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Chlorine Dioxide Mediated Oxidation of Sub-Bituminous Coal for Humic Acid Production

ABID NAZIR GILL[1], MUHAMMAD AKBAR[2], MUHAMMAD ABDUL QADIR[2], MUHAMMAD PERVAIZ[1] and AHMAD ADNAN[1,*]

[1]Department of Chemistry, Government College University, Lahore, Pakistan
[2]Institute of Chemistry, University of the Punjab, Lahore, Pakistan

*Corresponding author: E-mail: adnan_biochem@yahoo.com

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Humic acids are metastable degradation products of plant origin. These are used as soil conditioner to improve the texture of soil and uptake of nutrients. In nature, these are found in mineral deposits such as lignite or leonardite. However, these can also be prepared by the oxidation of low grade coals using a variety of oxidation processes. Different samples of coal were tested for their oxidizability to humic acids using chlorine dioxide as the oxidant. A sample of coal from Dukki area of Baluchistan gave maximum yield of humic acids. The coal sample was oxidized by chlorine dioxide produced *in situ* by the reaction between potassium chlorate, sulphuric acid and a reductant such as methanol or hydrochloric acid. Humic acids yield of 76 % was obtained at 65 °C when 100 g coal was treated with chlorine dioxide produced by the reaction between 8 g $KClO_3$, 30 g HCl and 50 mL 50 % H_2SO_4.

Keywords: Humic acid, Coal, Methanol, Chlorine dioxide.

INTRODUCTION

Humic acids are metastable polymeric intermediates of fossilization of plant materials subjected to air oxidation. These are polyphenolic polycarboxylates with carbonyl, alcoholic and other functionalities. In addition to carbon, hydrogen and oxygen these also contain small amounts of nitrogen and traces of other elements. Their molecular weights range from 2 to 300 KD. Characteristics like colour, percentage of carbon and cation exchange capacity change gradually with the increase in length of the polymer chain and degree of oxidation[1].

Humic acids are considered to be excellent soil conditioners. These not only improve the texture of the soil by improving its cation exchange capacity but also improve pH and organic content of the soil. Their water holding capacity by gelling with water molecules decrease the water demand. These substances have been reported to significantly increase the supply of vital micronutrients and available phosphorous to plants by chelation and bridging between root hair and nutrients involving their multi-active functionalaties[2-5].

Although humic acids occur naturally as outcrop in coal mines or in mineral deposits such as lignite or leonardite, these substances can also be prepared on industrial scale by oxidation of low grade brown coals[6]. Virtually it has now become the need of the hour to search for economically viable methods of preparation of humic acids because natural surces of humic acids are near to exhaust but their market demand is growing owing to their effectiveness.

Various methods of dry and wet oxidation of low rank coals have been investigated with oxidants like oxygen gas, alkaline $KMnO_4$, hydrogen peroxide, nitric acid, electrolytic oxidation *etc.*[7-12].

In present study attempts were made to oxidize the coal with chlorine dioxide (ClO_2), produced *in situ* by the reaction of $KClO_3$ with a reducing agents such as HCl, H_2O_2 or methanol, in the presence of excess H_2SO_4.

$$ClO_3^- + 2H^+ + e^- \longrightarrow ClO_2 + H_2O \quad E° = 1.152\ V$$

The reaction of chlorine dioxide with organic compounds takes place in two steps. In the first stage of the reaction, the ClO_2 molecule accepts an electron and chlorite ion is formed (ClO_2^-). In the second stage, ClO_2^- ion accepts 4 electrons to produce a chloride ion (Cl^-)[13].

$$ClO_2\ (aq) + e^- \longrightarrow ClO_2^- \quad E° = 0.95\ V$$

$$ClO_2^- + 2H_2O + 4e^- \longrightarrow Cl^- + 4OH^- \quad E° = 0.76\ V$$

Chlorine dioxide based oxidative production of humic acids has been found a promising way for the production of humic acids suggesting the possibility of the low rank coal for commercial production of humic acids.

EXPERIMENTAL

Preparation of coal sample: The coal samples from different mines of the Punjab and Baluchistan were collected in polyethylene bags. The samples were pulverized and sieved through 50 μm sieve.

Calculation of moisture content: Moisture content of the coal was determined drying the powdered sample of the coal in oven at 105 °C till content weight. The samples were weighed, completely ground to 200 mesh size and were carried out in separate crucibles. The crucibles were kept in an oven at 105 °C. Then the sample were cooled to room temperature and weighed again. The loss in weight is a measure of the moisture contents[14].

Calculation of ash contents: Ash contents were determined at 1200 °C. The crucible containg samples were heated in burner up to complete burning of compound. The residue was weighed which was the ash[14].

Calculation of volatile matter: The samples were crushed, weighed and kept in covered crucible. The crucibles were subjected to oven at 900 °C. The samples were cooled, the loss in weight tells about the loss of volatile matter[15].

Oxidation: For the oxidation of coal with chlorine dioxide, 100 g sample of pulverized coal was mixed with upto 10 g of potassium chlorate in 1 L flask equipped with magnetic stirring and hot plate to provide suitable temperature. Chlorine dioxide gas was produced *in situ* by adding activator (a mixture of sulphuric acid and hydrochloric acid or methanol). The treatment with ClO_2 was carried out at different temperatures for different time intervals.

Extraction of humic acids: The humic acids were extracted according to the standard procedure described by Jiang *et al.*[7] with modifications. One gram of coal was treated with 10 mL of 0.5 mol L^{-1} KOH at 70 °C for 2 h. The supernatant was filtered through 50 μm sieve and the coal residue was washed with distilled water until the supernatant was clear. The supernatant was acidified with concentrated H_2SO_4 to pH 1-2 and allowed to stand for 24 h. The precipitated humic acids were separated by centrifugation. The gel-liked humic acids were oven-dried at 60 °C and stored in desiccators.

FTIR spectra of the samples were recorded on KBr pellets (2 mg humic acids and 100 mg KBr) using FTIR spectrophotometer (Perkin Elmer)[16].

RESULTS AND DISCUSSION

FT-IR analysis: The FT-IR spectra of coal and humic acid were recorded on Perkin Elmer FTIR. The main difference in relative peaks was observed by comparing both spectra. In attached FT-IR spectrum of humic acid produced by the oxidation of coal (Fig. 1), the bending vibrations for OH group of carboxylic group were observed at 948 cm^{-1} and 1419 cm^{-1}. The IR stretching frequencies were also confirmed for carboxylic and hydroxyl groups. The stretching frequencies for free OH group were observed at 3530 cm^{-1} and for carboxylic OH group was found at 2930 cm^{-1}. The bending vibration for C=O was observed at 1760 cm^{-1}. These results can be visualized from the spectrum of humic acid (Fig. 1) and compared with spectrum of the unoxidized coal (Fig. 2).

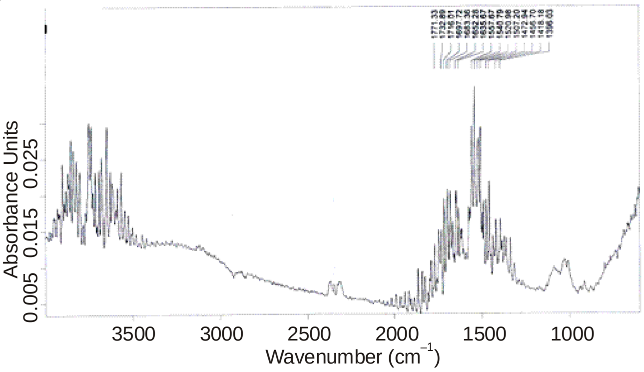

Fig. 1. FT-IR spectrum of humic acid

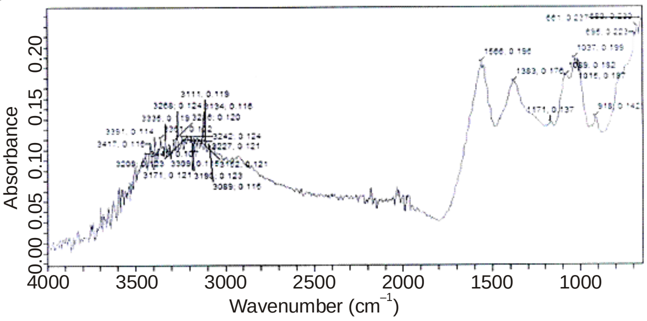

Fig. 2. FT-IR spectrum of coal

Nature of coal and oxidation: Nine samples of coal from different regions of Pakistan were analyzed for their composition, particularly the percentage of fixed carbon (Table-1). The coal samples from different areas were used for the production of humic acids by chlorine dioxide mediated oxidation. It was found that the highest yield of humic acid was found from the coal of region Dukki-2, Baluchistan which was 76 % on the dry weight basis.

Effect of concentrations of reactants on the yield of humic acids: The coal was oxidized with ClO_2, produced *in situ* by the reaction of $KClO_3$ with one of two reducing agents such as hydrochloric acid or methanol, in the presence of excess

TABLE-1
EVALUATION OF COAL FOR ITS OXIDATION

Sample No.	Mine location/Area	Total carbon (%)	Fixed carbon (%)	Volatile matter (%)	Total sulphur (%)	Ash (%)	Moisture (%)	Humic acid yield (%)
1	Dukki-l, Baluchistan	74	38.6	41.8	4.2	3.8	15.8	67
2	Dukki-2, Baluchistan	77	39.8	45.9	5.7	3.9	10.4	76
3	Dukki-3, Baluchistan	70	34	39	4.5	4.1	11.8	65
4	MDZ26, Chakwal	75	35.14	46.3	2.30	14.72	4.80	71
5	MDZ41, Chakwal	72	43.17	38.3	2.10	14.65	6.27	70
6	MDZ56, Chakwal	76	44.28	40.7	3.37	11.2	7.27	72
7	MDZ44, Chakwal	68	37.5	37.6	5.89	21	6.92	64
8	MDZ61, Chakwal	62	36.7	34.9	3.37	24.14	5.56	62
9	Hyderabad	59	33.68	36.4	3.8	26.73	3.2	60

H_2SO_4. The reaction flask contained 100 g pulverized coal, mixed with 2-10 g $KClO_3$ and 50 mL 50 % H_2SO_4. The reaction of ClO_2 with organic substances takes place in two steps. In the first stage of the reaction, the ClO_2 molecule accepts an electron and chlorite ion is formed (ClO_2^-). In the second stage, ClO_2^- ion accepts 4 electrons and chloride ion (Cl^-) is formed. The redox potential is the driving force for the oxidation of the coal to humic acids.

Effect of concentration of HCl: Fig. 3 shows the effect of changes in concentration of HCl using various fixed amounts of $KClO_3$. Hydrochloric acid was added to the reaction mixture over a range of 5 to 40 %. It was found that the conversion of coal to humic acids increased with increase in the concentration of HCl and reached a maximum value of 76 % when 30 g HCl was added to the reaction mixture having 8 g $KClO_3$, 50 mL 50 % H_2SO_4 and 100 g coal. A further increase in the concentration of HCl could not enhance the yield of humic acids.

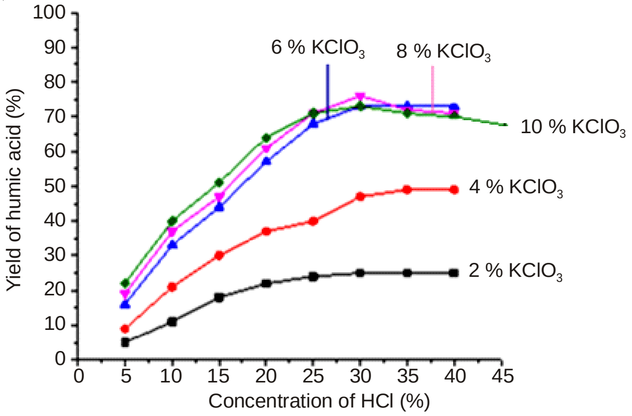

Fig. 3. Effect of concentrations of HCl on the yield of humic acid

Effect of concentration of $KClO_3$ (with HCl): Fig. 4 shows the effect of concentration of $KClO_3$ using various fixed amounts of HCl. The potassium chlorate was added to the reaction mixture over a range of 2 to 10 %. It was found that the conversion of coal to humic acids increased with increase in the concentration of $KClO_3$ and reached a maximum value of 76 % when 8 g $KClO_3$ was added to the reaction mixture having 30 g HCl, 50 mL 50 % H_2SO_4 and 100 g coal. A further increase in the concentration of HCl could not enhance the yield of humic acids.

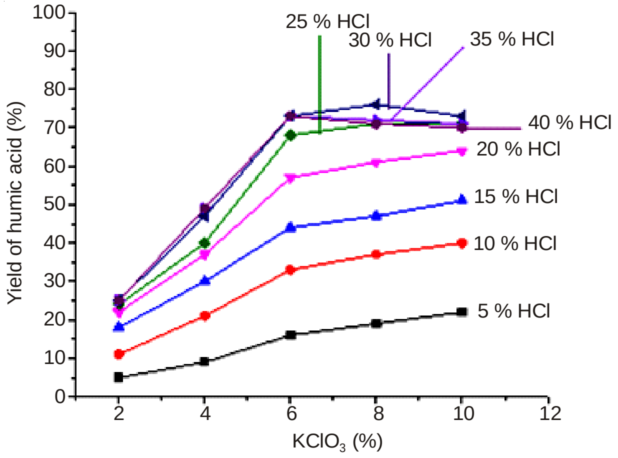

Fig. 4. Effect of concentrations of $KClO_3$ on the yield of humic acid

Effect of concentration of methanol: Fig. 5 shows the relationship between the concentration of methanol and the yield of oxidized humic acids. Methanol was added to the reaction mixture over a range of 5 to 30 %. It was found that the conversion of coal to humic acids increased with increase in the concentration of methanol and reached a maximum value of 72 % when 15 g methanol was added to the reaction mixture having 8 g $KClO_3$, 50 mL 50 % H_2SO_4 and 100 g coal. Higher amounts of methanol did not give better yield of humic acids.

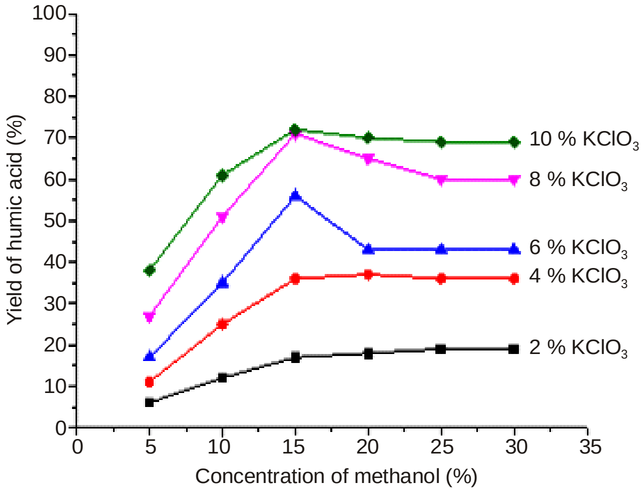

Fig. 5. Effect of concentrations of methanol on the yield of humic acid

Effect of concentration of $KClO_3$ (with methanol): Fig. 6 shows the relationship between the concentration of $KClO_3$ and the production of humic acids. Potassium chlorate was added to the reaction mixture over a range of 2 to 10 %. It was found that the conversion of coal to humic acids increased with increase in the concentration of $KClO_3$ and reached a maximum value of 75 % when 10 g $KClO_3$ was added to the reaction mixture having 15 % methanol, 50 mL 50 % H_2SO_4 and 100 g coal.

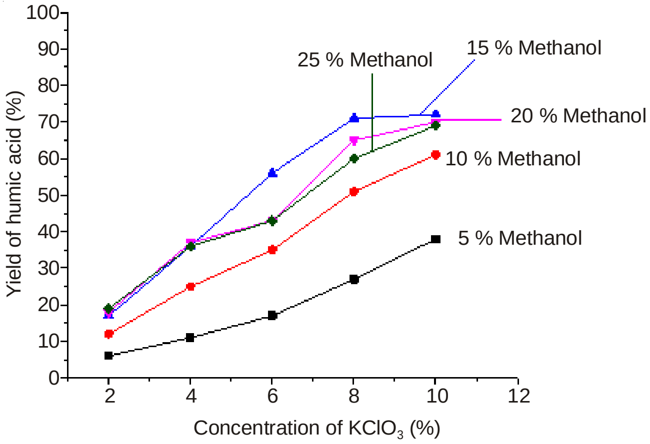

Fig. 6. Effect of concentrations of $KClO_3$ on the yield of humic acid

Effect of temperature: The effect of temperature on the production of humic acids using potassium chlorate and hydrochloric acid mixture was investigated. The temperature was found to affect the rate of formation and yield of humic acids during ClO_2 based oxidation of sub-bituminous coal. Fig. 7 shows that the yield of humic acid increased with increase in temperature up to 65 °C at which maximum yield

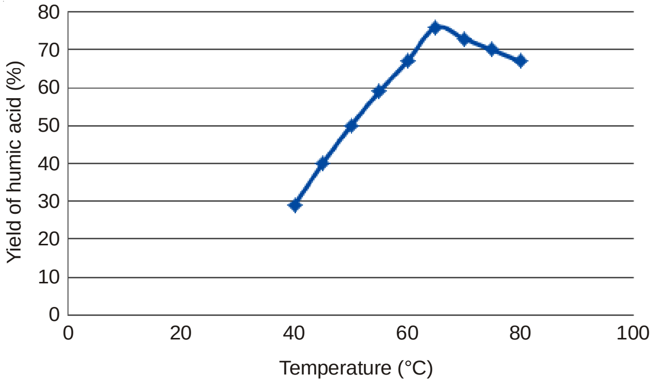

Fig. 7. Effect of temperature on yield of humic acid

of 76 % was obtained. Further increase in temperature could not enhance the oxidation yield. At higher temperatures ClO_2 gas was observed to evolve from the reaction flask.

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