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# Study of adsorption of phenol on activated carbons obtained from eggshells

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ABSTRACT

Adsorption process has been proven to be one of the best water treatment technologies around the world and activated carbon is undoubtedly considered as universal adsorbent for the removal of diverse types of pollutants from water. However, widespread use of commercial activated carbon is sometimes restricted due to its higher costs. Attempts have been made to develop inexpensive adsorbents utilizing numerous agro-industrial and municipal waste materials. Use of waste materials as low-cost adsorbents is attractive due to their contribution in the reduction of costs for waste disposal, therefore contributing to environmental protection. In this review, an extensive list of low-cost adsorbents (prepared by utilizing different types of waste materials) from vast literature has been compiled and their adsorption capacities for various aquatic pollutants as available in the literature are presented. It is evident from the literature survey that various low-cost adsorbents have shown good potential for the removal of various aquatic pollutants. However, there are few issues and drawbacks on the use of low-cost adsorbents in water treatment that have been discussed in this paper. Additionally, more research is needed to find the practical utility of low-cost adsorbents on commercial scale.

This work presents the synthesis of a series of activated carbons obtained from chicken eggshell to adsorb phenol solutions. Activated carbons were obtained from eggshells taking different parts, where a shell is activated without removing the membrane, another sample is obtained, and finally separating the sample membranes where the membranes are activated. The results obtained show that porous solids are obtained with areas, which allow the adsorption of phenol. For the adsorption studies was applied from aqueous solution Freundlich models, Langmuir and Toth. The phenol adsorption was adjusted to the Langmuir model. We did a scan with immersion microcalorimetry to establish if allowed to continue this type of research.



## 1. Introduction

Water is a source of life and energy, although millions of people worldwide are suffering with the shortage of fresh and clean drinking water. Industrial development has led to major problems of environmental pollution level. Large amounts of pollutants are released into bodies of water such as VOCs, metal ions, and a large amount of phenol and its derivatives, among others.

This rapid pace of industrialization, population expansion, and unplanned urbanization has contributed largely to the severe water pollution and surrounding soils.

Each of these contaminants is highly detrimental to ecosystems and human health.

The main sources of freshwater pollution can be attributed to discharge of untreated sanitary and toxic industrial wastes, dumping of industrial effluent, and runoff from agricultural fields. It is well known that 70–80% of all illnesses in developing countries are related to water contamination, particularly susceptible to women and children [1,2]. Pollutants discharged in wastewaters can be toxic to aquatic life and cause natural waters to be unfit as potable water sources. Several systems have been used to remove these contaminants with positive results. However in some cases the costs are high during the production of the solids to adsorb these contaminants or catalysts, which also are often used.

Water treatment process selection is a complex task involving the consideration of many factors, which include, available space for the construction of treatment facilities, reliability of process equipment, waste disposal constraints, desired finished water quality and capital and operating costs. The treatment of wastewaters to make them suitable for subsequent use requires physical, chemical and biological processes. A number of technologies are

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available with varying degrees of success to control water pollution. Some of them are coagulation [2], foam flotation [3], filtration [4], ion exchange [5], aerobic and anaerobic treatment [6,7], advanced oxidation processes [8], solvent extraction [9], adsorption [10], electrolysis [11], microbial reduction [12], and activated sludge [13–16]. However, most of them require substantial financial input and their use is restricted because of cost factors overriding the importance of pollution control.

Studies on the adsorption process of the activated carbons of phenol and the derivative compounds present in aqueous solutions have been carried out for some time and in fact still continue [2–5] showing that the process presents some complexities and is dependent on the solution characteristics, such as pH, force ionic, the grade of dilution and others. In turn, these characteristics influence the adsorption mechanism of the phenolic compounds [6]. The phenolic derivates are widely used as intermediates in the plastic synthesis, dyes, pesticides and insecticides, and their frequent presence in drinking waters and municipal and industrial waste sites represents a serious danger for the environment as well as – most alarmingly – for human health [7–9]. Furthermore due to the continuous search for sources of protein in the diet of humans, the egg has become one of them. The global production increases year by year, reaching about 72 million tons per year, of which 800.000 tons are produced in Colombia. This generates a significant production of waste of eggshells, which is used as fertilizer of soils.

However, a very interesting alternative use obtained from these eggshells is a porous solid that allows adsorb organic compound that pollute rivers.

In this work, the adsorption of phenol is studied in aqueous solutions on an activated carbon prepared from eggshell, in adsorption isotherm and immersion enthalpies at pH values between 3 and 11. The structures were characterized by determination of isotherms adsorption of $N_2$ at 77 K. Immersion enthalpies of the activated carbon are determined in phenol solutions in function of the concentration at pH of maximum adsorption, establishing a relationship between the quantities adsorbed and the enthalpic values of the solid–liquid interaction.

## 2. Materials

### 2.1. Starting materials

Discarded eggshells were collected from local restaurants. To prevent decomposition, eggshells were first washed in tap water, then boiled in distilled water, and finally dried at 105 °C in a hot air oven for 8 h. The membranes were separated from dried eggshells by hand.

The dried eggshells and its membranes were ground separately using a blender. The powdered materials were sieved to obtain particles of various size ranges. The sieved materials were tested for their adsorbent qualities without further chemical or physical treatment.

The materials were separated into three groups:

- a group to which the membranes were removed and the eggshells were activated alone,
- another group to which membranes were not separated and were activated along with the eggshells, and
- a third group that contained only membranes.

The samples were labeled: ESAC 1, ESAC 2, and ESAC 3 respectively. The Pyrolysis treatments (activations) were carried out in a horizontal tubular reactor made of quartz in furnace Carbolite™, Fig. 1, using in all cases 25 g of impregnated and dried material.

The treatment was done at a constant heating rate of 10 K $min^{-1}$ and with an argon (99.999% pure) flow of 30 STP $cm^3$ $min^{-1}$, which was kept during heating and cooling. An activation temperature of 973 K and a soaking time of 4 h were used. After cooling the solid pyrolysis residue to room temperature it was washed with milli-Q distilled water until lowering the conductivity of the washing liquids to <5 μS $cm^{-1}$ (measured with a pH/conductivity meter HP, model MARK 602). The resulting ACs were dried at 383 K for 24 h in a vacuum furnace.

### 2.2. Thermogravimetric (TGA) and derivative thermogravimetric

Derivative thermogravimetric (DTG) was realized for analyzing the eggshells in powder, using a thermal analyzer (Netzsch STA 409C) with ramping rate of 10 °C $min^{-1}$ from 30 °C to 900 °C under 30 mL $min^{-1}$ Nitrogen flow.

### 2.3. Characterization of the structures

All activated carbons are characterized by physical adsorption of $N_2$ at 77 K and $CO_2$ at 273 K using an IQ2 Quantachrome equipment, with prior outgassing at 250 °C for 3 h. The micropore volume is calculated by applying the Dubinin-Radushkevich equation and the surface area obtained by BET method. The samples are also characterized by immersion calorimetry in benzene (0.37 nm), using a Tian type equipment [17–20].

### 2.4. Determination of adsorption capacity of phenol from aqueous solution

In batch adsorption studies, working solutions were prepared from an aqueous phenol stock solution (with different initial concentrations from 45 mg $L^{-1}$ to 800 mg $L^{-1}$) by suitably diluting with distilled water. Absorbance calibration curves were performed against the concentration of aqueous solutions of phenol at a wavelength of 269 nm. To determine the adsorption of phenol on activated carbon prepared from eggshell are placed 500 mg of solid, glass bottles and 50 mL of an aqueous solution of phenol between 45 and 800 mg $L^{-1}$, adjusting the pH of solutions in value pH = 5.7 ± 0.2. The flasks were shaken at 150 rpm using an electric shaker, and maintained at 25 ± 2 °C for 48 h until the equilibrium was attained. The suspensions were then filtered, and residual phenol concentrations in the supernatant solutions, diluted to the appropriate level, were measured using a Milton Roy Spectronic Genesys SN, UV–vis spectrophotometer at $\lambda_{max}$ = 270 nm.

The concentrations of the solutions were determined by using the linear regression obtained by plotting a calibration curve for phenol over a range of concentrations. The amount of phenol uptake at equilibrium, $q_e$ (mg $g^{-1}$), was calculated by Eq. (1):

$$q_e = \frac{V(C_o - C_e)}{m} \quad (1)$$

where $V$ is the volume of the solution (L), $m$ is the amount of sorbent (g), and $C_o$ and $C_e$ are the initial and equilibrium concentrations in the solution (phenol, mg $L^{-1}$).

The experimental data were fitted to the linear equations of Langmuir and Freundlich isotherms to find out which one displayed the better fit value, and thus calculating the maximum adsorption capacity ($q_{max}$).

In order to adapt each system considered, at an adequate model that can reproduce the experimental results obtained, equations of Langmuir, Freundlich, Redlich–Peterson, Toth, Vieth–Sladek, Fritz–Schluender, Radke–Prausnitz and Temkin have been considered. Thus, the non-linearized forms of the different isotherm models are shown in Table 1.