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Characterization of the humic acid isolated from Thar coal mines, Sindh, Pakistan

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ABSTRACT

Pakistan is rich with 185 billion tons of coal reserves in all provinces but as fuel coal's rank is poor because excessive ash, evaporative contents, sulfur and wetness, these coals fall in the category of lignite to sub-bituminous rank but lignite make the largest share of coal which is rich with significant amount of humic acid that upgrade the agricultural topsoil for increasing Pakistan's crop production. The objective of this study was to investigate the larger extraction and characterization of humic acid from low rank coal of Thar (Sindh Province). Respective coal samples were initially oxidized with 2% HNO3 and then treated with 1.0, 2.5, 3, and 3.5% NaOH solutions for the extraction of humic acid. The 3.5% concentration of NaOH was found to be the optimum for the extraction of humic acid. The extracted humic acid was investigated for its quantitative assessment through UV-Vis spectrophotometer procedure. The humic acid determined by UV-Vis spectrophotometry was 32.23%. FTIR analyses of extracted humic acid samples have shown the presence of carboxylic, phenols, alcoholic, amines and ethers functional groups. Zeta potential analysis of humic acid was -20.3 mv, negative value indicating the larger number of negative ions than positive. In XRD analysis of humic acid samples the major peak *was obtained at 44.727170. The results of the study could be useful for selection of suitable coals for humic acid extraction.*

Keywords: *Coal squashed, Humification, characterization, quantitative assessment, FTIR analyses, centrifugation, Zeta potential analysis, XRD analysis*

1. INTRODUCTION

Humic substances are mostly placed in peat and brown coals (lignite), Humic acid, Fulvic acid and Humins are the major integrants of these humic substances. (*Fulcrum Health Limited. 2004*). Humic acids and related humates are among major fertilizers being used in the Middle East, Europe, and many Asian countries. The high purity liquid hummates are in the form of Na, K, Ca salts and Manganese, Zinc, Iron, Copper also along with these salts of humic acids. (*Mona Zara, Zeeshan Ahmad et al., 2017*). The crushed and ground solid coals are processed with different proportions of alkalis for extraction of humic acid which are a source of various chemical functional groups that modify the chemical properties of soil and stimulate the plant growth (*Demirbas, 2003; Erdogan et al., 2005*). Certain aromatic and amine groups are present in humic acids that are biologically activated for plant growth. The aromatic phenols (Ar-OH), carboxylates (COO-R), ketones (R-O-R), and hydroxyl groups (R-OH) improve ion exchange properties of the soils (Demirbas, 2002).

There are differing origins of these humates moving from dense dark coal, brown coal, peat and leonardite, peat is the first stage of coal, brown coal is lignite and leonardite is an average-brown coal that has nearly all multiplex and biologically active constituents of humic substances (*Canieren, et al. 2017).* The percentages of humic acid present in various sources are (a) black peat 10–40%, (b) sapropel peat 10–20%, (c) brown coal 10–30%, (d) compost materials 2–5%, and (e) soil sludge 1–5%. Different kinds of coal's humic acid depend on temperature, pH, the extracting agent and their concentration, time taken, grain size and drying procedure factors. Generally, low grade coals seem to be the major source of humic acid (*Demirbas, 2003; Fong and Mohamed, 2007*).

Pakistani coals fall in the category of lignite to sub-bituminous ranks but lignite makes the largest share of coal reserves of the country (Mustafa et al., 2016). The use of Pakistani coal for extraction of humic acid has been rarely investigated. The objective of this study was to investigate the extraction of humic acid from lignite coal from Thar, Sindh province of the country. The effect of NaOH concentration on extraction of humic acid has been investigated and the extracted humic acids were evaluated using standard UV-Vis spectrophotometry, Fourier transform infrared (FTIR) spectroscopy analysis, and Zeta potential analysis, XRD spectra.

2. Experimental

2.1. Preparation of coal samples

Bulk coal samples, weighing 20 kg each, were collected from the Thar borehole sample; it was cleaned and dried in an oven at 105°C, allowed to stand for about 24h. coal samples were squashed using a roller crusher and disc mill powdered. All samples by homogenized air dried and sieved for picking of particles smaller than 2mm (B. Saitol and M.M Seckler 2014). Then for experimental work samples weighing 1 kg were sealed in plastic bags for use in the test work using **sub-sampling methods** (*Mona Zara, Zeeshan Ahmad et al., 2017*).

2.2. Preparation of HNO3 and NaOH solutions

The active solutions of HNO3 and NaOH were newly prepared. The HNO3 (laboratory grade 65%

Concentrated) (Merck, Kenilworth, NJ, USA) was used to make 2% active solution of

HNO3 by dissolving 2mls of HNO3 in 100 ml de-ionized water. The NaOH solutions were prepared from 98% analytical grade NaOH (Merck) in the concentrations of 1, 2.5, 3, and 3.5% by adding 1, 2.5, 3, 3.5 mls of NaOH in 100 ml de-ionized water.

2.3. Acidic pretreatment of coal by HNO3

Firstly, the 50g coal sample for extraction of humic acid was oxidized by applying 100 ml of 2% HNO3 in the beaker and stirrer by using a magnetic stirrer for 1h. After that the mixture was filtered and washed to remove unreacted acid from the oxidized coal. The oxidized coal samples were dried in an oven at 40°C and the samples were preserved in sealed plastic bags to be used for extraction of humic acid.

2.4. Extraction of humic acid by NaOH

The oxidized coal weighing 2g should be added in portions with stirring to 1, 2.5, 3, and 3.5% NaOH solutions. The pH of suspensions must be sustained at alkali range and they were permitted to settle for 48h, the supernatants then filtered. Soluble humic acid is now put on a magnetic stirrer with addition of 6M HCl until the pH would become 2. Dissolved humic acids were isolated through centrifugation under 5000-6000 rpm at -4°C for 20 mins. Humic acid samples were preserved in air-sealed bottles for further test work.

3. Analysis

3.1. Characterization by UV/Visible Spectroscopy

For UV spectrophotometer characterization of extracted samples of humic acid, firstly the samples were cleaned and filtered by using Whatman filter paper # 42. Three standard solutions of different concentrations of 50, 100, and 200 ppm were prepared following the procedure which was adopted from Mohammadi et al. (2012) and a curve was obtained. The absorbance spectra of UV were taken out at 465 nm wavelength of spectrophotometer (Varian, Palo Alto, CA, USA). To obtain the percentage of humic acid contents in extracted samples the absorbency array regarding each try had matched standard curve.

3.2. Characterization by FTIR

In this technique the infrared region of light is used in the FTIR analysis machine (Simadzu, Kyoto, Japan). FTIR analysis is used for the detecting functional groups inside isolated HA sampling. In this technique the samples were cleaned and filtered by using Whatman filter paper. In an attenuated total reflectance cell of filtered sample up to 2–3 droplets was poured and fixed inside FTIR equipment near to perforation declaration about 4.5. IR radiation humps regarding humic acid had acquired afterward 100-scrutinizes.

3.3. Characterization by XRD

X-ray crystallography might be an active analytical method chiefly applied in order to calculate phase determination in regard to crystalline compounds also able to be informative about unit cell parameters. It may be a basic gadget as a probing framework regarding nano-materials. Analyzed matter was initially cleaned and filtered by using Whatman filter paper and finely pulverized, admixed to merge, also predictable majority configuration was figured by using special Rigaku Denki X-ray diffractometer in which x-rays are scattered from crystal lattice at angle of incidence *(Kumada and et al. 2014).*

3.4. Characterization by Zeta potential

It is the scientific term for electro-kinetic in colloidal dispersion. Particularly as it shows electric potential difference against ionic films anywhere on charged colloid ion and this expresses as millivolts (mv), ranging from -100 to +100 mv. This technique gives indication of charge present on a particle's surface, negative value means your particle is negatively charged and positive value means it is positively charged. Zeta potential of humic acid solution was measured by Malvin Zetasizer in which an emergence ray of light crossed by cuvette & lightened those particles which were present in sample and identified over 13° angle by detecting equipment. All clones in regard to each sample had examined through minimal or twice the assessments every 120 seconds interval of time *(Malvern, 2005).*

4. Results and discussion

Extraction of humic acid from low rank Thar coal with alkali was done by treating coal with four different percentages of NaOH, i-e, 1%, 2.5%, 3% and 3.5%.

4.1. Characterization of Extracted Humic Acid by Uv-Vis Spectrophotometer

Figure 1 Shows Humic Acid Contents Extracted from Thar Coal With four Different Concentrations of NaOH (1, 2.5, 3, and 3.5%). Among all four concentrations from each alkaline solution the 3.5% sample had judged optimum for extraction regarding humic acid is 32.25% from 3.5% NaOH.

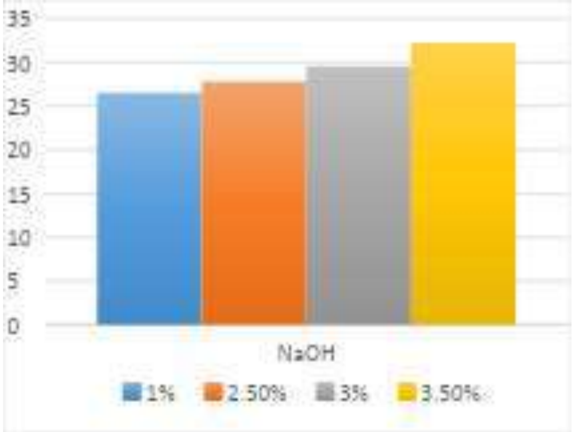


Figure 1. SPECTROPHOTOMETRIC DETERMINATION OF HUMIC ACID ISOLATED FROM THAR COAL SAMPLES.

Figure 2 shows the larger absorption peak of humic acids is obtained at 354nm and 2d taken from (*Aldrich)* as a standard graph which shows the larger absorption peak of humic acid at 357nm. These peaks are in the range of near UV (200-400) which shows the n-n* transitions occur in molecules containing double or triple bonds or aromatic rings. The UV-VIS absorption hump of all HAs from 3.5% NaOH solution showing E_4/E_6 ratios < 4.9-5 have made an estimation that they all have larger molecular weight also hydrophilic & double aromatized in kind (given within table 4.1).

Table 4.1 UV absorption data of HA

Samples	**A $_{436}$**	**A $_{465}$**	**A $_{665}$**	**E_4/E_6**
HA isolated from 3.5% NaOH	0.886	0.808	0.545	1.48
HA Standard (Aldrich)	0.571	0.457	0.101	4.52

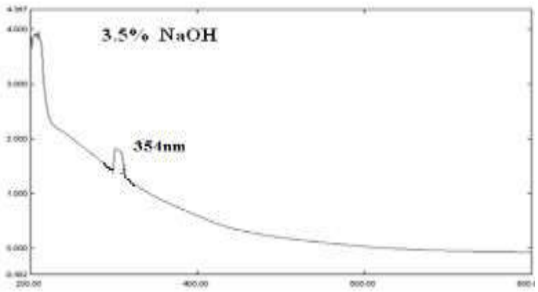


Figure 2a

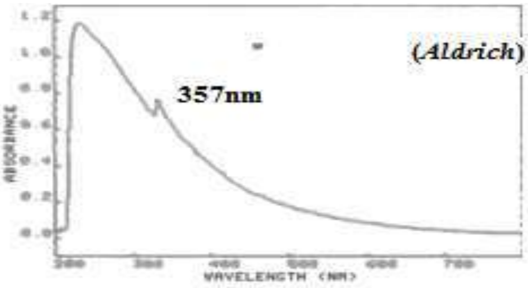
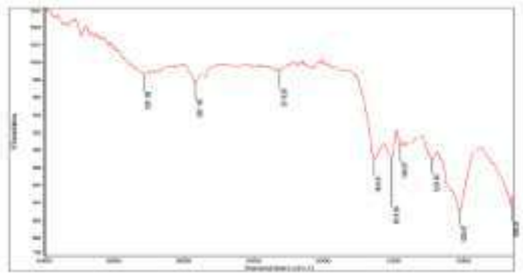


Figure 2b

4.2 Characterization of Extracted Humic Acid by FTIR spectroscopy

Figure 3a-3b reveals the FTIR analysis regarding the humic acid samples of coals along with 93% reference HA. **Figure 3a** demonstrated FTIR stretches regarding extracted HA through 3.5% NaOH. A deep absorption took place at 3259 cm−1 which donates bearing of alcoholic groups and amides N-H non-bonded. The peak shifted near 2337 cm−1 demonstrates bearing of C=C bond alkenes conjugation. The peak hump on 2110 cm−1 is associated mostly with presence of aromatic & COO- stretching. The lower peaks around 1551 cm−1 demonstrated bearing of symmetrical stretching of COO− group. A semi-sharp curve formed on 1219 cm−1 demonstrates varied oxygen containing clusters of compounds like -COOHs, -OH, and aromatized ethers) (Fong & Mohamed, 2007), whereas few litterateurs rationalize this advantageously to C-O stretching & also O-H distortion of COOH content (Chen et al., 2002). A peak showing curve at 1031 cm−1 rank affiliated through alcohol contents, carbohydrates & ethers indicates a tiny existence of all those functional groups inside humic poly-molecules in contrast through other oxygenated contents like carboxylic contents (Ma, 2004). The peak is shifting toward 909–700 cm−1. This range indicates amines NH2 (NH bending aliphatic amines).



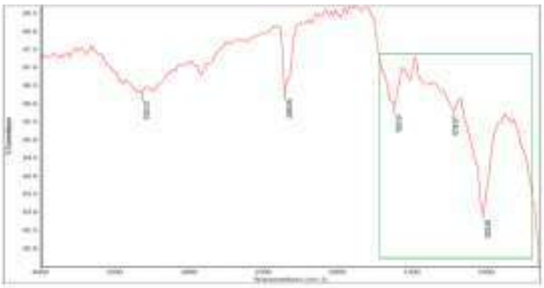
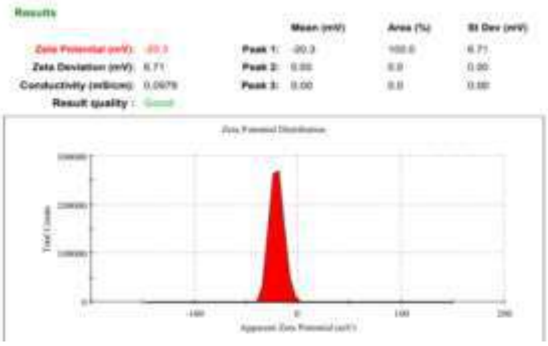


Figure 3a. (3.5%NaOH) **Figure 3b. (Aldrich)**

4.3 Characterization of Extracted Humic Acid by Zeta Potential

Figure 4 shows the Zeta potential analysis of the three humic acid samples of coal. As shown, maximum peak occur at -20.3 mv, highest negative value indicated the large number of negative ions present than positive in sample of humic acid extracted from 3.5% NaOH.



Results

Zeta Potential (mV): -20.3
Zeta Deviation (mV): 6.71
Conductivity (mS/cm): 0.0979
Result quality : Good

	Mean (mV)	Area (%)	St Dev (mV)
Peak 1:	-20.3	100.0	6.71
Peak 2:	0.00	0.0	0.00
Peak 3:	0.00	0.0	0.00

Figure 4. (3.5% NaOH)

4.4 Characterization of Extracted Humic Acid by XRD

Figure 5a shows the XRD analysis of the humic acid sample from 3.5% of NaOH. **Figure 5a** shows the absorption spectra of humic acid from 3.5% NaOH in which various °2Th values obtained at 12.287610, 24.993850, 29.461260, 38.613760, 44.727170 and 55.540240 but the major peak was obtained at 44.727170.

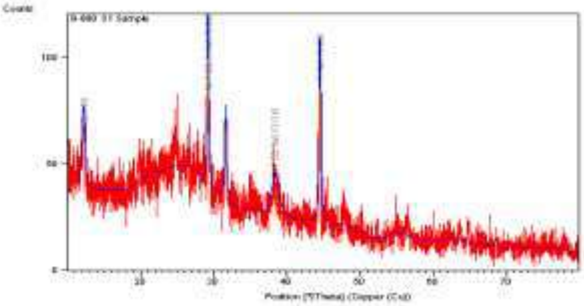


Figure 5. (3.5%NaOH)

5. CONCLUSIONS

Humic acid yield found 32.25% in 3.5% NaOH solution. The UV-VIS absorption spectrum regarding all Has test proportions has been identical to Has which were recorded within research articles that describe regular lowering of spectral ranges by increasing lemda. UV-VIS absorption band has shown the E_4/E_6 ratios of HA from 3.5% NaOH solution is < 4.9-5 have made an estimation that it has larger molecular weight also hydrophilic & double aromatized in kind. The FTIR band of Ha testing samples have shown curves regarding particular functional groups of Has recorded within research articles also identical to standard HA from Aldrich (literature) that has, a wide band about3400 cm−1 that denoting stretching of OH functional groups & sharp peak about 2900cm^{-1} aliphatic C-H group. Further curve within range of 1500-1624 cm^{-1} has shown aromatic C=C and C=O linkage of conjugated ketones also signify aromatized HA & curve within range of 1378-1428 cm^{-1} has shown a chain of carbon atoms & curve within range of 1000-1026 has shown C-OH of aliphatic O-H also polysaccharides. Whole consideration describes identifications within FT-IR absorption spectrum regarding all HAs excluding only 1 peak of 1454 cm $^{-1}$ which isn't addressed within standard humic acid spectrum. Zeta potential spectrum regarding all HAs from 3.5% NaOH solution is in the range of -30mv which indicates that the samples are stable. Whole consideration describes dissimilarities within XRD spectrum regarding all HAs excluding only 1 peak of 29.1 2 ° 2Th values which is in 3.5% of NaOH.

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