^{-1}); and C=O stretch of aldehydes similar to ethanol extraction (1729 cm^{-1}). The peaks relating to the CH stretch of aliphatic compounds (waxes, carboxylate, and fats) and adsorbed water were also observed, as in the other extraction phases.

Table 4 shows how much OM was extracted from each sample.

The FT-IR results of the samples differed between the stages of the sequential extraction, with some phases showing special peaks and some peaks being diminished at individual phases. The indications of the spectra of untreated samples and the treated phases are summarized for comparative purposes in Table 5.

4. Discussion

4.1. Characterization of peats

According to the von Post scale, Suteh PSF has the most highly humified peat among the three sites investigated, whereas the least humified peat was at Galougah CS. The minerals of Suteh PSF have been covered by OM of the peat swamp forest in the XRD results. In addition, XRD results showed quartz and Fe mineral components are common in all of the peats.

Based on the XRF results, Galougah CS has more sodium, chlorine, and magnesium than the other peatlands because it is located near the sea. The abundance of aluminum, silicate, and carbonate compounds at Ghaleh-ghafeh PS may be due to geological factors. Due to the higher rate of decomposition, the sulfur value for Suteh PSF is higher than that for the other sites. The amounts of some elements found in the samples in this work are compared with peat data from Germany, Finland, Canada, and the United States in Table 6. It can be seen in Table 6 that the amount of a particular inorganic species present varies considerably between regions, whereas the Suteh PSF and Galougah CS peats are fairly similar to the North American (USA and Canadian) peats, Ghaleh-ghafeh PS peat is more like the Finnish peats. Moreover, the composition and characteristic of Suteh PSF, Galougah CS, and Ghaleh-ghafeh PS was done with some peat in Canada. As presented in Table 7, percent of Nitrogen, Ash content (LOI), and pH of these peats and swamps were compared. In the case of nitrogen, Canadian peat content is more than Iranian peat but about the ash content, Iranian peats are completely different and higher than the Canadian peats.

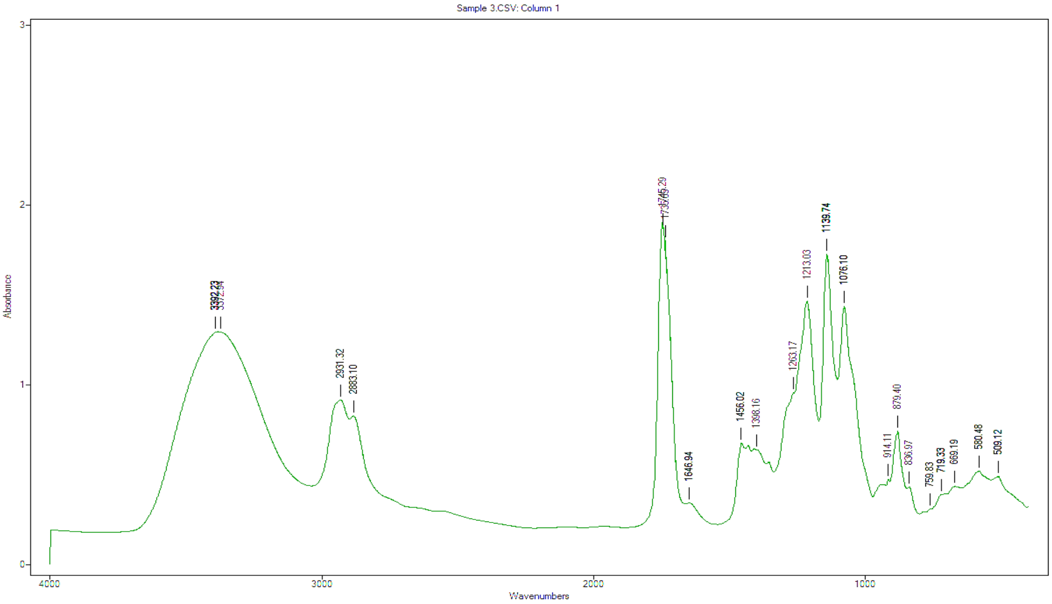


Figure 9. FT-IR spectra of the Phase 3 (dioxane) extraction.

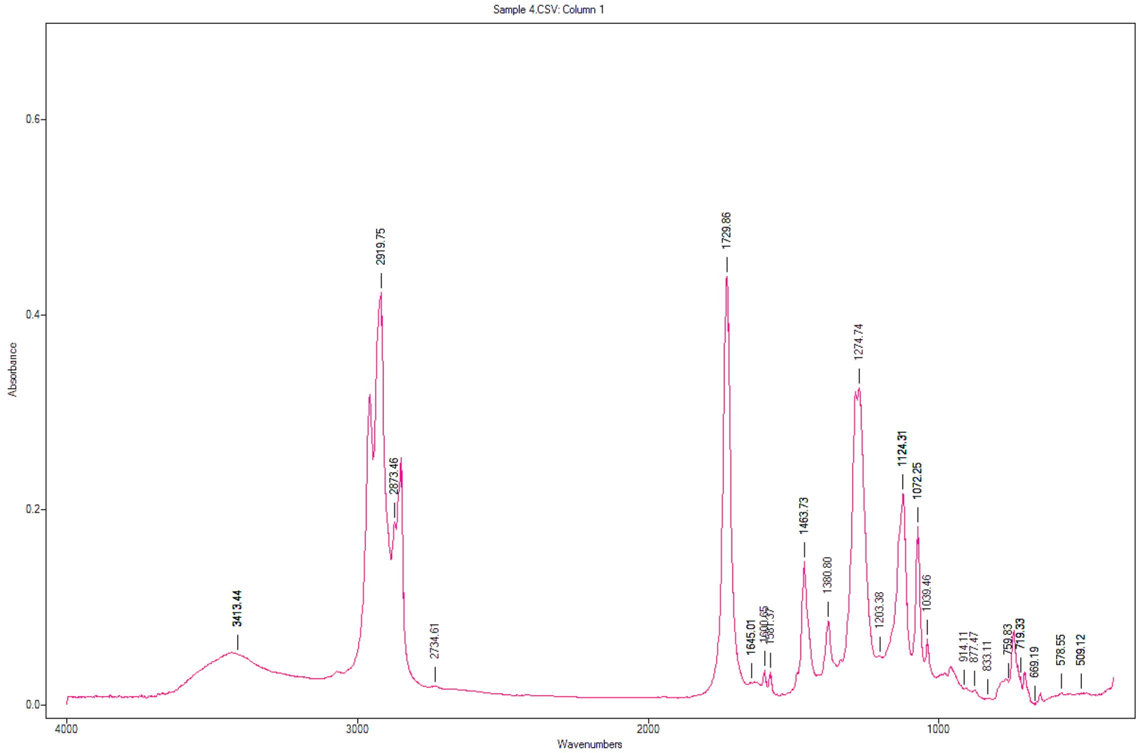


Figure 10. FT-IR spectra of the phase 4 (hexane) extraction.

Table 4. OM extracted from each sample.

	M1*	M2**	M1+M2	M1+M2 (110)	M1+M2 (550)	Water (%)	OM (%)
Su-15	1.251	24.771	26.022	26.009	25.462	1.03	43.72
Su-40	1.426	19.087	20.513	20.503	20.099	0.7	28.33
Gh-10	1.662	19.8	21.462	21.451	21.153	0.66	17.93
Gh-20	1.627	19.32	20.947	20.922	20.664	1.53	15.85
Ma-10	1.545	19.937	21.482	21.475	21.312	0.45	10.55
Ma-20	1.971	20.984	22.955	22.939	22.733	0.81	10.45

*Sample weight
** Crucible+sample weight

The FT-IR spectra are characterized by broad bands typical of natural OM due to the superposition of individual absorption bands [33]. Based on the FT-IR results, major absorbance bands include the OH stretch from water, carbohydrates and phenols, CH stretch of aliphatic compounds, a combination of C-O stretching and O-H deformation (Polysaccharides), aromatic C═C stretching of lignin and other aromatics, and C-H deformations of phenolic (lignin) structures.

4.2. Extraction procedure

Evidence of clay minerals, phenolic compounds, lignin and proteins, which were present in the original soil, did not appear in any of the extracts. On the other hand, all extracts exhibited OH stretching indicative of water, carbohydrates and phenols, aromatic C═C stretching reflecting the presence of lignin, and the aliphatic CH stretching associated with waxes, carboxylate, and fats. Free organic acid was present in the phase 1 (ethyl ether) extract only, whereas the C=O stretch indicative of aldehydes was apparent in phase 2 (ethanol) extract only, and evidence of cellulose and ketone in the phase 3 (dioxane) extract only. Other components of the original soil appeared at two or three of the four extraction phases. Seven different components were evident in the extracts at phases 1, 3, and 4, and eight components were detected at phase 2. Our technique and results are briefly compared with those of other workers in various parts of the world in Table 8.

Table 5. Comparison of FT-IR spectra in different phases of extraction.

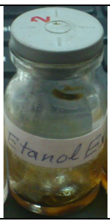
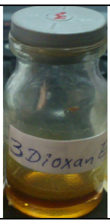
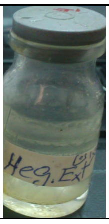
Spectrum	**Untreated sample**	**Ethyl ether extract**	**Ethanol extract**	**Dioxane extract**	**Hexane extract**
					
Clay minerals	✓				
C-O stretching (polysaccharide)	✓		✓	✓	✓
OH Stretch (water, carbohydrates, and phenols)	✓	✓	✓	✓	✓
Aromatic C=C stretching (lignin)	✓	✓	✓	✓	✓
C-H deformations (phenolic lignin)	✓				
CH stretch of aliphatic (waxes, carboxylate, and fats)	✓	✓	✓	✓	✓
Disulfide (proteins)	✓				
C-H compound (alkyne)		✓	✓		✓
C-O stretch (ether)		✓			✓
C–O stretch (humic acids)		✓	✓		✓
Free organic acid		✓			
Ester			✓	✓	
C=O stretch (aldehydes)			✓		
Cellulose				✓	
C=O stretch (ketone) or alcohol/glycol hydroxyl				✓	

Table 6. Comparison of elemental composition of this work and other country peats (after Dalouche et al. 1981; Delicato, 1996) [8, 1].

Material	**Germany (%)**	**Finland (%)**	**Canada (%)**	**USA (%)**	**This work**		
					Suteh (%)	**Ghaleh-ghafeh (%)**	**Galougah (%)**
CaO	20-45	1.5-4.6	1.3-42.7	2.3-47.8	7	1.3	16.5
Al_2O_3	1-11	1.3-5.1	3.3-23.1	5.1-16.6	5.93	9	7.1
SiO_2	10-45	50-72	7.9-38.8	42-91.2	41.9	56.4	30.2
Fe_2O_3	15-55	4.6-7.1	2.4-11.6	0.3-8.9	5.5	4.8	5
MgO	10-20	-	1.3-27.8	0.5-7	1.63	1.78	3.03
MnO	0.1-0.3	-	0.1-0.2	-	0.09	0.05	0.11
K_2O	0.1-2.5	-	0.4-2.8	0.2-2.8	1.85	1.88	1.47
Na_2O	0.2-5	-	0.3-2	0.1-2.9	0.06	0.31	1.56
P_2O_5	1-3	2.3-4.2	0-2.6	-	0.29	0.25	0.11

Table 7. Comparison of composition and properties of this work and other peat around the world studied by Levesque & Dinel (1977) [38].

	Gatineau Peat Moss (Quebec Canada)	**Cochrane Peat Bog (Ontario Canada)**	**Clothilde woody peat (Quebec Canada)**	**Ormstown Sedge-fen peat (Quebec Canada)**	**This study**		
					Suteh Peat swamp forest	**Ghaleh-ghafeh Peat swamp**	**Galougah coastal Swamp**
Nitrogen (%)	0.86	2.79	3.41	2.12	0.94	0.66	0.42
Ash (%)	6.4	6.2	10.9	7.1	33.26	22.9	17.1
pH	3.3	5.0	5.3	3.3	5.0	5.5	5.8

Table 8. Comparison between the results of this work with the results of some other studies in the same major.

Author (year)	Study subject/Solvent	Results
Hayes et al. (1975) [26]	Comparison of extractants (EDA, DMSO, DMF, sulpholane, pyridine) and properties of extracts.	Extractability increased in the general order: salts < organic chelating agents < dipolar aprotic solvents < pyridine < ethylenediamine (sodium hydroxide)
Senesi et al. (1983) [27]	Sequential extraction using ethyl ether, benzene, acetone, dioxane, THF, ethanol, DMF, pyridine, DMSO and formamide.	C, O, N and H (%, dry), plus transition of metal contents of the extracts determined. Three samples showed high C and H contents and low O content.
Schnitzer & Schuppli (1989) [39]	Sequential extraction using n-hexane, chloroform, $Na_4P_2O_7$, NaOH and distilled H_2O.	$Na_4P_2O_7$ solution extracts relatively more OM; OM is more easily extracted from soils low in clays than from those rich in clays.
You et al. (2006) [15]	Extraction using base with subsequent pH lowering and sequential pH extraction / NaOH-extraction and subsequent acidification to different pH (1 to 12).	Significant correlation between HA:FA ratio and the NaOH extractable%OC content; a significant amount of HA-associated OC was soluble in pH between 5 and 7.
Patti et al. (2010) [40]	Ionic liquid extractions of soil OM.	Level of nitrogen in the sample increased; ionic liquid Bmim Cl may function as a useful solvent for SOM
Osman & Saim (2012) [22]	Selective extraction of OM/application of sorbents in pressurised liquid extraction.	Nonpolar compounds (PAHs, chlorpyrifos, and pentachlorophenol) recovered in the first fraction using polar sorbents (like Florisil or alumina, and n-hexane); polar compounds (phenol and sterols) recovered in the second fraction using methanol.
Hernandez-Soriano et al. (2013) [41]	Organic soil was analysed by FTIR to determine changes in chemical composition after Biochar treatment.	FTIR showed polysaccharide (1035 cm^{-1}), aromatic (1600–1900 cm^{-1}) and aliphatic (2900 cm^{-1}) compounds; the spectra indicated that biochar provides a source of carbon with zero or small content of aromatic compounds and polysaccharides.
Baglieri et al. (2007) [23]	Proposed a method for the extraction of additional soil OM using $Na_4P_2O_7$ + NaOH + glycerol solutions.	Soil deprived of humic and fulvic acids; FTIR spectra of all the humic extracts were recorded in the range 3100–1250 cm^{-1}; aliphatic groups at 2922, 2853, 1460 and 1400 cm^{-1}; presence of amide I (1630 cm^{-1}); the AOM extracted by glycerol had a greater polysaccharide content.
This work	Sequential extraction using ether, ethanol, dioxane and n-hexane.	Clay minerals, phenolic compounds, lignin and proteins present in the original sample only; OH stretching of water, carbohydrates and phenols, aromatic C=C stretching of lignin, and the aliphatic CH stretching of waxes, carboxylate and fats appeared in all extracts; some compounds were apparent in only one phase, e.g. free organic acid in Phase 1 (ethyl ether), C=O stretch of aldehydes in Phase 2 (ethanol), cellulose and ketone in Phase 3 (dioxane).

The extraction of OM from soils is one of the unresolved problems in soil chemistry and biochemistry [39]. Based on this work, there appear to be some special advantages associated with the use of our chosen sequence of organic solvents on peat. For example, our results show that the protein present in the original sample does not appear in any of the extracts, which may offer an easy method for extraction of protein for medical usage, even though this is too speculative. One of the most important advantages of this technique is the availability and low cost of the organic solvents. In addition, this kind of treatment could be usefully transferred to the study of organic-inorganic complexes and could also find applications in improving our understanding of the OM portions of soils.

By the way, since in this work we just used FT-IR analysis to test the results of extraction of any phases, and using gas chromatography-mass spectroscopy (GC-MS) was impossible for the authors, it should be mentioned that some of the results of the extractants may be due to modification of the soil OM molecules.

5. Conclusions

In this work, the results of the characterization of the physico-chemical properties of three types of peats were compared. For this purpose, a highland peat swamp, a peat swamp forest, and a costal swamp in the Golestan Province, North of Iran, were considered. In conclusion, based on the above-mentioned point, the most important results are as follow:

- Based on the Von post degree of humification scale, Suteh PSF is decomposed more than Galougah CS and Ghaleh-ghafeh PS.
- Based on XRD, there was a presence of quartz, anorthite, calcium carbonate (calcite), chloritoid, and montmorilonite in Suteh PSF, a presence of quartz, anorthite, and kyanite in Ghaleh- ghafeh PS, and a large presence of quartz and magnesium silicate in Galougah CS.
- Galougah CS has more sodium, chlorine, and magnesium because it is located near the sea.
- The compounds of aluminum, silicate, and carbonate in Ghaleh-ghafeh PS were more than others, which may be due to the geological aspect.
- The sulfur value in Suteh PSF was more than the others, which may be related to the decomposing rate.
- Based on the FT-IR results, major absorption bands include the OH stretch from water, carbohydrates and phenols, CH stretch of aliphatic compounds, a combination of C-O stretching and O-H deformation (Polysaccharides), aromatic C=C stretching of lignin and other aromatics, and C-H deformations of phenolic (lignin) structures.
- The results of the comparison between the Iranian peat and the Canadian selected peat indicated that in case of nitrogen, the Canadian peat content was more than the Iranian peat but about the ash content, Iranian peat was completely different and higher than the Canadian peats, while pH of these ecological areas were approximately the same.
- The results of examining the amount of a particular inorganic species present varies considerably between the regions. For example, Suteh PSF and Galougah CS peats were fairly similar to the North American (USA and Canadian) peats, and Ghaleh-ghafeh PS peat was more like the Finnish peats.

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پتانسیل مواد ارگانیک پیت و خاک مرداب ایران و تعیین ویژگی‌های فیزیکوشیمیایی خاک‌های آلی

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چکیده:

هدف از این پژوهش، بررسی پتانسیل سه نوع مختلف پیت و خاک مرداب به عنوان منبع مواد ارگانیک (OM) واقع در استان گلستان است. مقایسه پیت‌ها برای بررسی درجه هوموسی شدن بر اساس مقیاس ون‌پست (von Post scale) انجام شده است. علاوه بر این، به منظور تعیین ویژگی‌های مینرالوژیکی و ژئوشیمیایی نمونه‌ها، روش‌های فلوئورسانس اشعه ایکس، دیفراکتومتری اشعه ایکس و طیف‌سنجی مادون‌قرمز (FT-IR) مورد استفاده قرار گرفتند. برای استخراج ترتیبی مواد ارگانیک خاک پیت سوته (Suteh)، از حلال‌های ارگانیک اتیل اتر، اتانول، دی‌اکسان ۱ و ۴ و n- هگزان در چهار مرحله استفاده شد. هر بخش استخراج شده توسط طیف‌سنجی مادون‌قرمز آنالیز شد و باقیمانده در مرحله بعد استفاده شد. نتایج حاصل نشان داد که مواد ارگانیک استخراج شده در هر مرحله متفاوت است، با این وجود، برخی ویژگی‌های طیفی نشان می‌دهند که لیگنیت‌ها، کربوهیدرات‌ها، فنول‌ها، واکس‌ها و چربی‌ها در تمام مراحل مشترک هستند؛ اما طیف جذبی اصلی نشان‌دهنده حضور پلی‌ساکاریدها، پروتئین‌ها، آلکین‌ها، هیومیک اسیدها، استرها، آلدئیدها و سلولزها در برخی از فازهای مشخص است.

کلمات کلیدی: طیف‌سنجی مادون‌قرمز، هیستوسول، کانی‌شناسی، خاک آلی، تالاب، استخراج ترتیبی.
