Phenol Adsorption from Crude and Active Coals

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Abstract
The aim of the present work is the removal of phenol by adsorption on a raw and activated crude or hard coal (C) with NaOH, ZnCl2 and H3PO4 in the region of Bechar (south-western Algeria). The development of adsorbents from precursors is inexpensive, requiring innovative techniques using concepts developed relevant to the physical handling, processing physical and chemical activation of coal into an activated coal, with the ability of fixing aromatic organic pollutants, namely phenol. The maximum surface area obtained from the activation with ZnCl2, H3PO4 and NaOH were 1000, 850 and 3000 m²/g, respectively. The results clearly showed that hard coal activation greatly improved phenol fixing. The rate of phenol adsorption by activated hard coal is much higher than those obtained from raw coal through its holding capacity. Activated carbon porosity with NaOH is much higher than those obtained from coal activated by ZnCl2 and H3PO4. Activated coal can be an effective means of confinement in industrial disposal sites, avoiding migration of organic pollutants contained in these wastes to groundwater via the adsorption phenomenon. The development of such effective barriers, based on local resources can help solve the problem of water contamination.

Keywords: Activated Coal, Crude Coal, Chemical Activation, Adsorption

1. Introduction
Phenol is a highly toxic and carcinogenic compound and its adsorption is very important to meet the environmental regulations.

The content of phenolic compounds in industrial waste water (about 200-2000 mg/L) is generally higher than the standard norms (mostly less than 0.5 mg/L) prepared for their release into the environment water [1].

Active Coal adsorption is one of the most effective technologies for removing organic substances and toxic dyes. Nevertheless, basic study of adsorption kinetics must be considered in advance. For an efficient adsorption process, the kinetic study allows the rapid removal of pollutants from the solution while the adsorption equilibrium is the ultimate capacity of adsorption [2].

In principle, the process for the preparation of activated carbons can be divided into two tests using physical and chemical methods. The physical method consists in the carbonization of precursors followed by gasification of coal resulting in steam or carbon dioxide [3-5].

The formation of a porous structure is obtained by the removal of a large amount of internal carbon mass.

The coal at high porosity can be obtained only at high levels of burned coal. The chemical method was carried out by carbonization of the raw material impregnated with a chemical reagent (eg. ZnCl2, H3PO4 and NaOH). Due to the properties of dehydrogenation, reagents favor the formation of chemical crosslink, leading to the formation of a rigid matrix, less prone to volatile loss and volume contraction during carbonization [6-8].

Adsorption is one of the most effective methods of advanced wastewater treatment that industries employ to reduce the hazardous waste organic and inorganic effluents. It is also used to remove toxic organic compounds and inorganic-contaminated groundwater [9-10].

In this work a sample coal was chosen as a precursor of activated carbons, in addition to various activating agents, including ZnCl2, H3PO4 and NaOH were used in the preparation. Changes in behavior during the carbonization of the samples treated with these reagents were...
rarely studied and have, to our knowledge, never been compared in the literature. In the above framework, this paper describes the influence of different chemical reagents on weight loss behaviors during carbonization, and the development of surface characteristics of carbons prepared with carbonization temperature.

2. Materials and Methods

An Algerian Coal from the region of Bechar was used as the starting material. The characteristics of the adsorbent used are shown in Table 1. Unless otherwise specified, the particle sizes of the coal used for carbon preparation were within a range of 0.2 mm.

2.1. Pyrolysis

About 45 g of Coal (0.2 mm) was heated to 1000°C in an atmosphere of the gases evolved during the pyrolysis process. Then, a quartz tube (i.d. 30 mm) carrying the sample was inserted into a horizontal tabular furnace between 40 and 450 mm long. After that, the quartz tube was connected to a tar condenser. At the beginning of each experiment, air was removed from the system by purging with N₂. The heating rate was 5°C min and the soaking time 30 min. The yields of Coke, tar and gas were determined, but the gases from pyrolysis were not analyzed.

2.2. Chemical Activation

As stated in the preceding section, chemical activation of the Coal was performed using ZnCl₂, H₃PO₄ and NaOH as reagents. The activation process was initiated in a 250 ml glass-stoppered flask by mixing 1 g of the as-received coal with a solution consisting of 50 g of water and 4.25 g of a chemical reagent. Then the flask was immersed in a constant-temperature shaker bath, with a shaker velocity of 100 rpm. The mixing was performed at 85°C and lasted for 3 h. After mixing, the Coal slurry was subjected to vacuum drying at 110°C for 24 h. The resulting chemical loaded samples were then carbonized in a horizontal cylindrical furnace (60 mm i.d) in N₂ atmosphere, with a flow rate of 100 ml/min. Carbonization was carried out by heating the samples at 30°C/min from room temperature to carbonization temperatures in a range of 400-900°C, followed by holding the samples at the carbonization temperature for 1 h before cooling under N₂.

After cooling, the carbonized products that were treated with ZnCl₂ or NaOH were then subjected to washing by stirring with 250 ml of 0.5 N HCl solutions at 85°C for 30 min, followed by filtration of the mixture. The acid-washed samples were then dried by vacuum at 110°C for 24 h to obtain the activated carbon products. As for the samples treated with H₃PO₄, an NaOH solution was used instead of the HCl solution in the washing process and the samples were leached by distilled water to reach a pH value less than 8.

In order to better understand the carbonization process, a thermo gravimetric analyzer (TGA, Perkin-Elmer TGA 7) was employed to monitor the volatile evolution behavior by heating the chemical-loaded samples from room temperature to 900°C at 30°C/min. A sample of 30-50 mg was used for each TGA analysis.

Specific surface areas and pore volumes of the carbon products were determined by gas adsorption. An automated adsorption apparatus (Micromeritics, ASAP) was employed for these measurements.

Next, adsorption of N₂, as probe species, was performed at 196°C. Nitrogen surface areas and micropore volumes of the samples were determined from the BET and Dubinin–Radushkevich (D-R) Equations, respectively. The amount of N₂ adsorbed at pressures corresponds to the total amount adsorbed at both micropores and mesopores; thereby subtracting of the micropore volume from the (D-R) Equation. The total amount of N₂ (determined at P/P₀ = 0.98 in this case) will provide the volume of the mesopore [11].

2.3. Kinetic studies

Experiments were conducted by contacting known amounts of different adsorbents with 200 ml of synthetic wastewater containing 70 mg/l of aqueous phenol solution.

The solution containing the adsorbents was left for 72 h. After the equilibrium time, the treated solution was cen-
trifuged and the supernatant solution was analyzed for initial concentration of phenol at $\lambda_{\text{max}} = 270$ nm using UV spectrophotometry.

### 2.4. Modeling the adsorption isotherm

Modeling of the equilibrium data was done using Freundlich and Langmuir isotherms [12].

**Langmuir Equation:** The Langmuir Equation is the most widely used two-parameter equation, commonly expressed

$$\frac{C_{eq}}{q} = \frac{1}{k_l q_m} + \frac{C_{eq}}{q_m}$$  \hspace{1cm} (1)

$$\frac{1}{x/m} = \frac{1}{q_m k_l} + \frac{1}{q_m C_{eq}}$$  \hspace{1cm} (2)

where:

- $C_{eq}$ = equilibrium concentration of adsorbate in solution after adsorption;
- $x/m$ = amount adsorbed per adsorbent unit weight; and
- $k_l$ and $q_m$ are the Langmuir constants.

From a plot of $C_{eq}/(x/m)$ versus $C_{eq}$, $k_l$ (mg/g) and $q_m$ (L/mg) can be determined from the slope and intercept, respectively. At equilibrium conditions, the adsorbed amount $x/m$ can also be predicted using the Freundlich Equation

$$\frac{x}{m} = k_F \cdot (C_{eq})^{1/n}$$  \hspace{1cm} (3)

where the parameters $k$ and $n$ can be obtained using the linear form

$$\log \frac{x}{m} = \log K_F + \frac{1}{n} \log C_{eq}$$  \hspace{1cm} (4)

where $K_F$ is an indication of the adsorbent capacity and $1/n$ is a measure of the surface heterogeneity, ranging between 0 and 1, becoming more heterogeneous as its value gets closer to zero. Using Equation (3) from the plot of log $x/m$ versus log $C_{eq}$, the parameters $n$ and $k$ were obtained from the slope and intercept, respectively.

Since the analysis of the isotherm is important in order to develop an Equation that accurately represents the results and which could be used for design purposes, two have been applied in this study, the Langmuir (1), Freundlich (2) out of the several isotherm Equations.

Adsorption model constants, the values which express the surface properties and affinity of the adsorbent, can be used for our Coal sample. The parameters in the models were estimated by nonlinear regression and by fitting transformed data to the linearized forms of the models.
complies with the Freundlich model with a regression coefficient of $R^2 = 0.98$

The constant characteristic $K_F = 1.01$; $n = 1.59$ and the isotherm follow the Equation $x/m = 1.01(C_{eq})^{0.62}$

The phenol fixing isotherm on Coal activated by ZnCl$_2$ obeys the Freundlich model with a regression coefficient of $R^2 = 0.98$

The constant $K_F = 0.23$; $n = 0.91$

$= > x/m = 0.23(C_{eq})^{1.09}$

The fixing of the phenol on coal activated by H$_3$PO$_4$ obeys the Freundlich model with a regression coefficient of $R^2 = 0.98$

The constant $K_F = 0.20$; $n = 0.85$

$= > x/m = 0.20(C_{eq})^{1.16}$

The phenol fixing on raw Coal obeys the Freundlich model with the regression coefficient $R^2 = 0.98$

The constant $K_F = 0.0033$; $n = 0.53$

$= > x/m = 0.0033(C_{eq})^{1.8}$

The value of the constant $1/n$ indicates the adsorption intensity

$n < 1$: weak adsorbent

$n > 1$: good adsorbent

$n \sim NaOH$ good adsorbent

$n \sim ZnCl_2$ good adsorbent

$n \sim H_3PO_4$ good adsorbent

$n \sim Crude$ weak adsorbent

Capacities of phenol adsorption on these coal samples can be classified as follows:

$n \sim NaOH > n \sim ZnCl_2 > n \sim H_3PO_4 > n \sim Crude$

There,fore, one can conclude that residual coal treated with NaOH gives the best results among the adsorbents studied.

Figure 3 is a typical plot obtained from investigation in phenol adsorption during equilibrium time of three different carbon types. It is evident that the rapid initial rate of adsorption decreases markedly within time and gave a gradual approach to an equilibrium condition, which was attained after 5 min of contact between phenol solution and activated carbon. It is noticed that after 05-min contact between phenol solution and activated coal with (NaOH; H$_3$PO$_4$; ZnCl$_2$), we obtained 62.4%; 43.08%; 24.87% of phenol retention respectively.

Figure 3 also shows a comparison of the adsorption capacity of the three types of carbon. The Coal activated with NaOH had obviously a larger adsorption capacity than the other two activated carbons.

4. Conclusions

The study of adsorption onto Coal activated carbon in a liquid-solid fluidized bed for phenol, gave rise to the following conclusions:

1. The order of adsorption capacities of adsorbents studied for phenol was in the following array NaOH > H$_3$PO$_4$ > ZnCl$_2$

2. The adsorption capacity of Coals increased after treatment with sodium hydroxide, phosphoric acid and zinc chloride.

3. Coal treated with sodium hydroxide was found to give better results among the adsorbents studied.

4. The adsorption isotherm obtained from Coals treated can be represented by a Langmuir and Freundlich Equations for phenol solute.

5. References


