Preparation and Characterization of Activated Dolochar for Adsorptive Desulphurization Process

Hariprasad.V.P, M.Biju, A.Nagarajan

***Abstract* —The objective of the following work is to understand the adsorptive desulphurization process of activated Dolochar (a carbonaceous material from sponge iron industry), it's preparation involving a novel compact process and to study the characterization methods to distinguish it from the available adsorbents , validate it's efficiency. The chemical impregnation of the dolochar was followed by pyrolysis activation which is carried out in a crucible with the support of a Nitrogen purging cylinder controlled by a gas flow-meter. The activity of the Virgin Dolochar and Activated Dolochar was determined by a comparison process of their Deadsorptive efficiency in a sulfur rich crude sample. The undiscardable Fixed Carbon in the sample is preserved and their activity is enhanced in the study.**

***Keywords*— adsorption, desulphurization, dolochar, pyrolysis.**

INTRODUCTION

The following study investigates the production of activated dolochar, an environment friendly adsorbent which are used in numerous industries. Activated carbon can be derived from many different sources and produced in varying production processes. The raw materials used, activation process, and process parameters determine the physical properties and performance characteristics of the resulting carbon. Modifying these activation properties determines the porosity and pore volume distribution of the carbon. The goal of this study is to detail a mass balance on the production of activated carbon and develop quick screening methods to observe and compare the effects of different precursor materials, chemical reagents, and process variables involved in this production process. To understand the adsorptive efficiency of the dolochar, an experimental set-up is also designed to verify the range of adsorption in a crude sample. This study also deals with adsorptive desulphurization to remove the sulphur content from a crude sample .Adsorptive desulphurization provides an alternative technology of particular interest due to its low energy consumption, availability of adsorbent, ambient operating temperature and pressure. It enables achievement of ultra-low sulphur concentration while incurring the least amount of negative effects on other fuel properties. Activated carbon's porous structure allows it to adsorb materials from the liquid and gas phase.

2) EXPERIMENTAL PROCEDURE

Dolochar available at AGNI steels Pvt Ltd Erode, Sangam Steels is collected in lumps at various intervals and made into a composite sample. A proximate analysis is made prior to using the collected dolochar for experimental trials. It was found an average of 45% carbon is present in dolochar. Also, the metal oxides like silica, alumina, and magnesia are present in considerable amount which will give an opportunity for stable surface sites. It is presumed that the active sites can be utilized to enhance the capabilities of adsorption**.** The experimental procedure can be summarized into following steps;

-Chemical Activation of the Dolochar
-Thermal Activation of the Dolochar
-Desulphurization of the crude sample using the Dolochar

Chemical Activation

Prior to the Thermal Activation process, chemical impregnation with acids like HCl, H_2sO_4 and H_3Po_4 and bases like NaOH, KOH, and salts like KCl, NaCl, $Zncl_2$ and Na_2CO_3 done in a digesting equipment and particularly with the help of magnetic stirrer come heater.

The dolochar was made into various fractions. A representative sample of (-16+pan) mess size is used for the activation purposes. The activation was done in two steps. First, around 100g of dolochar is taken in a 500ml beaker in six different sets. To each of the beaker, the following chemicals are added.

[1] 50% H_3PO_4 sol + 100g dolochar
[2] 50% KOH sol + 100g dolochar
[3] 50% NaOH sol + 100g dolochar
[4] 50% Na_2CO_3 sol + 100g dolochar
[5] 50% $ZnCl_2$ sol + 100g dolochar
[6] 50% KCl sol + 100g dolochar

Figure.1.Magnetic Stirrer cum Heater

The sample is then separated using Whatman Filter paper grade 42.

Figure.2.Filtration of the Dolochar

After activating, the carbon is separated using filtration process and then dried in a Dry Oven.

Figure.3.Process of Drying (Hot Air Oven)

Thermal Activation

An apparatus for the high-temperature thermal activation of the chemically impregnated dolochar is done in a closed chamber which is constructed from stainless steel. Nitrogen is purged into the chamber throughout the reaction. The various samples of dolochar were weighted (100 g) into silica crucibles and kept inside the chamber. The chamber is heated by the induction coil to reach temperatures of 200 to 400°C.

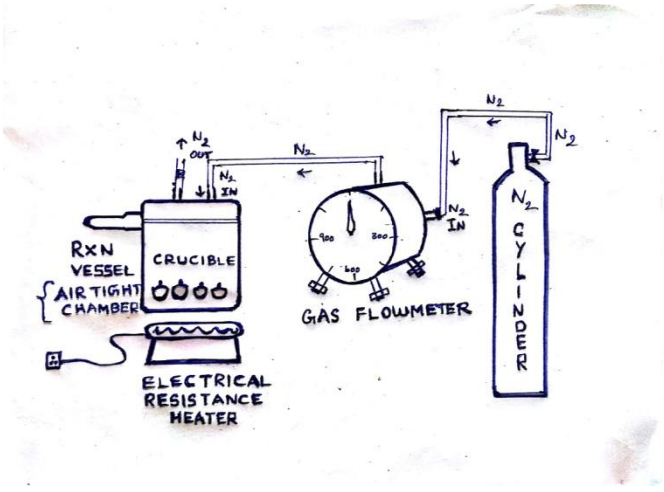

Figure.4.Pyrolysis Activation set-up

The activation reactor consists of a reaction chamber with dimensions of 15cm diameter and 12cm height aluminum alloy vessel with an inlet for the nitrogen gas and outlet for the exhaust gas. The heating is done by electrical resistance heater fitted with the thermocouple for measuring the temperature inside the reactor.

Various samples are taken in silica crucibles. The weights of various dolochar fractions are accurately determined. Nitrogen cylinder is used to purge the air inside the reactor assembly. A gas flow meter is used to measure the flow rate of nitrogen. The following readings are taken during the heating period. The maximum temperature of 300°C is reached in around 6min. The temperature-time history is as follows;

TABLE 1
PYROLYSIS HISTORY

S. No	Revolution	Time (sec)	Temperature °C
1	5	1min 6 sec	30
2	5	54 sec	88
3	5	1min 3 sec	145
4	5	1min 5 sec	200
5	5	3min 5 sec	300

Desulphurization Studies using Dolochar

To find the effectiveness of dolochar in adsorption of sulphur in petroleum crude, two experiments are designed. The first experiment uses dolochar without activation. In the second experiment the dolochar (-8+12 mess) is chemically activated and thermally pyrolyzed at 300°C is used as an adsorbent. The reaction kinetics of the adsorption process is studied by noting the adsorption of sulphur with time in both cases and the results are tabulated as follows;

TABLE 2
ADSORPTION STUDIES- VIRGIN DOLOCHAR/ACTIVATED DOLOCHAR

Time (min)	Output sulphur using Virgin dolochar (mg/kg)	Output sulphur using activated dolochar with Na_2CO_3 (mg/kg)
0	1.1	1.1
10	0.75	0.69
20	0.62	0.67
30	0.51	0.40
40	0.50	0.41
50	0.42	0.39
60	0.30	0.36
70	0.25	0.30
80	0.25	0.21
90	0.24	0.18

3) RESULTS

Characterization of Dolochar

The dolochar obtained is subjected to particles sieve analysis using various mess size screens from 4.75mm to 75µ

and a pan. A representative sample of cursed dolochar with -16+pan mess size is used throughout the experimental studies. A representative composition of dolochar is determined. It consists of about 45% fixed carbon, alumina, silica, ash and moisture constitute the rest. Chemical activation using KOH, H_3PO_4, NaOH, Na_2CO_3, $ZnCl_2$ and KCl were done. From the results obtained it was found chemical activation by phosphoric acid gives more active surface area.

Analysis of Effect of Activation

The effective increase in the adsorption capacity of the dolochar after various treatments are estimated by finding the iodine number and BET surface area the following are the values confirmed by chemical analysis at Coimbatore Institute of Technology, Coimbatore.

TABLE 3
EFFECT OF ACTIVATION

S. No	Material With Mess Size	Sample Details	Iodine Value mg/g	BET Surface Area m^2/gm
1	Virgin Dolochar -16+Pan	Untreated With Chemical	85.46	215
2	Dolochar -16+Pan	Treated With KCl	107.49	350
3	Dolochar -16+Pan	Treated With $ZnCl_2$	133.15	325
4	Dolochar -16+Pan	Treated With NaOH	142.49	400
5	Dolochar -16+Pan	Treated With Na_2Co_3	165.85	600
6	Dolochar -16+Pan	Treated With H_3PO_4	200	675

The above experimental results clearly show the activation of dolochar with phosphoric acid and sodium carbonate enhances the surface area of the dolochar which is evident from the iodine value obtained. The activation produces dominantly active micropores adsorptive capacity and the pyrolysis at 300°C of the various chemically treated dolochar is found to adsorb sulfur from synthetic petroleum crude. The desulphurization of synthetic crude is studied by using virgin dolochar and activated dolochar in two separate experiments. There is clear indication of increased adsorptive power for the activated dolochar.

Adsorptive Effectiveness of Dolochar

Experiment to find out the adsorption of sulphur from petroleum crude was designed. During the adsorption process, amount of sulphur removed by the adsorbent is analyzed and tabulated for both the experiments.

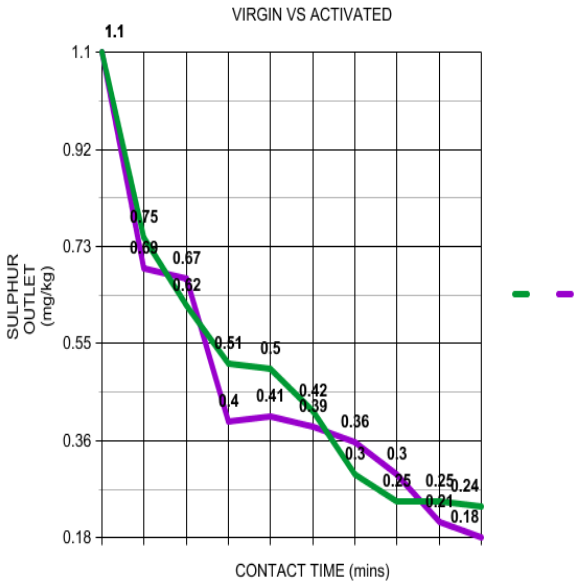

Figure.5. Virgin Dolochar v/s Activated Dolochar

The experiments proved removal of organic sulphur present in petroleum distillates is a reality. The surface area of dolochar fractions can be enhanced by chemical treatment with phosphoric acid and further micro-pores structure can be improved by pyrolysis treatment using nitrogen as purge gas. The advantage in the case of dolochar is the presence of metal oxide sites which gives pore channels for de mass transfer. The experimental data seems to fit well as pseudo-first-order kinetics. The surface area of phosphoric acid treated dolochar supports the desulphurization process with a direct impact on the adsorption. Ash and fixed content of the dolochar activated fractions show improved adsorption capacity. Ash is the inorganic, inert, amorphous and unusable part present in the activated carbon. Therefore to make dolochar as a useful adsorbent care must be taken.

Results of Activated Dolochar

TABLE 4
RESULTS OF ACTIVATED DOLOCHAR

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4) CONCLUSION

Dolochar wastes are generated by metallurgical industry contribute significantly towards the enhancement of environmental pollution. The handling, utilization and safe disposal of this solid waste are a major concern of the world. It contains around 45% fixed carbon which cannot be discarded. The sample was collected from AGNI steel industry and used as an adsorbent to remove sulfur and chromium. Firstly the virgin dolochar is used without activation. Further studies were undertaken to activate chemically and thermally to produce activated dolochar. It was found that treatment with phosphoric acid and pyrolysis at 300°C produces active dolochar which showed enhanced adsorptive capability. The results of the study revealed that there is an opportunity for employing dolochar as an adsorbate in case of petroleum crude with high sulphur content.

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Hariprasad.V.P pursued his B.E in Petrochemical Engineering from Anna University, Chennai, India. He is currently interning at Travancore Titanium Products Limited, Trivandrum, India.

M.Biju pursued his B.E in Petrochemical Engineering from Anna University, Chennai, India. He is currently enrolled in a Distribution and Control Systems programe.

A.Nagarajan is an Assistant Professor in the Department of Petrochemical Engineering, JCT College of Engineering and Technology. He is a Doctoral researcher at SSN College of Engineering, Chennai, India. He has a broad range of expertise in Environmental Science, Process Safety and Heat Transfer with hands –on experience in research and teaching for 8 years. He is currently performing his teaching duties in the faculty of Petrochemical Engineering.