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EXTRACTION OF THE HUMIC ACID FROM THAR LIGNITE COAL BY USING DIFFERENT SOLUTIONS

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Abstract

Malnutrition is one of the major world's problem to solve, for this purpose hundreds of scientists are working to find ways for advanced horticultural food mass production and harvesting more and more crops. Many of artificial fertilizers have been discovered to increase soil fertility but humic acid is natural one, which is present in coal (lignite), topsoil, tonic waters, garbage, kitchen midden or refuse heaps, oceanic & pond silts, peat marsh, carbon containing shales etc. HA is an agrochemical biotic acid which was aromatized by COOH-, R-OH-, OH-, R- clusters tied-up and can be specified via meteorological interpretation, as existence of acidulous, OH- & R-NH_2 groups even as acquired through the vast accumulation of lignite coal of Pakistan. So it is necessary to find a way for its extraction to get optimum production. For this initially coal from Thar (sindh) was oxidized with 2% HNO_3 then treated with 1.0, 2.5, 3, and 3.5% KOH and $Na_4P_2O_7.H_2O$ solutions for extraction of humic acid. The extraction of AH in KOH was 19.99% and in $Na_4P_2O_7.H_2O$ solution was 15.54%. That shows KOH found more optimum for HA extraction than $Na_4P_2O_7.H_2O$. Characterization techniques are important to understand structural properties by using useful advanced techniques such as UV-Vis spectrophotometry used for identifying compounds, FTIR analyses is used for study of active functional groups, Zeta potential is used to detect stability of compound and XRD analysis is used for textured analysis. This chapter discusses in detail the methods, sample preparation and extraction of humic acid from coal in two different solutions.

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1. INTRODUCTION

For a developing country, a big move in the direction of economic wealth is to exploit natural resources. On the prospective of coal Pakistan is a rich country but as fuel coal's rank is poor because of excessive ash. Overwork had been shown that crumbled immaterial coal of Pakistan has a significant amount of humic acid that could be made use of biotic plant food productively as to advance horticultural mass production (Mir et al., 2000. Humic acid and humactin deposits are lignites, brown coals, miscellaneous and others (Flaig et al., 1975; Lawson, 1989). On degradation of biotic stuff during the period considered thousands of years Humic acid will be formed in lignite (Flaig et al., 1975; Lawson, 1989). That's why the immaterial lignite coal which is the only coal originated in Pakistan, mostly possess top class humic acid that is extremely productive for upgrading topsoil's order and plant germination (Lee & Bartlett, 1976).

Humic acid supply appreciable capability for farming fulfillment and to take advantage from this HA then this research project would provide information to make use of ancient coal acquired HA in agricultural output & to diminish the addiction over chemical plant food , to distillation of HA through lignitic coals of Thar place of Pakistan, to theirs examination and characterization to determine the outcome of unrelated degrees of HA on agricultural crop development, to reaction of HA individually, to confirms excess reaction of HA & to interpret the working of theirs action.

2. Experimental

2.1. Preparation of coal sample

About 20 kg of coal samples was collected from Thar mines, Sindh Pakistan. It was clean and dried in the oven or sunlight. The sample was homogenized and sieved by a sieved shaker for separating smaller than 2mm coal particles (B. Saitol and M.M Seckler 2014). Then for experimental work nearly 5kg of sample was acquired using **sub-sampling method** in which a small amount of powered sample is taken from larger sample (*Mona Zara, Zeeshan Ahmad et al., 2017*).

2.2. HNO_3, KOH and $Na_4P_2O_7.H_2O$ solutions, Preparation

The active solutions of HNO_3, KOH and $Na_4P_2O_7.H_2O$ were newly prepared. 2 ml of HNO_3 (65%Concentrated, laboratory grade) (Merck, Kenilworth, NJ, USA) dissolve in 100ml di-ionized water and the alkaline solutions were prepared from 98% analytical brand (**Merck**) in the concentration scale of 1.0, 2.5, 3, 3.5% of KOH and $Na_4P_2O_7.H_2O$ in 100 ml de-ionized water.

2.3. Acidic pretreatment of coal by HNO_3

2.4. To begin with, coal samples for extraction of humic acid were oxidized in 2% HNO_3 to introduce functional groups and remove mineral impurities. Following mixing both coal and acid, the mixture was filtered and washed to remove unreacted acid from the oxidized coal after stirring for 1h. In the end the obtained sample was dried and collected for further work.

2.5. Humic acid extraction from coal

Humic acid extraction procedure was acquired from *Asing et al. (2004)*. The coal samples were put into the beaker along with prepared solutions of KOH and $Na_4P_2O_7.H_2O$ with different concentrations (1.0, 2.5, 3, 3.5%) and stirrer by using magnetic stirrer for 1h with 300 rpm *(Fabiana et al. 2018)* after it the suspensions were permitted to settle for about 48hrs and the supernatants were filtered and again stirring with addition of 6M HCl until the pH of mixture become 2. Separate the residues from supernatants through centrifugation under 5000-6000 rpm at -4°C for 20 minutes and wash with de-ionized water, dried it and then stocked in bottles for characterization.

3. Instrumentation

3.1. Characterization by UV/Visible Spectroscopy

For UV/Visible spectrophotometer characterization of extracted humic acid sample prepared three standard solutions of different concentrations of 50, 100, and 200 ppm by using method from *Mohammadi et al. (2012)* 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 and matched with standard curves.

3.2. Characterization by FTIR

For FTIR characterization of extracted samples of humic acid we used the FTIR analysis machine (Simadzu, Kyoto, Japan). It is used for the detecting functional groups inside isolated HA sampling. 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 is an analytical method mostly applied for calculating phase determination in regard to crystalline compounds also able to be informative about unit-cell parameters. It is useful for nano-materials, finely pulverized extracted HA sample admixed to merge, and 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

For Zeta potential characterization of extracted humic acid samples 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. Particularly it show electric potential difference against ionic films anywhere on charged-colloid-ion and this expresses as millivolts (mv), range from -100 to +100 mv, negative value stands your particle are negatively charged and positive value means it is positively charged *(Malvern, 2005).*

4. Results and Discussion

5. By using four different percentages of alkalis KOH and $Na_4P_2O_7.H_2O$, i-e, 1%, 2.5%, 3% and 3.5%, humic acid was extracted from low rank thar coal.

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 KOH and $Na_4P_2O_7.H_2O$ (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. 19.99% from 3.5% KOH and 15.54% from 3.5% $Na_4P_2O_7.H_2O$.

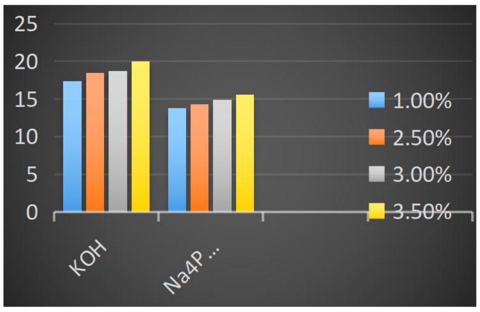
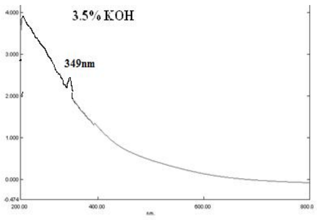
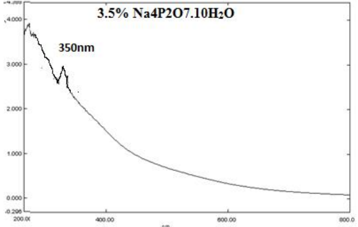


Figure-1. Spectrophotometric Determination Of Humic-Acid Isolated From Thar-Coal Samples.

Figure 2a-2b shows the larger absorption peak of humic acids is obtained at 354nm and 349nm **2c** 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.





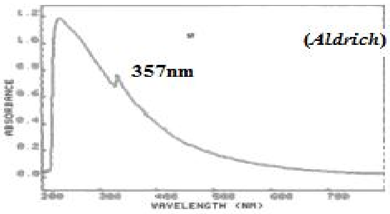


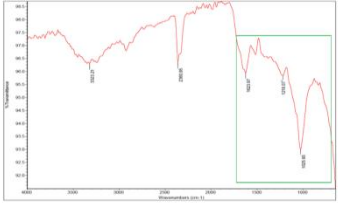
Figure 2a. (KOH) *Figure-2b. (Na4P2O7.H2O)* *Figure2c. (Aldrich)*

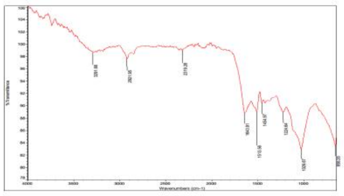
The “UV-VIS” absorption hump of all HAs from 3.5% KOH and Na4P2O7 solutions showing E_4/E_6 ratios < 4.9-5 have made an estimation that they all have larger molecular-weight also hydrophilic”& double aromatized in kind (given within table 4.1).

Samples	**A_{436}**	**A_{465}**	**A_{665}**	**E_4/E_6**
HA Isolated from 3.5 Na4P2O7	0.431	0.361	0.156	2.31
HA isolated from 3.5% KOH	0.997	0.908	0.602	1.50
HA-Standard (Aldrich)	0.571	0.457	0.101	4.52

4.2 Characterization of Extracted Humic Acid by FTIR spectroscopy

Figure 3a-3c reveals the humic-acid samples of coals along with 93% reference HA in the FTIR-analysis. **Figure 3a**, reference sample has the highest transmission density upon 3400 cm–1 that denotes stretching of OH-functional groups (Dick et al., 2002). **Figure 3b**, shows absorption spectra for humic acid from 3.5% KOH 1570–1577, 1375 and 1090 cm–1 are the major peaks shows C=C ring and coo– stretching, C-H functional groups and Si-O functional groups and metal oxygen stretching *(Chen et al., 2002; oskars and maris, 2012)*. **Figure 3c,** demonstrated FTIR stretches regarding extracted HA through 3.5% Na4P2O7 Similar peaks containing less deep spectrum were found in Na4P2O7 sample.





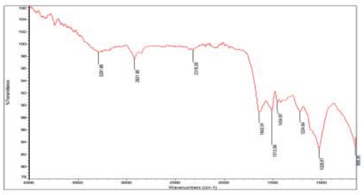
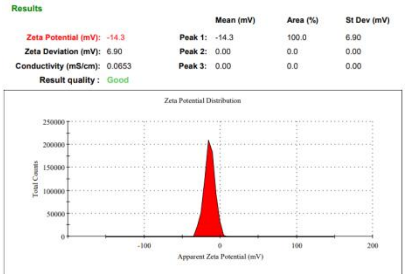


Figure-3a. (Dick et al., 2002) *Figure-3b. (KOH)* *Figure-3c. (Na4P2O7)*

4.3 Characterization of Extracted Humic Acid by Zeta Potential

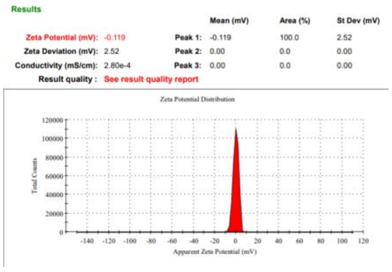
The Zeta potential analysis of the two extracted humic acid samples from coal are shown in **Figure 4a–4b.** As shown in **Figure 4a** shows the Zeta potential spectra of extracted humic acid from 3.5% KOH highest peak at -14.3mv, which indicate more negative ions are present than positive at the boundaries b/w solid molecules of that sample. **Figure 4b** shows absorption spectra for humic acid from 3.5% Na4P2O7 in which the maximum peak occurs at -0.119mv means it has less number of negative ion compare to other samples but still have more negative ions than positive.



Results

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-14.3	Peak 1:	-14.3	100.0	6.90
Zeta Deviation (mV):	6.90	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm):	0.0653	Peak 3:	0.00	0.0	0.00
Result quality :	Good				

Figure 4a (3.5%KOH)



Results

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-0.119	Peak 1:	-0.119	100.0	2.52
Zeta Deviation (mV):	2.52	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm):	2.80e-4	Peak 3:	0.00	0.0	0.00
Result quality :	See result quality report				

Figure 4b (3.5% Na4P2O7)

4.4. XRD Characterization of Extracted Humic Acid

The XRD analysis of the two extracted humic acid samples from coal from 3.5% of KOH and Na4P2O7 solutions are shown in **Figure 5a–5b.** As shown in **Figure 5a** shows the XRD pectra of humic acid from 3.5% KOH there were also a number of different peaks occur at 12.207530, 29.199520, 31.609230, 38.393110 and 44.500420 but the two major peaks were obtained at 31.609230 and 44.500420. **Figure 5b** shows absorption spectra for humic acid from 3.5% Na4P2O7 there were also various °2Th values obtained at 23.561880, 28.271060, 33.465950, 38.429790, 40.470650, 44.649230, 64.956420 and 78.166400 but the major peak was obtained at 44.64923 of angles

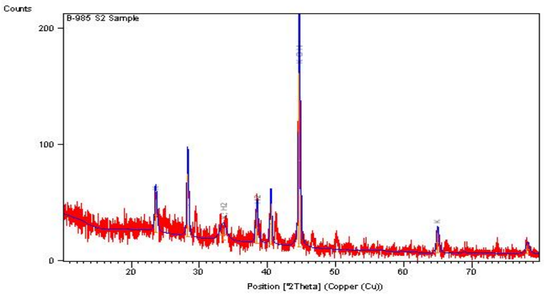


Figure 5a (3.5%KOH)

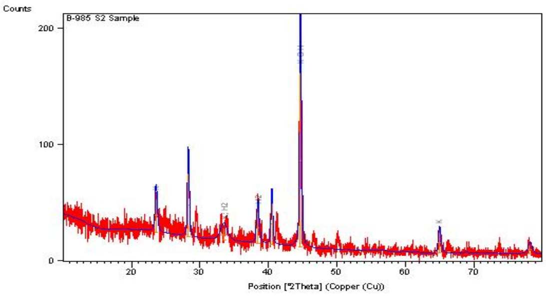


Figure 5b (3.5% Na4P2O7)

5. CONCLUSIONS

Humic acids yield was found 19.99% in 3.5% KOH solution > 15.54% in 3.5% Na4P2O7.H2O solution UV-VIS" absorption-band has shown the E_4/E_6 ratios of both samples from 3.5% KOH and Na4P2O7.H2O solutions are < 4.9-5 have made an estimation that they all have larger molecular-weight also hydrophilic"& double aromatized in kind. In the FTIR-analysis the peaks in 3.5% KOH sample were deeper than those in 3.5% in Na4P2O7.H2O and that may comparatively show higher percentage of humic acid presence in 3.5%KOH sample. Zeta potential technique is mainly used for determining the molar mass of complex compounds. Greater value of zeta potential indicates the larger number of moles/ molecules present in the sample. Among all two samples of humic acid, the humic acid from 3.5% KOH (-14.3mv) was found to be the more negative ions holding than3.5% Na4P2O7.H2O (-0.119 mv). Both XRD absorption spectra of humic acid from 3.5% KOH and Na4P2O7.H2O solutions show almost similar peaks that indicate that almost the same entities were present in all three samples but with different intensities.

6. REFERENCES

Anon. (1999). Humic acids and their sodium salts. European Agency for the Evaluation of Medicinal Products, (Summary report). UK: EMEA

Antosovd, B.; Novak, J.; Kozler, J.; Kubicek, J.; Kimmerovd, I. Methodic for testing biological activities of humic substances in higher plants. In Reactive and Functional Polymers Research Advances; Nova Publishers: Ústí nad Labem, US, Chech Republic, 2008; 191.

Canieren, O.; Karaguzel, C.; Aydin, A. Effect of physical pre-enrichment on humic substance recovery from leonardite. Physicochem. Probl. Miner. Process. 2017, 53, 502–514.

ENVIROMATE TM (2002). Effects of humic acid on animals and humans 1–15. Texas: Enviromate Inc.

Fulcrum Health Limited (2004). Humifulvate-a natural active ingredients.1–43. Budapest: Humifulvate science

Gil-Sotres, F., Trasar-Cepeda, M.C., Ciardi, C., Ceccanti, B.,Leiros, M.C., 1992. Biochemical characterization of biologi-cal activity in very young mine soils. Biology and Fertility of Soils 13, 25–30.

Gonzales-Sangregorio, M.V., Trasar-Cepeda, M.C., Leiros, M.C., Gil-Sotres, F., Guitian-Ojea, F., 1991. Early stages of lignite mine soil genesis. Changes in biochemical properties. Soil Biology and Biochemstry 23, 589–595.

Hayashi, J.-I.; Li, C.-Z. Structure and properties of Victorian brown coal. In Advances in the Science of Victorian Brown Coal; Elsevier: Victoria, VIC, Australia, 2004; 11–84.

Huang, P.-M.; Wang, M.-K.; Chiu, C.-Y. Soil mineral–organic matter–microbe interactions: Impacts on biogeochemical processes and biodiversity in soils. Pedobiologia 2005, 49, 609–635. [CrossRef]

Insam, H., Domsch, K.H., 1988. Relationship between soil organic carbon and microbial biomass on chronosequences of reclamation sites. Microbial Ecology 15, 177–188.

Karaman, M.; Turan, M.; Tutar, A.; Dizman, M.; ¸Sahin, S. Possible Use of Leonardite-Based Humate Sources as a Potential Organic Fertilizer. In Functions of Natural Organic Matter in Changing Environment; Springer: Berlin, Germany, 2013;. 1061–1065.

Kline, S.W.; Wilson, C.E., Jr. Proposal for Experimentation with Arkansas Lignite to Identify Organic Soil Supplements Suitable to Regional Agricultural Needs; Preliminary Draft; Arkansas Tech University: Russellville, AR, USA, 1994

Lawson, G.J., Steward, D., 1989. Coal humic acids. In: Aiken, G.R., McKnight, D.R., Wershaw, R.L., MacCarthy, P.C. (Eds.), Humic Substances II) Wiley-Interscience, New York,641–686.

Lehmann, J.; Kleber, M. The contentious nature of soil organicmatter. Nature 2015, 528, 60. [CrossRef] [PubMed]

Leiros, M.C., Gil-Sotres, F., Ceccanti, B., Trasar-Cepeda, M.C., Gonzalez-Sangregorio, M.V., 1993. Humification processes in reclaimed open-cast lignite mine soils. Soil Biol-ogy and Biochemistry 25, 1391–1397.

Leiros, M.C., Gil-Sotres, F., Ceccanti, B., Trasar-Cepeda, M.C., Gonzalez-Sangregorio, M.V., 1993. Humification processes in reclaimed open-cast lignite mine soils. Soil Biol-ogy and Biochemistry 25, 1391–1397

Malik, A., Scullion, J., 1998. Soil development on restored opencast coal sites with particular reference to organic mat-ter and aggregate stability. Soil Use and Management 14, 234–239.

Nardi, S.; Pizzeghello, D.; Schiavon, M.; Ertani, A. Plant biostimulants: Zhysiological responses induced by protein hydrolyzed-based products and humic substances in plant metabolism. Sci. Agric. 2016, 73, 18–23. [CrossRef]

O'donnell, R. The auxin-like effects of humic preparations from leonardite. Soil Sci. 1973, 116, 106–112. [CrossRef]

Orsi, M. Molecular dynamics simulation of humic substances. Chem. Biol. Technol. Agric. 2014, 1, 10. [CrossRef]

Pettit, R.E. (2002). Organic matter, humus, humate, humic acid, fulvic acid and humin: Their importance in soil fertility and plant health, 1–24. Texas: A & M University.

Roberts, J.A., Daniels, W.L., Bells, J.C., Burger, J.A., 1988. Early stages of mine soil genesis in a southwest Virginia spoil lithosequence. Soil Science Society of America Journal 52, 716–723.

Rose, M.T.; Patti, A.F.; Little, K.R.; Brown, A.L.; Jackson, W.R.; Cavagnaro, T.R. A meta-analysis and review of plant-growth response to humic substances: Practical implications for agriculture. In Advances in Agronomy; Elsevier: Victoria, VIC, Australia, 2014; Volume 124, 37–89.

Rumpel, C., Ko¨gel-Knabner, I., Knicker, H., Skjemstad, J.O., Hu¨ttl, R.F., 1998. Types and chemistry of organic matter of rehabilitated mine soils in Lusatia (Germany). Geoderma 86, 123–142.

Schafer, W.M., Nielsen, G.A., Nettleton, W.D., 1980. Mine soil genesis and morphology in a spoil chronosequence in Mon-tana. Soil Science Society of America Journal 44, 802–807.

Schulten, H.-R.; Plage, B.; Schnitzer, M. A chemical structure for humic substances. Naturwissenschaften 1991, 78, 311–312. [CrossRef] [PubMed]

Stott, D.; Martin, J. Synthesis and degradation of natural and synthetic humic material in soils. Hum. Subst. Soil Crop Sci. Sel. Read. 1990, 37–63. [CrossRef]

Stroo, H.F., Jencks, E.M., 1982. Enzyme activity and respira-tion in mine soils. Soil Science Society of America Journal 46, 548–553.

Tahiri, A.; Delporte, F.; Muhovski, Y .; Ongena, M.; Thonart, P.; Druart, P. Change in ATP-binding cassette B1/19, glutamine synthetase and alcohol dehydrogenase gene expression during root elongation in Betula pendula Roth and Alnus glutinosa L. Gaertn in response to leachate and leonardite humic substances. Plant Physiol. Biochem. 2016, 98, 25–38. [CrossRef] [PubMed]

Tan, K.H. Humic Matter in Soil and the Environment: Principles and Controversies; CRC Press: Boca Raton, FL, USA, 2014.

Teichm€ uuller, M., Teichm€ uuller, R., 1975. Stachs Texbook of Coal Petrology. Gebruder Borntrager, Berlin (Chapter 2).

Wershaw, R. Model for humus in soils and sediments. Environ. Sci. Technol. 1993, 27, 814–816. [CrossRef]

Yang, C.-M.; Wang, M.-C.; Lu, Y.-F.; Chang, F.; Chou, C.-H. Humic substances affect the activity of chlorophyllase. J. Chem. Ecol. 2004, 30, 1057–1065. [CrossRef] [PubMed]