ASEAN Journal of Science and Engineering

JURNAL UPI

Journal homepage: http://ejournal.upi.edu/index.php/AJSE/

Comparative Study on Extraction of Humic Acid from Pakistani Coal Samples by Oxidizing the Samples with Hydrogen Peroxide

Muhammad Asif [1 2]

[1]Department of Environmental Science, COMSATS University Islamabad, Abbottabad Campus-Pakistan
[2]Institute of Energy and Environmental Engineering, University of the Punjab, Lahore-Pakistan
Correspondence: E-mail: 03047092647asif@gmail.com

ABSTRACT

Humic Acid is soil conditioning agent, which is used for improving the soil chemistry, plant root growth and related metabolism. Pakistan is an agricultural country and about 70% of population is directly or indirectly linked to the agricultural sector. Coal is considered one of the most appropriate raw materials for humic acid. The yield of extracted humic acid from coal is inversely proportional to the rank of coal. Since, majority of Pakistani coals are of low rank, extraction of humic acid from indigenous coal may be one of the non-fuels uses of coal. Three different coal sample from Thar, Dukki and Chamalong coalfields were treated with 3% H2O2 solution for determining the impact of oxidation on humic acid yield. The yield of humic acid from H2O2 treated samples were as follows; 2.5% for Chamalong coal sample, 16.5% from Dukki, and 35% from Thar coal sample. Thar coal sample, being the lowest in rank among all experimented coal samples, yielded higher fraction of humic acid.

ARTICLE INFO

Article History:
Submitted/Received 21 Apr 2021
Revised 17 May 2021
Accepted 17 Jul 2021
Available online 19 Jul 2021
Publication date 01 Mar 2022

Keyword:
H2O2 oxidation,
Low rank coal,
Humic acid from coal

1. INTRODUCTION

Majority of Coal utilization process consist on direct coal combustion either in power sectors, cement industries or utility boilers. Major drawback of coal combustion is an emission of large number of air pollutant into environment. There are total 187 air pollutant in which 84 air pollutants (Kumar-Tayi *et al.,* 1985) are emitted only from coal. Coal produces large number of SOx, NOx, CO2, CO, particulate matter, bottom ash and unburnt hydrocarbons which effects the environment in different ways. The alternative way of coal utilization may be its conversion into value added chemicals and alternative fuels (Kumar-Tayi *et al.,* 1985), which may have some less environmental effect of coal utilization as compared to its combustion. There are a number of chemicals which may be (Schobert, 2014) extracted from coal due the heterogeneity in the nature of coal and diversity of compounds which may be extracted from coal, due to uncontrolled reaction mechanism during coal conversion. During the pyrolysis of coal beside the gaseous and solid products only Tar may contain more than thousands of chemicals (Wang *et al.,* 2013), but these chemicals are present in so little amount that the extraction cost may be unfeasible under current economic scenario. Coal liquefaction and gasification process are highly costly due to which their adoption in Pakistan under current situation is highly impossible. We have only single option of coal utilization that is combustion but due to environmental restriction we cannot adopt such combustion technology to use our indigenous coal. Pakistan has round about 184 billion tons reserves of coal (Malkani and Mahmood, 2016) which is low rank lignite coal and a very small quantity of sub bituminous coal. Where this low rank coal has low heating value but as well it may be good feed stock for production of different chemicals (Li *et al.,* 2012). We can produce benzene, phenols, graphene quantum dots, and humic acid (Miura, 2000) from the coal of different rank. Low rank indigenous coal may be a good option for the extraction of humic acid which is soil conditioning agent and can increase the fertility of the land which is important factor for the better growth and high yields of crops . According to the Pakistan energy year book of 2018, 24.7% coal is used in power generation, 4.4% coal is blended with imported coal for coke production in steel industry, 21.9% coal is used in brick kilns and 53.4% is used in cement industry. The total consumption of coal in Pakistan is 17.98 million tones but the annual production is 4.3 million tones.

Pakistan is agricultural country, about 70% of population of Pakistan (Abedullah *et al.,* 2009) directly or indirectly is associated with this profession. If we increase the production rate of crop or the per acre yield of crops than above mentioned percentage of dependence of population on agricultural may be increases, due to which the problem of unemployment in Pakistan may be decreases. The better growth of crop is highly dependent on the availability of nutrient (Khaled and Fawy, 2011) which are necessary for the better growth of plants. Due to high demand of agricultural product the soil is unable to absorb these nutrients so rapidly from environment, So it is highly necessary to provide some essential nutrients to soil for proper crop growth, for which we have needed a large quantity of fertilizer (Kopittke, 2019) for agricultural use. Fertilizers industries in Pakistan for the production of urea and other chemical fertilizer is still using methane cracking process for the production of Hydrogen for the synthesis of Anomia which is an important chemical for fertilizer preparation, But unfortunately we have already consumed our natural gases resources which was about 19 trillion cubic feet and now it left behind only 10.5 trillion cubic feet. Now we are importing about 21% of our natural gas consumption. Due to unavailability of raw material, we are importing a significant portion of fertilizers from other countries.

DOI: http://dx.doi.org/10. 17509/xxxxt.vxix
p- ISSN e- ISSN

Imported fertilizer are very costly due to implementation of heavy taxeswhich are unaffordable for the former of low level, due to which our crop yield is very low as compared to other neighboring countries. The only solution of this problem is provision of fertilizer to the former at low cost which is only possible when we synthesis the required fertilizer from our indigenous resources. Pakistan has been gifted by Allah with its mineral resources and coal resources but due to lack of research work and miss management, Pakistan is not properly growing as we were expecting. We have about 184 billion of tons coal resources which can meet the total energy demand of Pakistan for more than three hundreds of years (Mahmood *et al*., 2014). Major coal field is thar coal reserve which is a low rank lignite, a highly suitable for the production of Humic Acid and other chemicals. There is a need of attention of the researchers and universities that they have to think about the positive use of our indigenous coal. Similar attempts were also adopted by many research centers for the extraction of Humic Acid from coal. Institute of Physical and Applied Chemistry, Faculty of Chemistry, Brno University of Technology extracts humic acid from coal (Kucerik *et al*., 2004). The sample of lignite used in this study was obtained from Mir mine located near Hodonín in the south-eastern part of Moravia, Czech Republic. The overall yield of recovered products was ca. 33.9% (relative to the weight of the initial HAs). It consisted principally of hydrophilic molecules. Shenfu subbituminous coal and pretreated sample with H2O2 were subjected to oxidation with NaOCl at 30C for 5h. The results showed that the pretreatment with H2O2 significantly increased the yields of water-soluble species, (Wang *et al*., 2018) especially benzene carboxylic acids and long-chain alkane dioic acids, but substantially inhibited the formation of chloro-substituted alkanoic acids. The introduction of oxygenated functional groups to SFSBC by the pretreatment, could be responsible for the increase in the yields. In 2015 humic acid was extracted in center for coal technology by fungal treatment with the yield of 57% humic acid (Haider *et al*., 2015) but fungal treatment is a complex process and not easily adoptable in Pakistan at commercial scale. In 2017 in our center humic acid was extracted from various lignite coal sample by the treatment of HNO3 and KOH solution but the yield was about 24% to 29% (Zara *et al*., 2017) again which was not economically feasible due to having less humate contents. In china the humic acid was extracted by lignite coal by treatment with sodium pyrophosphate and sodium hydroxide solution (Cheng *et al*., 2019) but the yield was about 39% which was economically not a feasible due having less humate contents.

Many other researchers also tried for the extraction of Humic acid from coal, but still there is no any option that can be adopted in Pakistan for the extraction of Humic acid from coal at commercial scale. So, there is a need of further research in this field that make us able to develop any mechanism by which we would commercialize the process of extraction of humic acid from our local coal reserves. So, there is need of this work and our research objectives are also to produce a Humic Acid from indigenous coal reserves at low cost and that process would be able for applicable at commercial scale. Humic Acid is formed naturally by buried plant after the transformation of plant debris into peat, there is a stage between the peat and lignite (Ibarra and Juan, 1985) in which plant matter transformed into Humic Acid. Thar coal reserves is a pre-mature low rank lignite coal very close to the Humic acid stage (Zara *et al*., 2017), due to which the production of Humic Acid from the Thar may be useful process. In this research work thar, Dukki and Chamalong coal was subjected for the extraction of Humic Acid by treatment of pulverized coal sample with 3% of hydrogen peroxide solution as an oxidizing agent, because we have to oxidize the lignite coal to go back into its previous stage as coalification is a reduction process. As the Humic Acid is soluble in alkali solution, so the oxidize coal samples were dissolved in alkali solution (NaOH) for the extraction of pure Humic

DOI: http://dx.doi.org/10.17509/xxxx.vxix
p- ISSN 2776-5938 e- ISSN 2776-6098

Acid. Thar coal shows the highest yield of humic Acid about 35% from all other three coal sample which was subjected for the extraction of Humic Acid under the same experimental setup. Suggesting that in future the Thar coal may be good alternative feed stock for the extraction of Humic Acid.

2. METHODS

2.1. Sample Collection

Coal samples of Dukki Chamalong and Thar were collected from coal research lab of Institute of Energy and Environmental Engineering. University of the Punjab, Lahore. Schematic representation of step for extraction of humic acid from raw coal samples are also given below **Figure 1**.

2.2. Sample Preparation

The sample were grinded into -60 mesh size by the help of mortal and pestles and size classification was performed by Taylor series sieve shaker with the sieves of ASTM standards. This -60mesh coal (250um) coal samples were packed into air tight plastic bags for further usage.

2.3. Characterization of Raw Coal Sample

Proximate composition of three coal samples was determined according to ASTM standards methods. Moisture was determined according to ASTM (D3173), by drying the coal samples at 110 C for one hour. Fraction of volatile component was determined by (D3175), heating the coal samples at 950C for 7 min in an inert atmosphere, and Ash content was measured by (D3174), heating the coal samples at 750 for 4 hours in an oxidizing.

2.4. Oxidation of Coal Sample by H2O2

Lab scale H2O2 solution with the purity of 35% was diluted to concentration of 3% used for the oxidation of coal. The coal to solution ratio was adjusted about 1:30. The coal samples see **Figure 2** was mixed thoroughly with the help of magnetic stirrer for about one hour and the solution was allowed to settled for the period of 14 days for the completion of the process of oxidation. After 14 days the coal samples were filtered and dried in an oven at 40C.

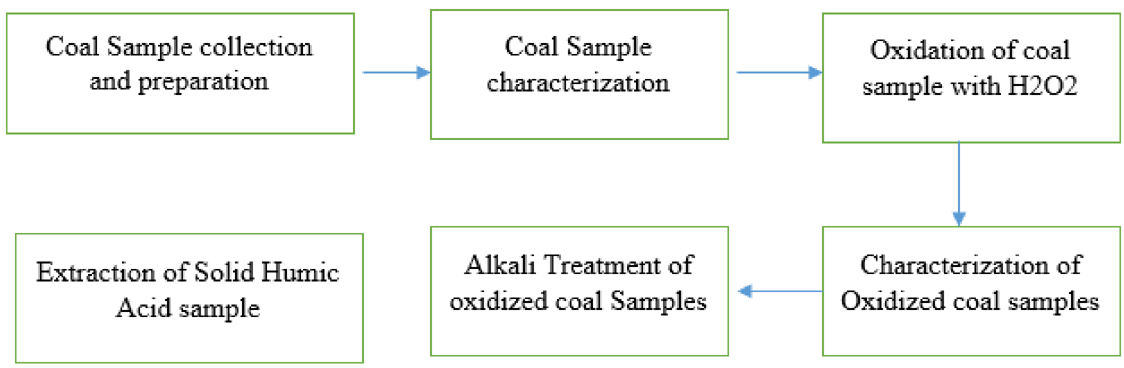

Figure 1. Schematic diagram for the extraction of humic acid from coal samples

DOI: http://dx.doi.org/10.17509/xxxxt.vxix
p- ISSN 2776-5938 e- ISSN 2776-6098

Figure 2. Oxidation of coal sample with hydrogen per oxides

2.5. Extraction of Humic Acid from Oxidized Coal Samples

The extracted humic acid was impure and containing mixture of sodium hydroxide and humic acid, for estimating the exact concentration of humic acid, the mixture was treated with 6 Molar solution of HCl. The pH of the solution was maintained about 1.8 and solution was left for overnight for the precipitation of humic acid sample in acidic medium. On next morning the solid humic acid content was separated by the centrifuge. The liquid fraction was separated out and solid residue was allowed for drying at 45C in an inert drying oven.

2.6. Purification of Humic Acid samples

The extracted humic acid was impure and containing mixture of sodium hydroxide and humic acid, for estimating the exact concentration of humic acid, the mixture was treated with 6 Molar solution of HCl. The pH of the solution was maintained about 1.8 and solution was left for overnight for the precipitation of humic acid sample in acidic medium. On next morning the solid humic acid content was separated by the centrifuge. The liquid fraction was separated out and solid residue was allowed for drying at 45C in an inert drying oven.

2.7. Yield of Humic Acid

The yield of extracted humic acid was calculated on the basis of the amount of oxidized coal samples that was subjected for the extraction of humic acid, with the help of following formula 1.

$$\text{Yield of Humic acid} = \frac{wight\ of\ solid\ humic\ acid\ content}{weight\ of\ the\ oxidized\ coal\ sample} \times 100 \quad (1)$$

3. RESULTS AND DISCUSSION

3.1. Results of Proximate Analysis

Three coal sample subjected in proximate analysis are given in **Figure 3** which showed that the thar coal sample contains considerable portion of moisture and ash content, due to which it showed lower GCV value. Thar being a low rank coal is highly suitable for the its conversion into alternative fuel option or chemical feed stock.

Raw coal samples and residual coal samples, both were subjected for proximate analysis, in which raw coal samples showed the lower amount of moisture and volatile matter but higher amount of fixed carbon and GCV as compared to residual coal samples. In residual coal samples the trends of the different constituent were observed same, the highest moisture content was observed in Thar coal sample while highest Ash content was observed was observed in Chamalong coal samples, (Mukherjee *et al*., 2001) the similar results were also

DOI: http://dx.doi.org/10.17509/xxxx.vxix
p- ISSN 2776-5938 e- ISSN 2776-6098

reported by many other researchers in different articles. Hydrogen per oxide treatment also performed the process of leaching chemical coal cleaning process for the reduction of mineral matter or ash content. But this treatment also dissolved some amount carbon, which caused the decreased in GCV of residual sample as compared to raw coal sample, (Saikia *et al.*, 2014) which is one the main disadvantage of chemical coal cleaning process reported by many researchers.

3.2. Effect of Hydrogen Per Oxide Solution on Coal Samples

Hydrogen per oxide is being an oxidizing agent, oxidizes the coal sample by breaking its aromatic molecular structure, converting into aliphatic or branched chain. It increased the oxygenated linkage in the coal sample which are closely related to the structure of Humic Acid. Hydrogen per oxide treatment of coal results in dissolution of coal sample into the solution, hence the amount of fixed carbon in residual coal sample was decreased and oxygen content was increased, due to which the GCV of coal sample was decreased. The percentage dissolution by hydrogen per oxide treatment has shown in **Figure 4** which is inversely proportional with the rank of the coal. That is why the thar coal sample being a lowest in rank showed the highest dissolution about 29 wt% while Chamalong is being higher in rank among these three samples showed the lowest dissolution about 7.5 wt%. and Dukki coal sample showed the 21% dissolution in hydrogen peroxide solution. It was also observed that the ash content also decreased by hydrogen peroxide treatment because it also performed the action of coal cleaning by leaching the inorganic content for the purification of coal sample. Many other researchers also used the solution of hydrogen peroxide for chemical cleaning and desulphurization of coal.

3.3. Yield of Extracted Humic Acid

When the purified solid samples were dried, then the yield of humic acid was calculated which was reported about Chamalong coal sample was higher in rank among these three so it produced a little yield of humic acid about 2.5wt%, Dukki coal sample was medium in rank so it produced 16.5wt% yield of humic acid while Thar coal sample was lower in rank among all the coal sample that produced higher amount of humic acid about 35wt%.

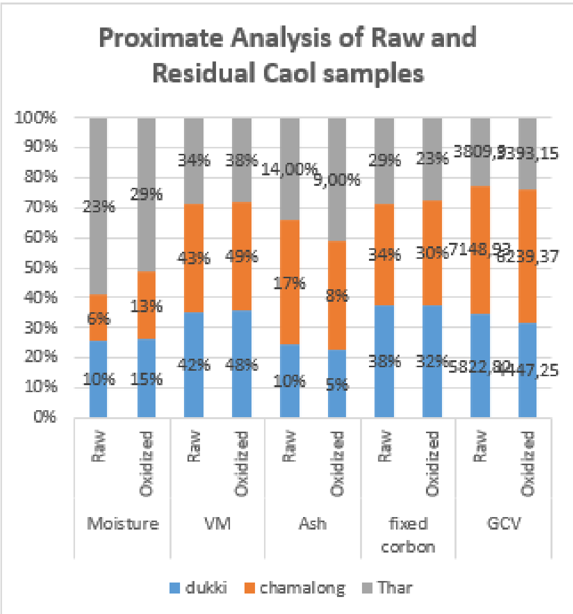

Figure 3. Results of proximate analysis of raw coal samples

DOI: http://dx.doi.org/10. 17509/xxxxt.vxix
p- ISSN 2776-5938 e- ISSN 2776-6098

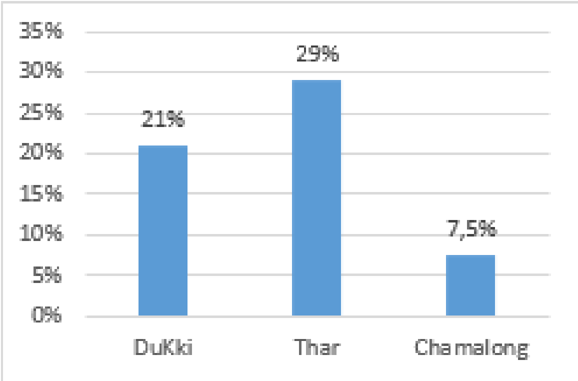

Figure 4. Percentage Dissolution of Coal Samples by H_2O_2

4. CONCLUSION

Three different coal sample Chamalong, Dukki and thar were oxidized for the extraction of humic acid by alkali treatment. Oxidation of coal samples by hydrogen per oxide treatment reduced the ash content and fixed carbon by dissolving the coal sample. In this study it has been observed that lower rank coal samples produced a good yield of humic acid by this experimental process. The highest yield of humic acid about 35% was observed in thar coal sample and lowest yield about 2.5% was observed in Chamalong coal sample while Dukki coal sample showed the medium yield about 16%. On the basis of this research work it can be suggested that thar coal sample being a low rank coal may be good raw feed stock for the extraction of humic acid at commercial scale.

5. ACKNOWLEDGEMENTS

In this research work Miss. Maham Abbas (my fellow) helped me in idea refining, Dr. Naseer sheikh, Senior teacher of our institute helped me in designing the experimental setup, Mr. Abdul Wahab a senior student of institute helped me in coal sample collection, Mr. Ali Arshad student in institute helped me in FTIR graph interpretation and Mr. Nadeem lab Assistant helped me during experimental work.

6. AUTHORS' NOTE

The author states that there is no conflict of interest regarding the publication of this article. The author confirms that the paper is free from plagiarism. There are still many shortcomings and need further research from this article so that the resulting battery is used like a conventional battery.

7. REFERENCES

Abedullah, N., Khalid, M., and Kouser, S. (2009). The role of agricultural credit in the growth of livestock sector: A case study of Faisalabad. *Pakistan Veterinary Journal*, *29*(2), 81-84.

Kopittke, P. M., Lombi, E., Wang, P., Schjoerring, J. K., and Husted, S. (2019). Nanomaterials as fertilizers for improving plant mineral nutrition and environmental outcomes. *Environmental Science: Nano*, *6*(12), 3513-3524.

DOI: http://dx.doi.org/10.17509/xxxx.vxix
p- ISSN 2776-5938 e- ISSN 2776-6098

Cheng, G., Niu, Z., Zhang, C., Zhang, X., and Li, X. (2019). Extraction of Humic Acid from Lignite by KOH-Hydrothermal Method. *Applied Sciences*, *9*(7), 1356.

Haider, R., Ghauri, M. A., and Akhtar, K. (2015). Isolation of coal degrading fungus from drilled core coal sample and effect of prior fungal pretreatment on chemical attributes of extracted humic acid. *Geomicrobiology Journal*, *32*(10), 944-953.

Ibarra, J., and Juan, R. (1985). Structural changes in humic acids during the coalification process. *Fuel*, *64*(5), 650-656.

Khaled, H., and Fawy, H. A. (2011). Effect of different levels of humic acids on the nutrient content, plant growth, and soil properties under conditions of salinity. *Soil and Water Research*, *6*(1), 21-29.

Kucerik, J., Kovar, J., and Pekar, M. (2004). Thermoanalytical investigation of lignite humic acids fractions. *Journal of Thermal Analysis and Calorimetry*, *76*(1), 55-65.

Kumar-Tayi, G., Rubin, E. S., and Lincoln, D. R. (1985). Cross-media environmental impacts of air pollution regulations for a coal liquefaction process plant. *Journal of the Air Pollution Control Association*, *35*(1), 35-40.

Li, X., Ashida, R., and Miura, K. (2012). Preparation of high-grade carbonaceous materials having similar chemical and physical properties from various low-rank coals by degradative solvent extraction. *Energy and Fuels*, *26*(11), 6897-6904.

Mahmood, A., Javaid, N., Zafar, A., Riaz, R. A., Ahmed, S., and Razzaq, S. (2014). Pakistan's overall energy potential assessment, comparison of LNG, TAPI and IPI gas projects. *Renewable and Sustainable Energy Reviews*, *31*(2014), 182-193.

Malkani, M. S., and Mahmood, Z. (2016). Coal Resources of Pakistan: entry of new coalfields. Geological Survey of Pakistan, *Information Release*, *981*(2016), 1-28.

Miura, K. (2000). Mild conversion of coal for producing valuable chemicals. *Fuel Processing Technology*, *62*(2-3), 119-135.

Mukherjee, S., Mahiuddin, S., and Borthakur, P. (2001). Demineralization and desulfurization of subbituminous coal with hydrogen peroxide. *Energy and Fuels*, *15*(6), 1418-1424.

Saikia, B. K., Dutta, A. M., and Baruah, B. P. (2014). Feasibility studies of de-sulfurization and de-ashing of low grade medium to high sulfur coals by low energy ultrasonication. *Fuel*, *123*, 12-18.

Schobert, H. (2014). Production of acetylene and acetylene-based chemicals from coal. *Chemical Reviews*, *114*(3), 1743-1760.

Wang, P., Jin, L., Liu, J., Zhu, S., and Hu, H. (2013). Analysis of coal tar derived from pyrolysis at different atmospheres. *Fuel*, *104*(2013), 14-21.

Wang, Z., Ding, J., Xie, P., Chen, Y., Wan, Y., and Wang, S. (2018). Formation of halogenated by-products during chemical cleaning of humic acid-fouled UF membrane by sodium hypochlorite solution. *Chemical Engineering Journal*, *332*(2018), 76-84.

Zara, M., Ahmad, Z., Akhtar, J., Shahzad, K., Sheikh, N., and Munir, S. (2017). Extraction and characterization of humic acid from Pakistani lignite coals. Energy Sources, Part A: Recovery, *Utilization, and Environmental Effects*, *39*(11), 1159-1166.

DOI: http://dx.doi.org/10. 17509/xxxxt.vxix
p- ISSN 2776-5938 e- ISSN 2776-6098