



Petroleum Coke Carbon, Characterization, and Environmental Application

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Abstract: Activated carbons were prepared from petroleum coke of Khartoum Refinery Company delayed coke unit (KRC-DCU) by chemical activation methods with KOH as active agent, It has been found that under the identical experimental conditions the porous carbon obtained was about 68–61% in yield, Iodine Number and Methylene Blue around 1248.1-1242 mg/g and 43- 51mg/g respectively, The results showed that the carbon obtained from coke by KOH activation in ratio 1:4-1:5 Coke: KOH and 60 min activation time is less in time and cost in comparison to the traditional methods. It also observed that the adsorption of Zn^{2+} on petroleum active carbon depends on the pH of solutions, contact time, and doses of adsorbent. Adsorption of Zinc+2 from water was found to fit Freundlich isotherm model with a linear curve and $R \approx 0.9731$.

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1. Introduction:

Activated Carbon (AC) and Carbon Molecular Sieves (CMS), are characterized by a high specific surface area and high pore volume in the carbon matrix. They can adsorb molecules in liquid and gaseous phase. CMS is used in several areas of science and technology and in many industries. AC belongs to the family of advanced carbon materials, due its microspore characteristics, such as high surface area, high adsorption capacity and high reactivity (González, Molina-Sabio, & Rodriguez-Reinos, 1994; Bansal, Donnet, & Stoeckli, 1988).

The conventional process to produce CMS and AC use as raw materials: carbon from fossil origin, such as coal and anthracite; biomass precursors, such as wood and cellulose fibers; synthetic materials, such as carbon fibers and carbon fibers felts, and others. The process consists in the carbonization of raw materials at temperatures between 600 °C and 650 °C, followed by a partial gasification or activation with air, steam or carbon dioxide, between temperatures of 800 °C and 900 °C, to develop an appropriate porous structure (Walker, 1968; Coutinho, Rocha, & Luengo, 2000; Metcalfe, Kawahata, & Walker, 1963) were the first to describe a production of CMS, when they activated anthracite, using CO₂ as activating agent.

The produced sieve was employed to separate n-butane, isobutane, and n-pentane. Petroleum coke is a residue with high carbon content and low ash

content. Due to its practically amorphous structure, it is a material of little commercial value, being considered a troublesome residue, both to economically and to the environment. Therefore, the use of petroleum coke for the production of AC and CMS, through physical activation and/or chemical activation, is a promising way to use this residue.

Zinc is one of the most important heavy –metal pollutants in waste water and treated water (WHO, 1971). It is leached in water, mainly, from corrosion of galvanized metals (Faust & Aly, 1998) and when used as a micronutrient in agriculture. Its removal from water using different types of activated carbons and has, therefore, been the subject matter of several investigations (Marzel, Seco, Gabaldon, Ferrer, 1996).

The objective of the present work is to evaluate how process parameters affect the porosity of the AC from the delayed coking unit of Khartoum Refinery Company (KRC) obtained by chemical activation (Rand, Hosty, West, & Marsh, 1989). In addition to the first objective the second one, is to study the adsorption of zinc ion from an aqueous solution in to activated carbon experimentally with different parameters.

2. Material and Methods:

The chemical activation experiments were carried out impregnating 1 g of petroleum coke with an aqueous solution of potassium hydroxide (KOH).



The resultant mixture was then evaporated at 150 C° and heated up by an electric furnace with heating rate control 25C°/ min and temperature control with different activation times starting from 30, 45 and 60 min (Chunlan, Shaoping, Yixiong, Shuqin, Changhou, 2005). Afterward, all the activated carbon produced were washed with hydrochloric acid (10%) then with hot and cold distilled water to remove the alkali metal and ashes until the filtrate neutralized.

2.1. Active carbon Sample:

Active carbon sample characterize by (FT- IR) to present main function group of active carbon, Characterization was performed using an Infrared spectrophotometer FT, IR 84005 Shimadzu, in wavelength 4000 to 400 fig (1).

Information about the structure of activated carbons can be obtained by the adsorption characteristics of different adsorbates, such as methylene blue and iodine. Adsorption experiments of these molecules are easy and habitually done to characterize activated carbons for the purpose of obtaining information on the adsorption capacity of the materials.

Iodine Number (IN):

The iodine value, defined as the amount of iodine adsorbed per gram of activated carbon at an equilibrium (European Council of chemical manufacturers, 1986). The iodine number is determined according to the ASTM D4607-94 method.

Methylene blue number (MBN):

The methylene blue number is defined as the maximum amount of dye adsorbed on 1.0 g of adsorbent was measured according to the procedure established by the (European council of Chemical Manufacturers Federations., 1986) The remaining concentration of methylene blue is analyzed using a UV/Vis spectrophotometer SHIMADZU 1800.

2.2 Adsorption capacity of Zinc (+2) Method:

500 cm⁻³ of 120 (ppm) Zinc (+2) volumetric flasks. A 100 cm⁻³ of each was mixed in 250 cm⁻³ beakers with 0.01, 0.03, 0,06,0.09 and 0.12 g, the mixtures were stirred for 15 min and allowed to settle for 48 hrs. before they were filtered. The residual metal ion concentration of the filtrate was determined using Atomic adsorption spectrometer ICE 3000 series Thermo Scientific-USA and presented table 1 and figures 1 and 2.

2.3 Effect of equilibrium time and pH method:

A carbon dose of 0.1 g was added to 50 cm³ solution the pH of each sample was adjusted to 2,4,6,8

and 10 consequently using 5 M Hydrochloric acid and 5 M Ammonium solution, calibrated pH-meter was used to measure the pH of the samples by (pH meter model 3305 Jenway UK). The final concentration of each sample was measured using Atomic absorption.

2.4 Evaluation of Data:

The removal percentage of active carbon was calculated according to equation:-

$$\text{Metal removal\%} = (\text{Co}-\text{C})/\text{Co} \times 100 \quad (1)$$

Where Co and C are initial and final concentration (mg/l) of the metal ions solution contact with the mass of carbon.

The amount of Zn²⁺ adsorbed by active carbon was determined by using mass balance equation

$$q_e = (v (\text{Co}-\text{C}))/m \quad (2)$$

Where q_e is the metal concentration on the zeolite carbon (mg/l) at equilibrium, C is metal concentration in solution (mg/l) at equilibrium, Co is initial metal concentration in solution (mg/l), v is volume of initial metal solution used (ml) and m is mass of zeolite used (g) (Shahmohammadi-Kalalagh, 2011).

3. Results and Discussion:

3.1. Activated carbon yields:

Results show that the ACs yield mainly depends on the amount of activation agent added, results in the table (1) showed that, the increasing of the activation agent amount increased the yield, due to the sufficiency of the activation agent loaded on the coke during impregnation which prevents volatilization of carbon during activation.

Table (1): Results of yield different activation times.

KOH: Coke	Yield % (30 min)	Yield % (45 min)	Yield % (60 min)
1:1	58.20	21.20	28.40
2:1	45.10	25.30	22.00
3:1	45.00	52.10	50.00
4:1	N/A	N/A	68.70
5:1	N/A	N/A	61.00

3.2 FT-IR spectroscopic:

FT-IR study of the produced carbon is shown in Figure 1. The sample showed four major absorption bands at 2900-3500 cm⁻¹, 1300-1750 cm⁻¹, 1000-1250 cm⁻¹ and 450-900 cm⁻¹. A wide band with two maximum peaks can be noticed at 2930 and 3450 cm⁻¹.

1. The band at 3452 cm⁻¹ is due to the absorption of water molecules as a result of an O-H stretching mode of hydroxyl groups and adsorbed water while the band at 3037 cm⁻¹ is attributed to C-H interaction with the surface of the carbon. However, it must be indicated that the bands in the range of 3200-3650 cm⁻¹ have also been attributed to the hydrogen-bonded OH group of alcohols and phenols (Yang & Lua, 2003; Puziy et al., 2003). In the region 1300-1750 cm⁻¹, amides can be distinguished on the surface of the activated carbon which has two peaks at 1640 and 1450 cm⁻¹. These functional groups were obtained during the activation process as a result of the presence of ammonia and primary amines that usually exist. Moreover, the band at 1525 cm⁻¹ may be attributed to the aromatic carbon-carbon stretching vibration. The two peaks at 1143-1193 cm⁻¹ yield the fingerprint of this carbon. The sharp absorption band at 1087 cm⁻¹ is ascribed to either Si-O (Misra, Tyagi, Singh, & Misra, 2006).

The band at 1143 cm⁻¹ can also be associated with ether C-O symmetric and asymmetric stretching vibration (-C-O-C- ring) (Wu et al., 2004).

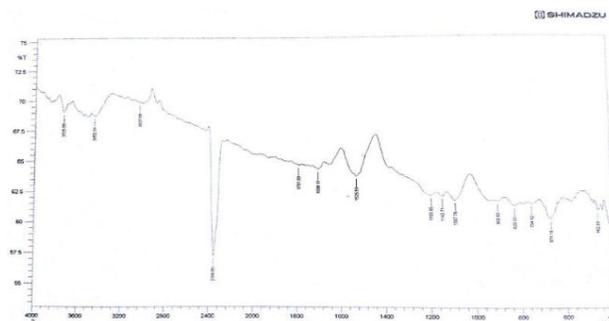


Fig (1). IR Spectrum of Activated carbon.

3.3 Effect of activation time on iodine number and methylene blue adsorption:

The process parameters, such as activation time, also have much effect on the pore structure of the final products results are presented in table no 2 and 3 and. As can be observed by changing the activation time the behavior of iodine number and methylene blue becomes more influenced, it was evidenced that the yield of activated carbon increased with increasing of activation time. The iodine number and methylene blue increased gradually too when the Activation time increased gradually, and the reason is that more diffusion can occur during activation and more reaction time (Wu et al., 2004).

Table (2): Results of Iodine Number at different activation time.

KOH: Coke	IN mgg-1 (30 min)	I N mgg-1 (45 min)	IN mgg-1 (60 min)
1:1	211.50	93.20	64.88
2:1	267.00	326.00	460.70
3:1	760.50	823.30	1119.50
4:1	N/A	N/A	1248.10
5:1	N/A	N/A	1242.40
0:1	N/A	N/A	260.00

Table (3): Results of Methylene blue number at different activation times.

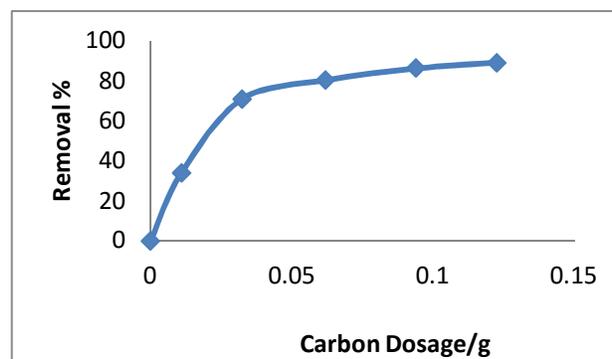
KOH: Coke	MB mgg-1 (30 min)	MB mgg-1 (45 min)	MB mgg-1 (60 min)
1:1	4.00	5.00	4.40
2:1	7.70	23.60	16.40
3:1	11.80	32.60	43.00
4:1	N/A	N/A	46.00
5:1	N/A	N/A	51.60
0:1	N/A	N/A	1.50

3.4 Zinc (+2) adsorption on activated carbon:

Many parameters affect on adsorption like carbon doses, pH, contact time and temperature of the medium.

3.4.1 Effect of carbon doses:

Zinc (+2) removal increases with the increasing of carbon doses. Data presented in Figure 2 can be used to determine the required carbon dosage to the desirable treatment concentration. However, the remaining solution concentration changed on treatment with different weights of the package -based



activated carbon, the high adsorption capacity as much as 382 mg/g was obtained.

Fig (2). Effect of Carbon dosage on adsorption removal of Zinc²⁺.

3.4.2 The effect of pH:

Very important parameter in adsorption, the study of effect of pH using different solution pH value from 2 to 10 at room temperature and 120ppm,

activated carbons had higher adsorptive capacities at pH 4, at pH 2 also the adsorptive capacity of activated carbon is high. However, increasing in the pH of the solution to 6, 8 and 10, Adsorption equilibrium time was also investigated after different contact time starting with 24 hrs. for each pH and it found that with the increasing in the contact time the amount of impurities adsorbed were also increased and reached the equilibrium after 72 hours.

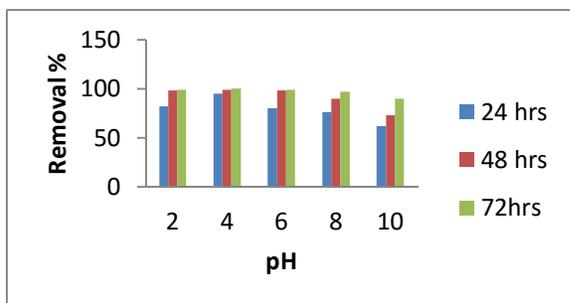


Fig (3) Effect of pH on adsorption of Zn²⁺ after different equilibrium times

3.5 Adsorption isotherms:

Freundlich model supposes that uptake or adsorption of metal ions occurs on the heterogeneous surface by monolayer adsorption. The equation of this model is described following like this

$$q_e = K_f(C_e)^{1/n} \quad (3)$$

The Freundlich equation can be linearized by taking logarithms and constants can be determined. The above equation can be linearized as follows:

$$\text{Log}(q_e) = \log(k_f + 1/n \log(C_e)) \quad (4)$$

Where k_f and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The initial concentrations of Zn²⁺ were varied and the adsorbent dose was kept constant in order to determine the equilibrium isotherms.

The constants k and $1/n$ were 1.25 and 0.509 respectively were found, the position and slope of the isotherm line revealed the performance of the activated carbon. The representation of the experimental data by Freundlich equation resulted in a linear curve with $r \approx 0.9731$. Generally, higher isotherm line means that the carbon has better adsorptive capacity than the lower line and carbon that has a higher x/m value at a specified equilibrium concentration, which was 368 mg/g (5.6 mmol/g).

Table (4): Zinc (+2) adsorption on activated carbon.

Carbon Wt.	C _e	Log C _e	x/m	Log x/m	Removal %
0.0109	39.7	1.598	368.3486	2.566259	66.91
0.0323	35.86	1.554	260.4954	2.4158	70.11
0.062	23.96	1.379	154.9032	2.19006	80.03
0.094	16.73	1.223	109.8617	2.040846	86.05
0.1225	13.35	1.125	87.06122	1.939825	88.87

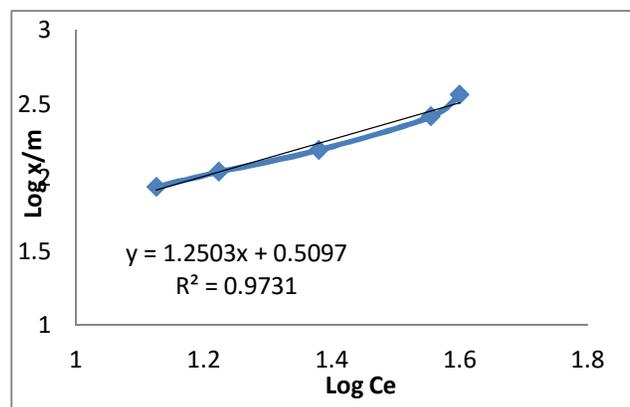


Fig (4). Freundlich linear adsorption isotherm of Zn²⁺.

4. Conclusion:

The results of this study show that it is feasible to prepare activated carbons with relatively high iodine value (1248.10 mg/gm) and methylene blue value (51.0 mg/gm) from petroleum coke by direct chemical activation using potassium hydroxide as the activation agent. And capable of using in adsorption of heavy metals from waste water and the obtained activated carbon has higher adsorption capacity towards Zinc (II), the obtained isotherm was found to fit Freundlich isotherm model.

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