

Activation of Petroleum Coke

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Mini Review

Volume 3 Issue 9

Received Date: March 05, 2019

Published Date: March 21, 2019

DOI: 10.23880/ppcj-16000182

Abstract

Activated carbon is among the best and most used materials for the adsorption and removal of pollutants. Petroleum coke may be activated by either a physical or chemical process, with a significant increase of its surface area. The activated coke may be effectively used as an adsorbing agent for the treatment of polluted water and natural gas.

Keywords: Petroleum coke; Activation; Adsorption

Introduction

Activated carbon is among the best and most used materials for the adsorption and removal of pollutants. Its adsorption efficiency is in general a function of its porosity, surface area and activity, with the surface area as a determining factor in most cases. In particular, activated carbon may be used for the removal of organic and other contaminants and pollutants dissolved in water that often lead to discoloration and objectionable smells. Previous work carried out at the chemical engineering department of A-Baath University has demonstrated the effectiveness of using commercially-available activated carbon powder for the adsorption of several different pollutants from water [1]. Adsorption of aromatic compounds by activated carbon is an irreversible process as indicated by several studies [2]. The adsorption process may however be made reversible facilitating thereby the desorption process by the use of suitable kinds of activated carbon. On adsorbing large quantities of materials, the carbon becomes less active and incapable of further adsorption. The spent carbon can, however, be easily re-activated in most cases and re-used by a simple heating procedure to a high temperature.

In lieu of the high-price commercially-available active carbons, petroleum coke may be effectively used for the adsorption of hydrocarbon and other pollutants and in

the treatment of natural gas and water [3]. In general, however, the surface area of green petroleum coke is rather low, which impairs significantly its adsorption efficiency. The surface area averages for Syrian petcoke for example between 0.04 and 0.23 m²/g, which is very low compared to the surface area of commercially-available active carbons, ranging between 950-1150 m²/g. Activation of petcoke is therefore a necessary procedure before it can be used efficiently in the treatment of Natural gas or polluted water. Activation of petroleum coke for the production of activated carbon can be an important process for upgrading low-quality petroleum coke.

Activation of Petroleum Coke

Activation is a process whereby the pores of the carbonaceous material are enlarged and the overall porosity and the surface area are increased (110). This is achieved by burning off the pyrolysis products formed during the carbonisation process. Activation processes can be either physical or chemical. Physical activation processes are more often favoured over chemical processes for economical and practical reasons and for the fact that no chemicals are required or used. In physical activation processes, the coke is normally heated with steam or carbon dioxide or it may be subjected to mild oxidation in air at moderate temperatures (600 K)

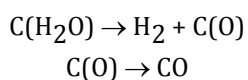
[4]. The coke may also be pre-treated prior to the activation step with an appropriate catalyst but this doesn't seem to lead to the improvement of its surface area [5].

Petcoke may be activated by heating in an inert atmosphere with steam to a high temperature at atmospheric pressure. Its surface area will thus be increased to a value that is comparable to the surface area of commercially available activated carbons. Published work indicates that activation with steam leads to the enlargement of micropores and their coalescence to form mesopores [6]. Both micropores and mesopores are normally formed in coke in the temperature range 875-1175 K. The surface area of coke will increase with increased temperature up to 1225 K, but further increase of temperature leads to the decrease of the surface area according to the results obtained by a group of Korean researchers [7].

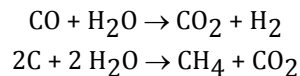
On the other hand, the increase in surface area is directly dependent on the residence time. The available evidence indicates that the effective increase in the surface area is achieved after a residence time of four hours but the maximum increase in surface area occurs after six hours (105). Other workers, however, found that the surface area starts to decrease after four hours [8]. It was argued that increasing the activation time leads at first to the appearance of a greater number of reaction sites between the carbon and steam, and this continues until the activation time reaches four hours, but afterwards if the heating continues further, oxidation reactions set in leading to the combustion of pore walls and subsequent decrease of the surface area.

The increase in the surface area of the activated coke is further related to the degree of desulphurization at the high activation temperatures [9], as desulphurization involves the breakup of the carbon-sulphur bonds and the formation of pores at the activation sites where sulphur and other inorganic matter are removed. The rate of desulphurisation reaches a maximum at 1150 K, and then decreases, and very high heating temperatures would then be required for further desulphurisation.

The reactions that take place during the activation of coke are similar in general to the reactions of steam gasification of carbonaceous materials which include the following reactions [5]:



Other reactions are also involved in which carbon dioxide, hydrogen and methane are formed:



The hydrogen and methane yields and also the ratio of carbon monoxide to carbon dioxide are both dependent on the activation temperature and pressure. There is evidence to indicate that the surface carbon catalyses the transformation reaction of carbon monoxide to carbon dioxide and it is a known fact that the ratio of carbon monoxide to carbon dioxide is directly related to the increase in the surface area of the activated coke.

Activation of Syrian Petroleum Coke

Of the available types of Syrian petroleum coke, the porous sponge coke is to be preferred to other types of coke for activation and utilization as an adsorbent [10]. Work done on this type of coke indicated that it may be possible through activation to increase the adsorption capability of the coke tenfold [11].

For the activation of Syrian petroleum coke, samples of sponge coke were heated in an electric tube furnace with a silicon carbide heating element. The furnace tube was of 59 mm diameter and the length of the heated section was 250 mm. The samples were placed in the middle of the heated section which was provided with a PtRh-Pt thermocouple. The furnace was heated to a temperature of 725 K before placing the coke samples where the heating rate was controlled at 3.5°C/min. The samples were heated with steam to a high temperature (1200 K) at atmospheric pressure in an atmosphere of nitrogen. After six hours of heating, the coke samples were left to cool in the furnace in an atmosphere of nitrogen. As a result of this activation, the surface area of the coke increased to a maximum value of 788-879 m²/g [3,12,13].

Chemical methods leading to a significant increase in microporosity may also be used for the activation of petcoke. Such methods include fusion with potassium hydroxide and treatment with sodium hydroxide [14]. When petcoke was treated with potassium hydroxide (in 1/10 ratio), Ottawa obtained an activated coke with increased surface area (up to 3000 m²/g). The coke potassium impregnation was the main factor in the activation process [9]. Activated carbon with a high surface area (up to 1600 m²/g) was also obtained by

treating anthracite with such compounds as HClO_4 and $\text{Mg}(\text{ClO}_4)_2$ [15].

Activation of Syrian petroleum coke was carried out by heating with potassium hydroxide. This was selected as the best method for obtaining activated coke with a high surface area. A small sample (5 g) of coke was placed in a porcelain crucible to which a proportionate amount of solid potassium hydroxide was added and the mixture heated in an oven at a temperature of 400°C for four hours. The coke sample was then removed from the oven and washed with a liter of deionised water to remove all traces of the alkali and then placed in an Erlenmeyer to which half a liter of aqua regia was added. The mixture was then stirred and heated for 12 hours, after which it was again washed with deionised water on a Buchner funnel at reduced pressure to neutralize the filtrate ($\text{pH} = 7$), and then heated in the oven at a temperature of 400°C for a further four hours [16].

Activated Coke as an Adsorbing Agent

Activated coke may be effectively used as an adsorbing agent for the treatment of polluted water and natural gas. Adsorption of hydrocarbon compounds by activated carbon is one of the most effective methods for water treatment as it is easily possible for the activated carbon and hydrocarbon molecules to bond together

Activated carbon particles can selectively adsorb hydrocarbon molecules from water particularly if such molecules are larger and not polar since carbon is attracted to hydrocarbon molecules and oils more than to water. The ability of activated carbon to adsorb dissolved hydrocarbons in water is related to the diffusion of the adsorbed particles towards the outer carbon surface and their later diffusion inside the pores. The three most relevant properties of the activated coke used in this way are its porosity, surface area and activity, with the internal surface area being the chief property that determines its adsorption effectiveness. The adsorption effectiveness of carbon is also a factor of the relative sizes of the pores and the adsorbate molecules as the force of attraction between the carbon and the adsorbate molecules increases as the size of the adsorbate molecules approaches that of the pores and when the size of the pores is just sufficient for the adsorbate molecules to penetrate through. Additionally, the activated coke must be granular of a sufficient particle size as work with Syrian petcoke indicated that coke fines are not as effective in the treatment of water polluted with hydrocarbons, and particularly organic hydrocarbons [13].

Of the many water pollutants, the organic compounds are in general easiest to adsorb, especially phenol and mononuclear organic solvents such as benzene, toluene and nitrobenzenes. Other pollutants may also be adsorbed by the activated coke including chlorinated organic and other hydrocarbon compounds such as chlorobenzene, chlorophenol and chloronaphthalene and also carbon tetrachloride, chloroalkyl ether and hexachlorobutadiene. Polynuclear organics and other high-molecular weight compounds, amines, pesticides, herbicides¹ and dyes may also be easily adsorbed.

In general, the separation and removal of hydrocarbon molecules from water can be achieved by any of three processes, namely adsorption, filtration of the larger particles and by the deposit of the molecules on the external surface of the activated carbon.

In practice, water may be treated by either of two procedures: viz. stirring or filtration. In the stirring procedure, the coke is added to the water and the mixture is thoroughly stirred. As a result of stirring, however, flocculation of coke particles may occur leading to loss of adsorbability effectiveness of the coke. In the filtration procedure, on the other hand, the water is made to flow over the coke granules. This procedure is often preferred because of its simplicity, although greater accumulation of the adsorbate at the inlet than at the outlet would mean that not all coke layers will be equally utilized; this may be compensated for, however, by increasing the amount of coke used and/or increasing residence time.

Activated petcoke was found to be an effective adsorbent for the treatment of water polluted with naphtha or other petroleum products. The optimum conditions for the treatment of polluted water using activated Syrian petcoke were found to be at a low temperature (25°C) and a residence time of 15 hours. Using an appropriate adsorbate to adsorbent ratio at the optimum conditions resulted in a separation efficiency of 86% [3]. At higher temperatures the adsorption and separation efficiency was reduced. This is probably due to the fact that the adsorption process is exothermic. Furthermore, increasing the temperature increases the volatility of the adsorbate and reduces the possibility of its adsorption by the coke.

Similar results were obtained when water polluted with benzene and toluene was treated with activated

¹DDT, aldrin, chlordane, BHCs, heptachlor.

Syrian petcoke. The separation efficiency of a mixture of organic compounds was not found to differ significantly from their separation efficiency when they form a part of a petroleum product such as naphtha. In both cases, the separation efficiency was found to increase with increased amount of the coke used and reduced concentration of the organic compound. On the other hand, the separation efficiency for toluene was found to be greater by about 5-16% than that of benzene [13]. This is most probably due to the molecular size difference of the two compounds, as the size of the molecules of the organic compounds has a significant effect on its adsorbability by activated carbon [13].

Activated petcoke may also be used as an adsorbent for the adsorption of acidic gases (mainly CO₂) from natural gas. When Syrian natural gas with acidic gases volume content of 3.6% was treated with activated petcoke at atmospheric pressure and at a low optimum temperature of 25°C, a high percentage of the acidic gases was removed (about 70 %) demonstrating the viability of the utilization of a cheap and available source (Syrian delayed coke) for the treatment of natural gas. Better adsorption ratios could also be obtained by carrying the adsorption process at higher pressures or lower temperatures [12]. Complete elimination of carbon dioxide may be achieved if the pressure is increased up to 20 bars and the temperature reduced to 0°C [12,17].

Reactivating the used coke is not economically recommended as it is not possible to completely remove the adsorbed acidic gases and certain residual amounts of the acidic gases will remain in the coke after re-activation. Consequently, the adsorption efficiency of the activated coke will decrease rapidly with reactivation; the rate of decrease being often a function of the surface area of the coke. For this reason, cokes of high surface area are seldom re-activated [18].

Conclusion

Petroleum coke may be activated by either a physical or chemical process. In the physical process, the coke may be activated by heating in an inert atmosphere with steam to a high temperature at atmospheric pressure. In the physical process, the coke may be activated by treatment with a suitable chemical such as molten potassium hydroxide. Activated petcoke was found to be an effective adsorbent for the treatment of water polluted with naphtha or other petroleum products. Activated petcoke may also be used as an adsorbent for the adsorption of acidic gases (mainly CO₂) from natural gas.

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