# Activated nanoporous carbon from walnut shell as promising phenol adsorbent for wastewaterTreatment

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## Introduction:

Activated carbon is predominantly an amorphous solid with a large internal surface area and pore volume. It consists of a basic structural unit building up of condensed aromatic basal plan. Annually huge amount of biomass produce in agro industry [1]. These biomasses can change to the better product by means of best method. One of these methods is producing activated carbon. In addition to high cost of activated carbon, many researchers have studied the feasibility of less expensive activated carbon by using cheaper raw materials [2]. Phenols and its derivatives constitute a widespread of water pollutant. These compounds usually find in the waste waters of industrial like as petroleum industry, coke production and agro industrial process. There are lots of methods for removing phenol from waste water such as chemical oxidation, sedimentation, filtration, adsorption, osmosis and ion exchange, but adsorption with activated carbon is an effective method used extensively for the removal of phenolic compound from aqueous solutions [3]. Adsorption of phenol in activated carbons has been intensively investigated [4], but relatively less work is reported related to modified carbons [5]. The main goal of this literature is to provide the effect of $CO_2$ modification of activated carbon prepared from walnut shell for improvement of phenol adsorbent.

## 2-Exprimental technique

The walnuts shell used for the preparation of nano porous adsorbent was collected from an agriculture waste industry. It was reduced to a size of 2–3.5 mm by means of a hammer mill. The sized shell was washed with distillated water to remove the water-soluble impurities and surface adhered particles. Then the filtered materials were dried at the oven in 80 $^o$C over night to eliminate moisture. At the first step of activation, the starting material was mixed into a boiling solution containing zinc chloride with weight ratio of (R=0.75, 0.82, 1) to walnut shell. In all experiments, heating rate, activation temperature and nitrogen flow rate were kept constant. The mixture was then dried at 110$^o$C to prepare the impregnated sample. In the second step, the resulting chemical loaded sample was placed on a quartz, which was then inserted in a quartz tube (i.d=30 mm). The impregnated sample was heated up to activation temperature 450 $^o$C under

$N_2$ flow (300 ml.min$^{-1}$) at the rate of 5 $^o$C/min$^{-1}$ and hold at the activation temperature for 55 min but in modification by $CO_2$ stream activated time increase to 5hr at $CO_2/N_2$ ratio 5% under total flow of 300 ml/min. After that samples (RC) were cooled down under $N_2$ flow, 0.5N HCl, hot water and finally cold distilled water to remove residual organic and mineral matters and then dried at 110$^o$C as a final step. The study of phenol adsorption took place in a constant temperature bath (20$^o$C) under continuous shaking. Ultra pure phenol was obtained from Merck. Adsorption equilibrium studies were conducted using the bottle-point isotherm technique by placing a known quantity of the adsorbent (0.1 gr) in glass bottle containing 50 ml of an aqueous solution of phenol at various concentrations (0–1000 mgL$^{-1}$). Titrisol solution (analytical grade, obtained from Merck), was also added at concentration of $10^{-3}$M in order to provide sufficient buffer capacity and adjusting pH of the contaminated during phenol adsorption for all adsorbents. The phenol concentration in the wastewater was monitored using a UV–visible spectrophotometer (WTW) working at 500 nm. The quantity of phenol adsorbed qt on apatite was calculated as the difference between the initial $C_0$ and the instant concentration C(t), $q_t= (C_0-C(t)V/m)$ (m and V are adsorbent mass and the volume of the contaminated solution, respectively). All measurements were performed in duplicate and experimental errors were found below 8%.

## 3-Results and discussion:

The effect of chemical ratio ($ZnCl_2$ to nutshell ratio) on BET surface area, micropoure volume and Total pore volume of activated carbons are shown in table.1.2. It can be seen that pore evolution is different before and after $CO_2$ modification. Before modification, micropoure area and micropoure volume decrease with increasing in chemical ratio. It was observed that an excess amount of $ZnCl_2$ significantly enhance the process of pore widening and formation of the micro- and mesoporouse structure by promoting externally located devolatilization process. In $CO_2$ Modification, reaction of Oxygen molecules in $CO_2$ with Carbon, intensify micropore characteristic of adsorbent by widening and/or formation of new pores, another effect related to creation of functionalize group. Several studies have shown that phenol adsorption is dependent on both the porosity and the presence of surface group [6].

The results of batch experiments reveal that adsorption capacity of modified activated carbon increase by increasing chemical ratio. From fig 1 and 2, it was observed that this effect is brilliant in samples with lower adsorption capacity because small molecule such as phenol molecule can absorb on micropores and modification increase fractional microprosity [7].

Another reason is related to functional groups on basal plan such as carboxyl, carbonyl and other groups which create in activated carbon during modification. Especially introduction of acidic functional groups may cause the π-electrons to be

removed from the carbon matrix, leading to a decrease in the strength of the interactions between the aromatic ring of the phenol molecule and the carbon basal plane [8]. In fact low percent of $CO_2$ and formation of new pores with appropriate diameter relieves the effect of functional groups and increase the effect of porosity on phenol adsorption.In fig.2 the effect of pH for the best adsorbent show that at pH near $pK_a$ maximum uptake of phenol acquired. This effect is nearly same as conclusions which Carlos Moreno-Castilla obtains in his work on adsorption of organic molecules from aqueous solution on carbon materials [9].

**Table.1**: Properties of prepared activated carbon

| properties | R=0.75 | R=0.82 | R=0.1 |
|---|---|---|---|
| Bet Surface Area($m^2g^{-1}$) | 1430.9 | 1496.3 | 1325.1 |
| Micropore area($m^2g^{-1}$) | 1034.13 | 995.63 | 785.83 |
| Total pore volume($cm^3g^{-1}$) | 1.03 | 1.1 | 1.07 |
| Micropore volume($cm^3g^{-1}$) | 0.703 | 0.671 | 0.432 |
| Average pore diameter(Å) | 11.13 | 13.36 | 14.22 |
| Fractional Microprosity (%) | 68% | 61% | 40% |

**Table.2**: properties of modified activated carbon

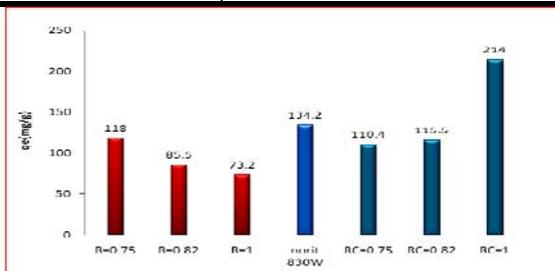| properties | RC=0.75 | RC=0.82 | RC=0.1 |
|---|---|---|---|
| Bet Surface Area($m^2g^{-1}$) | 1532.9 | 1551.4 | 1665.1 |
| Micropore area($m^2g^{-1}$) | 923.3 | 1086.7 | 1034.1 |
| Total pore volume($cm^3g^{-1}$) | 1.11 | 1.18 | 1.45 |
| Micropore volume($cm^3g^{-1}$) | 0.613 | 0.696 | 0.883 |
| Average pore diameter(Å) | 13.14 | 15.54 | 18.16 |
| Fractional Microprosity (%) | 55% | 58% | 62% |



**Fig 1**. Adsorption capacity of activated carbon at pH=7 and $C_0$= 1000 ppm.



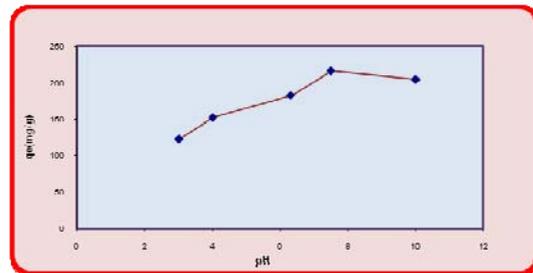**Fig 2**: Adsorption capacity of phenol on prepared activated carbon (RC=1) Verses solution pH.

**4-Conclution**

Activated carbon with various characteristics and tailored adsorption capacity were produced by the application of different $ZnCl_2$/precursor ratio. $CO_2$ modification presented significant effect on adsorption capacity which is related to creation of functional group and formation or widening of new pores. Because $CO_2$ fraction in activation step is not a lot, Dioxide gasification cannot create much acidic group which can decrease adsorption capacity, But gasification can evaluate the activation step and cause increase in adsorption capacity. Thus, activated carbon (RC=1) with the highest surface areas and the most developed porosity has the highest adsorption capacity (214 mg/g) at optimum pH for phenol adsorption.

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