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ADSORPTION OF 4-CHLOROPHENOL AND HYDROQUINONE FROM AQUEOUS SOLUTION ONTO ACTIVATED OIL BEAN SEED SHELLS

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Abstract

Phenolic compounds such as 4-Chlorophenol and Hydroquinone are among the hazardous pollutants which appear in almost all chemical and petrochemical effluents from industries. This study investigated the adsorption of 4-Chlorophenol and Hydroquinone from aqueous solution using activated oil bean seed shells (OBSS). Two different activated carbon was prepared from the seed shells of Ukpaka, Pentaclethra macrophylla benth, using two activating agents ($ZnCl_2$ and H_3PO_4) respectively. The effects of contact time were evaluated using an oscillatory shaker and a Uv Spectrophotometer. Adsorption increased as the contact time increased with the optimum achieved at 50 minutes (for $ZnCl_2$ activated oil bean seed shells) and 40 minutes (for H_3PO_4 activated oil bean seed shells). The rate constant was determined using first order kinetics. The rate constant k was calculated to be -0.005 moles per minute, and-0.004 moles per minute for 4-Chlorophenol and Hydroquinone concentration at 30 mg/l respectively using $ZnCl_2$ activated carbon, and -0.0094 moles per min for 4-Chlorophenol, and -0.012 moles per minute for Hydroquinone using H_3PO_4 activated shells of oil bean seeds. The result revealed that $ZnCl_2$ activated oil bean seed shells was more efficient in the adsorption of 4-Chlorophenol and Hydroquinone from an aqueous solution.

1. Introduction

Phenolic compounds in wastewaters are hazardous pollutants that appear in almost all chemical and petrochemical effluents from industries. These compounds are mostly by-products of industrial processes, including pharmaceutical, pesticide, paint, and solvent production, and wood, paper, and pulp processing, additionally, because of the widespread agricultural use of these compounds as herbicides, insecticides, and fungicides.

Phenolic compounds, including 4-Chlorophenol, have been detected in many sources of wastewater and drinking water (Anku and Govender, 2017). These chemicals transform other moieties that can even be more harmful than the original compounds. These transformations are usually due to their interaction with physical, chemical, biological, or microbial factors in the water (Kulkarni S. and Kaware D., 2013).

Consumption of liquids, including drinking water, containing a high concentration of phenol results in problems with the gastrointestinal tract and muscle tremor with difficulty in walking (Anku, W. W., Mamo, M. A., & Govender, P. P., 2017). Application of products containing a high concentration of phenol to the skin causes blisters and burns on the skin; heart, kidneys, and liver damage may occur with exposure to high levels of phenol. Because of their tendency to readily oxidize to quinone radicals, which tend to be more reactive, catechols have the tendency to cause DNA damage or arylation, destroy some proteins in the body, and disrupt the transportation of electrons in energy-transducing membranes. Caffeic and dihydrocaffeic acids, in the presence of copper, also cause damage to DNA. Chlorophenol poisoning causes mouth burning, throat burning, and necrotic lesions in the mouth, stomach, and oesophagus. It also induces abnormal temperature and pulse fluctuation, weak muscles, and convulsions (Gosselin R. E., Smith R. P., and Hodge H. C., 1984) . Other effects of chlorophenol poisoning include damage to the liver, kidneys, lungs, skin, and the digestive tract. Hydroquinone also damages chromosomes. Para-cresol and 2,4-dimethyl phenol have been classified as chemicals with the potential of inducing carcinogenic effects (Zhang L., Wang Y., Shang N. and Smith M. T., 1998)

1.1. Chlorophenols

4-Chlorophenols are synthetic organic compounds, obtained on large, industrial, and commercial scales by chlorinating phenols or hydrolyzing them (Tazik, M., Dehghani, M.H., and Yaghmaeian, K., 2023). It consists of the benzene ring, -OH, and chlorine atoms. It is used or formed because of the activity of some industries, mainly chemical, textile, pharmaceutical, and metallurgical.

Molecular formular; C_6H_4ClOH

Physical description

P-chlorophenol appears as white crystals with a strong phenolic odor.

4-Chlorophenol is an active ingredient in formulations of Polychlorophenols used as wood preservatives for homes, and as an additive to paints and stains (WHO, 2008).

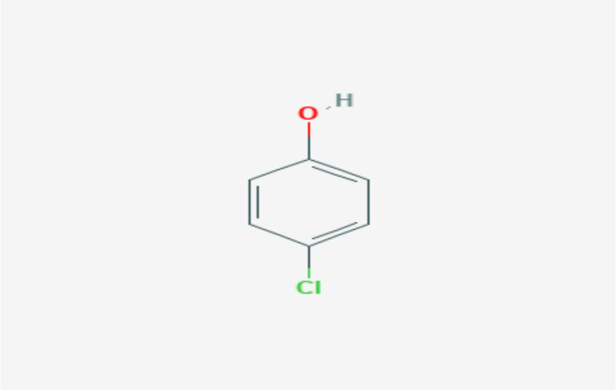

Figure 1: Structure of 4-Chlorophenol

1.2. Hydroquinone

Hydroquinone is a major Benzene metabolite, a well-known hepatotoxic and carcinogenic agent associated with malignancy in occupational environments. Human exposure to hydroquinone can occur through dietary, occupational, and environmental sources.

Chemical formula: $C_6H_6O_2$

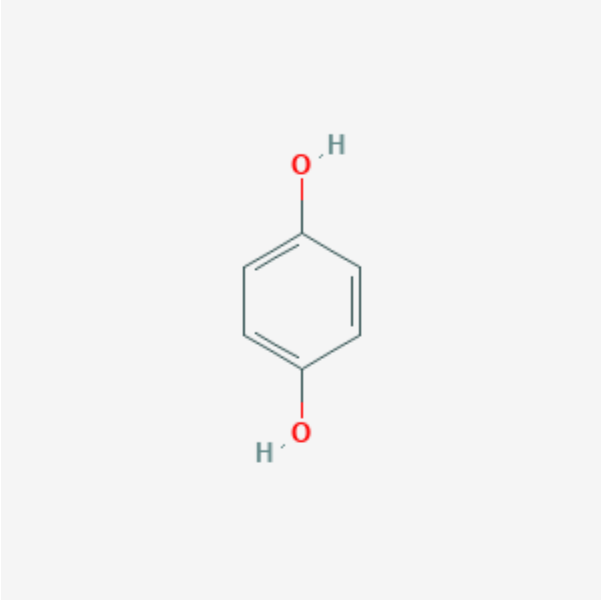

Figure 2: Structure of Hydroquinone

1.3. Adsorption

Adsorption is a surface phenomenon that occurs when a gas or liquid solute accumulates on the surface of a solid or liquid, forming a molecular or atomic film. It is a separation process in which molecules tend to concentrate on the surface of an adsorbent because of van der Waals forces, which exist between the molecules (Ujile A., 2014). It arises due to the presence of unbalanced or residual forces at the surface of liquids or the solid phase. These residual unbalanced forces tend to attract and retain the molecular species with which they meet the surface. Adsorption is a term that is completely different from absorption. While absorption means uniform distribution of the substance throughout the bulk, adsorption happens at the surface of the substance. When both adsorption and absorption processes take place simultaneously, the process is called sorption. The adsorption process involves two components:

a) Adsorbent: the substance on the surface of which the adsorption takes place.
b) Adsorbate: the substance that is being adsorbed on the surface of the adsorbent

Adsorbate + adsorbent = Adsorption

Forces of attraction exist between the adsorbate and adsorbent, and due to these forces of attraction, heat energy is released. So, adsorption is an exothermic process. If the adsorbent and adsorbate are contacted long enough, an equilibrium will be established between the amount of adsorbate adsorbed and the amount of adsorbate in solution. Adsorption isotherms describe the equilibrium relationship. There are two basic manufacturing processes for activated carbons, which include physical (thermal) and chemical activation methods (Giraldo and Moreno-Pirajan, 2008). While, physical adsorption also called physisorption, is a process in which the electronic structure of the atom or molecule is barely perturbed upon adsorption, in chemical adsorption there is a strong force between the adsorbate and adsorbent by chemical bonds, chemical adsorption is accompanied by release of energy because the adsorbates lose their translational freedom when they get to the surface of the adsorbent.

Ajayi and Olewale (2009), working on the thermal and chemical activation of Carnarium Schweinfurt nutshell, reported that the chemical method of activation using KOH leads to higher porosity formation and higher adsorptive capacity at relatively higher temperatures than thermal formation of the tars, as well as lesser gasification. The adsorption capacity of activated carbon depends on various factors such as temperature, surface area of adsorbent, activation of the solid adsorbent, solubility of adsorbates, pH of solution, and nature of adsorbent.

Adsorption using activated carbons has been described as an effective separation process for treating industrial and domestic effluents. Ansari and Mohammad-Khan (2009 asserted that it is widely used as an effective physical method of separation to eliminate or lower the concentration of a wide range of dissolved pollutants (organics or inorganics) in the effluent. It has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation, and insensitivity to toxic pollutants. It also does not involve formation of harmful substances (Wang and Li, 2007). Timurah K., Hussein M., Zainal Z., and Rusli R. (2015) used pit soil to prepare activated carbon using H_3PO_4 and $ZnCl_2$ activation at 500 °C for 3hr. They characterized these activated carbons and observed that the activated carbon produced using H_3PO_4 possesses a more crystalline structure than the activated carbon prepared using $ZnCl_2$ activation. On the other hand, Timur, S., Kantarli, I. C., Onenc, S., and Yanik, J. (2010) reported that activated carbons obtained from oak cup pulp using $ZnCl_2$ have higher phenol adsorption capacities than those obtained for activated carbons produced with H_3PO_4. They suggested that this best performance was related to the lower amount of acidic surface groups on activated carbon.

2. METHODS

2.1. Materials used

Reagents: 0.5M sodium hydroxide and hydrochloric acid solutions for adjustment of pH.
Activating Agents: Phosphoric acid, zinc chloride.
Adsorbent: Oil bean seed shells.
Adsorbate: 4-Chlorophenol, Hydroquinone.

Instruments: Air drying oven, digital weighing balance, Jenway 3510 pH meter, mechanical shaker, thermostated water bath, ultraviolet spectrophotometer, muffle furnace. All chemicals were obtained from chemical stores at Head Bridge, Onitsha, except for the 4-Chlorophenol, which was obtained from a reliable chemical store at Port Harcourt.

2.2. Sample Collection, Preparation, and Activation

The oil bean seed shells used in this work were bought from oil bean sellers in Eke, Ekwulobia, Aguata Local Government Area, Anambra State, and Oye Akokwa, Ideato Local Government Area, Imo State.

The oil bean seed shells were thoroughly washed using clean water, dried, and ground into smaller particles. The ground particles were divided into two equal parts, 1000 g each, and treated with 20 % zinc chloride and 20 % phosphoric acid, respectively. This was to activate before carbonizing (chemical activation). The raw materials were drained after 24 hours, dried, and carbonized in a muffle furnace at a temperature of 450 ^{o}C for 30 minutes to give an activated carbon (Akpan, U., Chubu, J.M., and Olutoye, M.A., 2015).

The activated carbon produced was washed with 0.5 M sodium hydroxide solution, rinsed thoroughly with distilled water, and dried in an oven at 110 ^{o}C. It was sieved with a 250-um mesh sieve and stored in an airtight container until use.

2.3. Effect of contact time on the adsorption of 4-Chlorophenol and Hydroquinone onto activated oil bean seed shells.

0.3 g of Oil bean seed shell was added to a conical flask containing 30 mg/l of 4-chlorophenol solution diluted with 50 ml of distilled water in six different conical flasks at pH 6.5 and temperature 30 ^{o}C. The flask containing the sample was suspended in a mechanical shaker and agitated for various times, 10, 20, 30, 40, 50, 60, 70, and 80 minutes.

After agitation, the sample was allowed to settle for 30 minutes and then filtered through Whatman filter paper No.110. The absorbance of the filtrates was read using a UV spectrophotometer. A plot of the amount of 4-Chlorophenol adsorbed against contact time for oil bean seed shell samples was obtained. The same method was used for effect of contact time on adsorption of Hydroquinone onto oil bean seed shell (Zhang J., Li Y., Zhang C. and Jing Y., 2008). The equilibrium amount of 4-Chlorophenol or Hydroquinone per unit mass of adsorbent, q_e (mg/g), was calculated using the equation below.

$$q_e = \frac{(Co - C_e)\,v}{W} \quad \ldots\ldots\ldots (1)$$

Where v (L) is the volume of the solution, and w (g) is the mass of the dry adsorbent.
C_o = initial concentration (mg/l) of 4-chlorophenol or hydroquinone.
C_e = Concentration (mg/l) of 4-chlorophenol or hydroquinone at equilibrium.

To study the kinetics of the adsorption process, the concentration of each of the 4-chlorophenol and hydroquinone solutions was determined at intervals of time, and the amount of each adsorbate adsorbed at time t.

$q_{t = (}$mg/g) was also calculated using equation (2).

$$q_t = \frac{(C_o - C_t)\,v}{W} \quad \ldots\ldots\ldots (2)$$

Where V (L) is the volume of the solution, and w(g) is the mass of the dry adsorbent.

Where C_t (mg/l) is the 4-chlorophenol or hydroquinone concentration at time t.

3. RESULTS AND DISCUSSION

3.1. The result of the effect of contact time on the adsorption of 4-Chlorophenol and Hydroquinone from aqueous solution using activated oil bean seed shells

The effect of contact time on the adsorption of 30 mg/l of 4-Chlorophenol onto oil bean seed shells activated with $ZnCl_2$ was presented in Tables 3.10, 3.20, 3.30, and 3.40. Figures 3 and 4 show rapid adsorption of 4-Chlorophenol onto oil bean seed shells from 2.73 mg/g to 3.15 mg/g at 10 minutes and 20 minutes, respectively. Beyond 20 minutes, the amount of 4-Chlorophenol adsorbed onto oil bean seed shells increases gradually and reaches a maximum adsorption of 3.92 mg/g and 3.35 mg/g at 50 minutes (for the salt activated carbon) and 40 minutes (for the acid activated carbon) respectively for 4-Chlorophenol and a maximum of 3.80 mg/g and 4.47mg/g for Hydroquinone. The fast uptake of 4-Chlorophenol molecules at the beginning of the adsorption time may be attributed to the availability of large numbers of vacant sites on the adsorbent surface. With the increase of contact time, these vacant sites were saturated with 4-Chlorophenol. Yusef, O., Abadi, Nourmoradi H., and Taheri, A. (2015) reported that the optimum contact time of 40 minutes was established for the removal of 4-Chlorophenol from aqueous solution using activated carbon synthesized from Aloe Vera green wastes.

Table 3.10. Effect of contact time on the adsorption of 30 mg/l of 4-Chlorophenol onto $ZnCl_2$ activated carbon shells of oil bean seed.

Contact Time (mins)	Absorbance (A) at equilibrium (nm)	4-Chlorophenol concentration in equilibrium supernatant liquid (mg/l)	4-Chlorophenol Adsorbed at equilibrium (mg/l)	Amount of 4-chlorophenol adsorbed at equilibrium (mg/g)
10	0.140	13.65	16.35	2.73
20	0.120	11.10	18.90	3.15

Contact Time (mins)	Absorbance (A) at equilibrium (nm)	4-Chlorophenol concentration in equilibrium supernatant liquid (mg/l)	4-Chlorophenol Adsorbed at equilibrium (mg/l)	Amount of 4-chlorophenol adsorbed at equilibrium (mg/g)
30	0.150	10.70	19.30	3.25
40	0.095	9.00	21.00	3.50
50	0.07	6.50	23.50	3.9
60	0.07	6.50	23.50	3.92
70	0.07	6.50	23.50	3.92
80	0.07	6.50	23.50	3.92

Table 3.20: Effect of contact time on the adsorption of 30 mg/l Hydroquinone onto $ZnCl_2$ activated shells of oil bean seed.

Contact time (mins)	Absorbance(A) at equilibrium (nm)	Hydroquinone concentration at equilibrium supernatant solution (mg/l)	Hydroquinone adsorbed at equilibrium (mg/l)	Amount of hydroquinone adsorbed (mg/g)
10	0.150	12.20	17.80	2.96
20	0.115	9.50	20.50	3.42
30	0.085	7.00	23.00	3.83
40	0.055	4.40	25.60	4.27
50	0.040	3.20	26.80	4.47
60	0.040	3.20	26.80	4.47
70	0.040	3.20	26.80	4.47
80	0.040	3.20	26.80	4.47

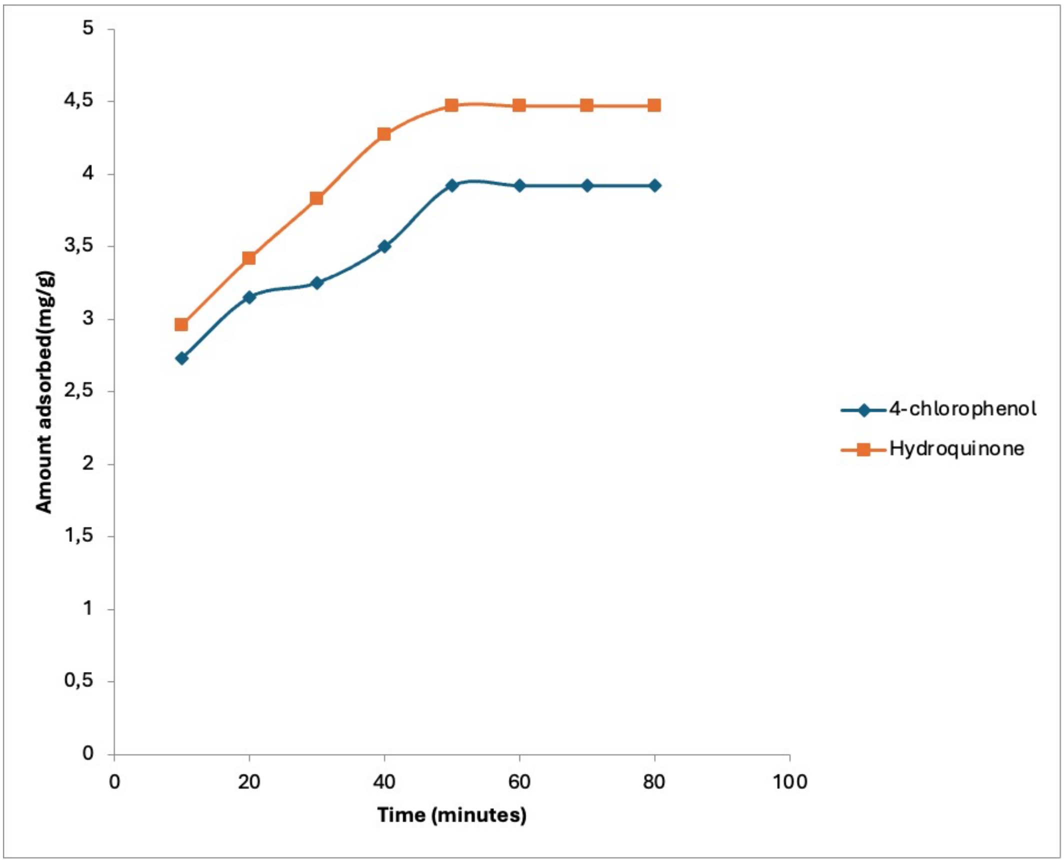

Figure 3: Plots of the effect of contact time on the adsorption of 30 mg/l of 4-Chlorophenol and Hydroquinone onto $ZnCl_2$ activated oil bean seed shells.

Table 3.30: Effects of contact time on the adsorption of 4-chlorophenol onto H_3PO_4 activated shells of oil bean seed.

Contact time (mins)	Absorbance at equilibrium (nm)	4-Chlorophenol concentration in equilibrium supernatant liquid (mg/l)	4-Chlorophenol concentration at equilibrium (mg/l)	Amount of 4-chlorophenol adsorbed at equilibrium (mg/g)
10	0.155	14.9	15.10	2.51
20	0.130	12.6	17.40	2.90
30	0.115	11.0	19.00	3.17
40	0.105	9.90	20.10	3.35
50	0.105	9.90	20.10	3.35
60	0. 105	9.90	20.10	3.35
70	0.105	9.90	20.10	3.35
80	0.105	9.90	20.10	3.35

Table 3.40: Effect of contact time on the adsorption of Hydroquinone onto H_3PO_4 activated oil bean seed shell.

Contact time (mins)	Absorbance(A) at equilibrium (nm)	Hydroquinone concentration in equilibrium supernatant liquid (mg/l)	Hydroquinone adsorbed at equilibrium (mg/l)	Amount of Hydroquinone adsorbed (mg/g)
10	0.170	14.00	16.00	2.60
20	0.130	10.50	19.50	3.25
30	0.100	8.00	22.00	3.60
40	0.090	7.20	22.80	3.80
50	0.090	7.20	22.80	3.80
60	0.090	7.20	22.80	3.80
70	0.090	7.20	22.80	3.80
80	0.090	7.20	22.80	3.80

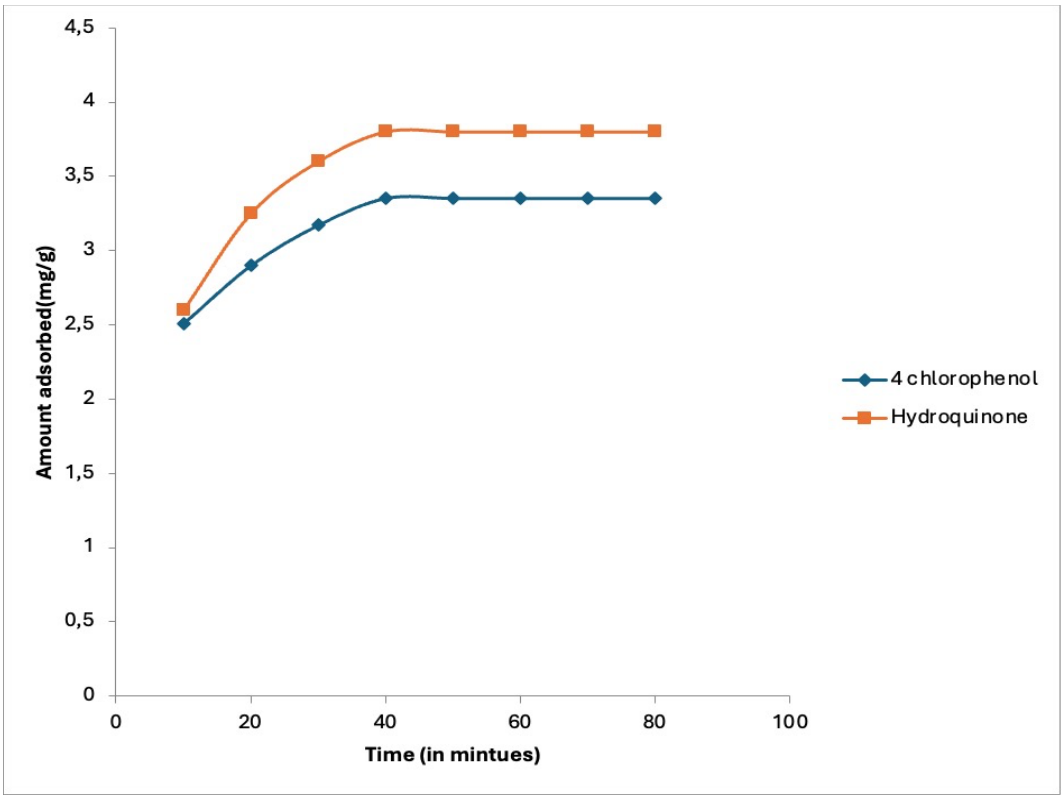

Figure 4: Plots of the effect of contact time on the adsorption of 4-Chlorophenol using H_3PO_4 activated shells of Oil bean seed.

3.2. Adsorption kinetics for a plot of 4-Chlorophenol and Hydroquinone

The rate constant for adsorption of 4-Chlorophenol and Hydroquinone onto activated oil bean seed shells was determined using first-order kinetics

In (C_0/C_t) = K_t
Where C_0 is the initial 4-chlorophenol and hydroquinone solution concentration
C_t is the concentration at time t
K_t is the rate constant

A plot of In (C_0/C_t) versus t yielded a straight line from the slope of which the rate constant k, was calculated to be -0.005 moles per min, and-0.004 moles per min for 4-Chlorophenol and Hydroquinone concentration at 30 mg/l respectively using $ZnCl_2$ activated carbon, and -0.0094 moles per min for 4-Chlorophenol, and -0.012 moles per minute for Hydroquinone using H_3PO_4 activated shells of oil bean seeds.

Table 3.50. First-order kinetic table for the adsorption of 4-Chlorophenol and Hydroquinone onto $ZnCl_2$ activated oil bean seed shells

Time(mins)	$lnC_o/Ct.$ 4-Chlorophenol	lnC_o/Ct Hydroquinone
10	0.604	0.525
20	0.460	0.378
30	0.430	0.262
40	0.360	0.157
50	0.246	0.120
60	0.246	0.120
70	0.246	0.120
80	0.246	0.120

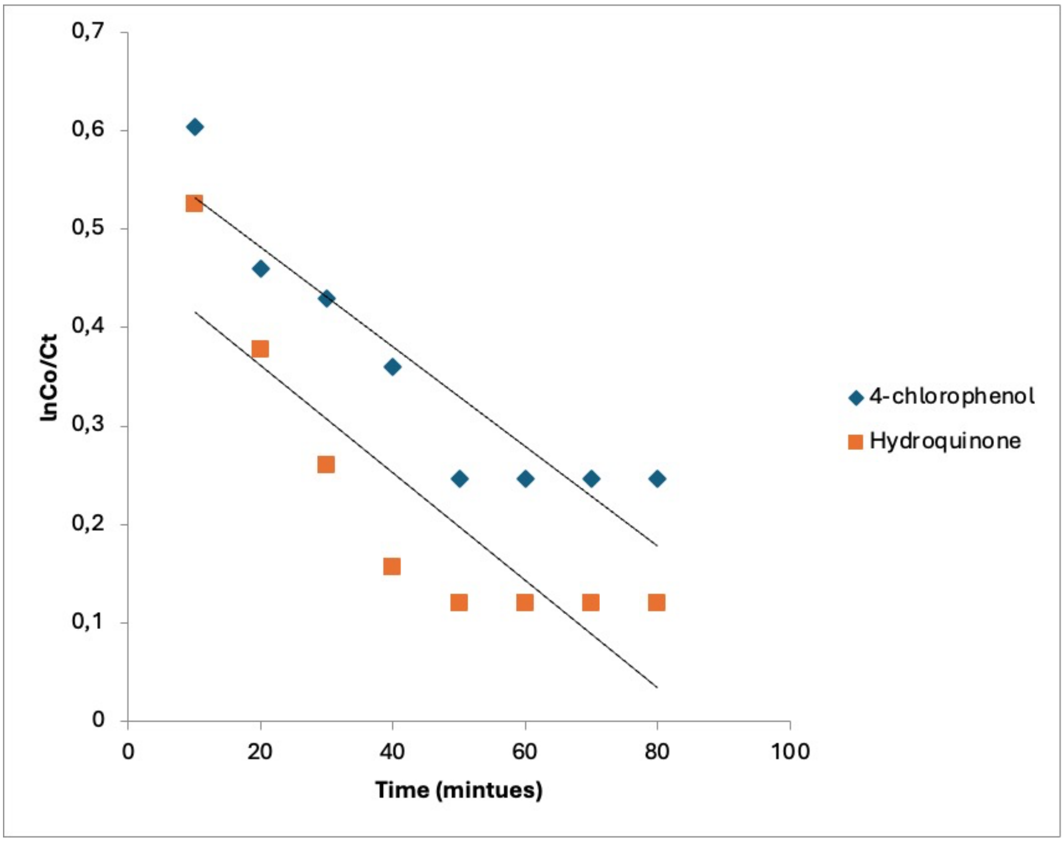

Figure 5. First-order kinetic plots of the adsorption of 4-Chlorophenol and Hydroquinone onto $ZnCl_2$ activated oil bean seed shell.

Table 3.60: First-order kinetic table for the adsorption of 4-Chlorophenol and Hydroquinone onto H_3PO_4 activated oil bean seed shell

Time (mins)	$\ln C_o/C_t$ 4-Chlorophenol	$\ln C_o/C_t$ Hydroquinone
10	0.683	0.628
20	0.542	0.430
30	0.451	0.262
40	0.399	0.270
50	0.399	0.270
60	0.399	0.270
70	0.399	0.270
80	0.399	0.270

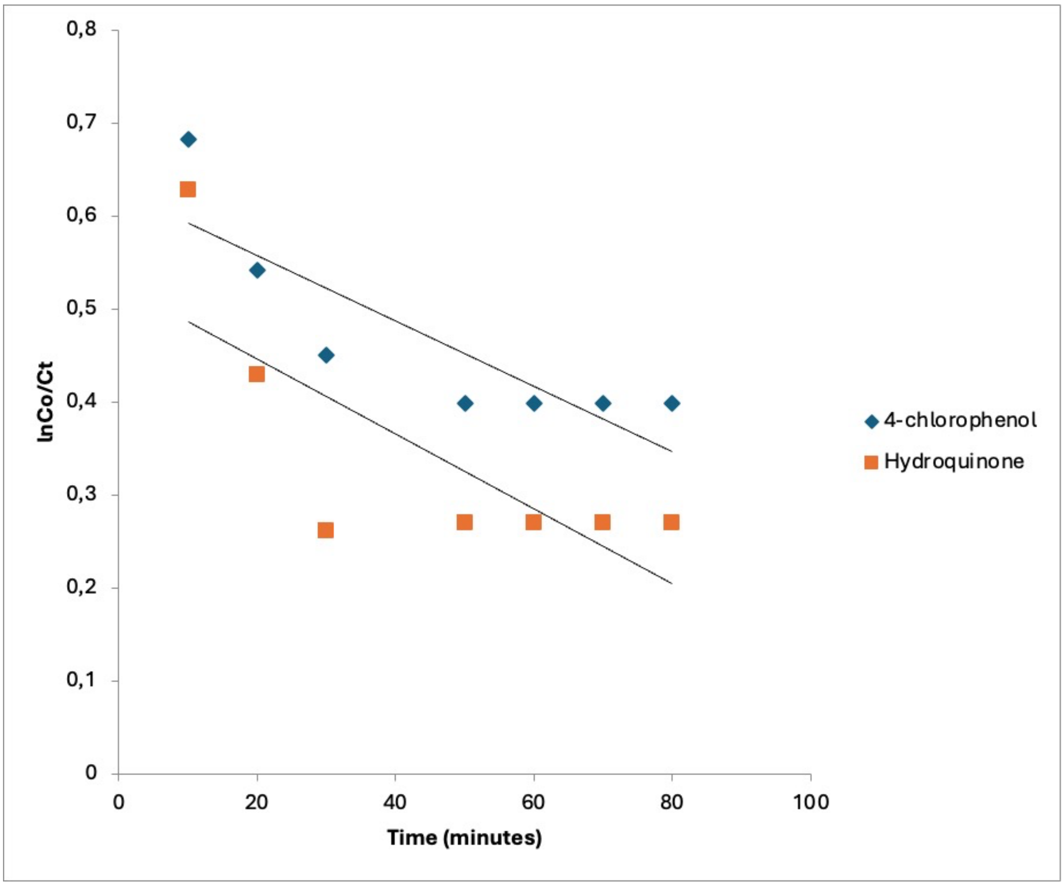

Figure 6:.First-order kinetic plots of the adsorption of 4-Chlorophenol and Hydroquinone onto H_3PO_4 activated oil bean seed shell.

4. CONCLUSION

This study indicates that oil bean seed shell is a good adsorbent for the removal of toxic solvents from wastewater. The kinetic study indicates that hydroquinone and 4-Chlorophenol was adsorbed onto oil bean seed shells rapidly within the first 20 minutes, while equilibrium was established within 50 minutes (for $ZnCl_2$ activated oil bean seed shells), and 40 minutes (for H_3PO_4 activated oil bean seed shells) for both concentrations of hydroquinone and 4-Chlorophenol studied respectively. The results showed that $ZnCl_2$-activated oil bean seed shells were more efficient in the adsorption of 4-Chlorophenol and Hydroquinone from aqueous solution. Jacob A., Tijani A.,Oluwole. And Hamisu S., (2015), working on the treatment of wastewater by activated carbon developed from Borassus aethiopium, using H_3PO_4 and $ZnCl_2$ activation, and by varying the concentration of the solutions, also reported that $ZnCl_2$ activated carbon exhibited better adsorption than H_3PO_4 activated carbons.

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