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Solar Photocatalytic Degradation of Phenol Using Cocos Nucifera (Coconut) Shells as Adsorbent

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Abstract

Cocosnucifera (coconut) shell powder was used as the adsorbents for the removal of phenol from aqueous solutions. Degradation efficiency has been evaluated using photocatalysis and adsorption processes at ambient temperature. Photolysis was performed to study the effect of light on the degradation of phenol at ambient temperature while adsorption process was carried out without utilizing solar illumination. Effect of initial concentrations of phenol (50, 75, 100 and 150 mg/l), TiO_2 loading (4, 8, 16 and 20 %), and composite mass (adsorbent + TiO_2) (1, 3, 5 and 8 g) were investigated using UV-Visible spectrophotometric technique. The results obtained indicate that phenol removal increases with time and concentration of the catalyst (TiO_2) and decreases with increase in initial concentration of phenol and composite mass. Combination of UV irradiation with TiO_2 loading gave a degradation efficiency ranging from 78.36 - 82.76 % while UV irradiation with composite (catalyst- Cocosnucifera) mass gave a degradation efficiency ranging from 63.12 - 79.32 %. The efficiency of the processes of degradation of phenol followed the trend: photocatalysis>photolysis> adsorption. The kinetics studies of the degradation fitted the Langmuir and pseudo-second–order models.

Keywords: Adsorption, *Cocosnucifera*, Photocatalysis, Photolysis, Titanium dioxide

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Introduction

Water pollution caused by pollutant such as phenol has posed a significant threat to the marine environment and public health because of their high toxicity and further accumulation in the food chain, and its persistence in nature [1]. The compounds penetrate ecosystems as the result of drainage off the municipal or industrial sewage to surface water [2].

Phenol may also occur naturally in aquatic environments from the decomposition of aquatic vegetation [3] and recent research has proven the use of variety of adsorbents such as coconut shells, fruit stones, coir pith, bagasse, bamboo, rice husk, and cotton stalks, *etc*in removing phenol from wastewater [4, 5]. Coconut shell is a potential precursor for the production of activated carbons due to its excellent natural structure and low ash content. Conversion of coconut shells into activated carbons which can be used as adsorbents in water purification or treatment of industrial and municipal effluents would add value to agricultural commodities, help reduce the cost of waste disposal, and provide a potentially cheap alternative to existing commercial carbons [6, 7].

Various technologies have also been applied to eliminate phenolic compounds from waste waters. Some of these processes include: photo-fenten degradation [8 - 10], adsorption [11-13], photocatalysis [14, 15] and biodegradation [16,17].

The present research shows systematic laboratory investigations of the removal of phenol from aqueous solutions using *Cocosnucifera*shells as adsorbent and TiO_2 (catalyst), and different kinetic models were fitted to the experimental data. The main objective of this research is to investigate the efficiency of phenol degradation from wastewater via solar photocatalysis, photolysis and adsorption processes, with *Cocosnucifera*shells used as adsorbent in the photocatalysis and adsorption processes.

Materials and Methods

Coconut shells and various chemicals used for analysis were sourced within Nigeria. Phenol was obtained from Med-lab Scientific Enterprise, Port Harcourt with 99.5 % purity. Wastewaters of different concentrations of phenol were synthetically prepared using distilled water. TiO_2 used is 98 percent pure.

Coconut Shell Preparation

The coconut shell used as adsorbent was first washed with deionized water to remove the debris attached to the shell and thereafter dried at a temperature of 100°C for 5 hours. After grinding, it was cooled at ambient temperature and then sieved to obtain average particle size of (0246 - 0074mm)[18]. The adsorbent was then stored in a dessicator for further used.

Photocatalysis Experiment

For photocatalysis experiment, phenol solution of different concentration (50, 75, 100, and 150 mg/l) was treated with known weight of adsorbents-catalyst composite. All experiments were carried out using 150 ml conical flask to ensure maximum penetration of solar UV rays [21]. The adsorbent with different TiO_2 loading (4, 8, 16 and 20 percent) was added into the phenol wastewater solution. The flask was then exposed to sunlight for photocatalysis reaction to take place daily between 09:30 to15:00 hours for a period of 5 days at ambient temperature (27±1 ºC).

After illumination for the specified period, the suspension was centrifuged and the supernatant was analyzed for its phenol content by spectrophotometric techniques [22] using Varian UV-VIS spectrophometer at a wavelength of 270 nm, and the amount of phenol degraded in (percent) was calculated using the equation [23]:

$$\text{Percentage degradation} = \frac{C_i - C_f}{C_i} x100 \qquad 1$$

where C_i is the initial concentration before degradation and C_f is the concentration after degradation.

Control experiment for photolysis was also done. In this experiment the phenol synthetic wastewater was exposed to the sun without the adsorbents and catalysts present and its concentration determined as mentioned above.

Adsorption Experiments

In adsorption experiment the conical flask was covered with opaque material to prevent the penetration of solar irradiation and its concentration calculated as mentioned earlier in photocatalysis experiment.

Results and Discussion

Effect of Phenol Concentration on the Degradation of Phenol

In order to investigate the effect of initial concentration of phenol on its degradation, series of photocatalysis, adsorption and photolysis experiments were carried out at various concentrations of phenol (50, 75, 100 and 150 mg/l). For these experiments, a 4 % TiO_2 loading – 1 g adsorbent composite mass was used.

Figure 1 indicates the variation of amount of phenol degraded with contact time for aqueous solution containing 75 mg/l of phenol. It is shown that the degradation of phenol was at maximum using photocatalysis experiment as compared to photolysis and adsorption. This is due to the present of more hydroxyl radicals from illumination of sun rays and catalyst. This observation is similar to result obtained by Rahmani*et al*. [21]. The same trend was obtained for other initial concentrations of phenol.

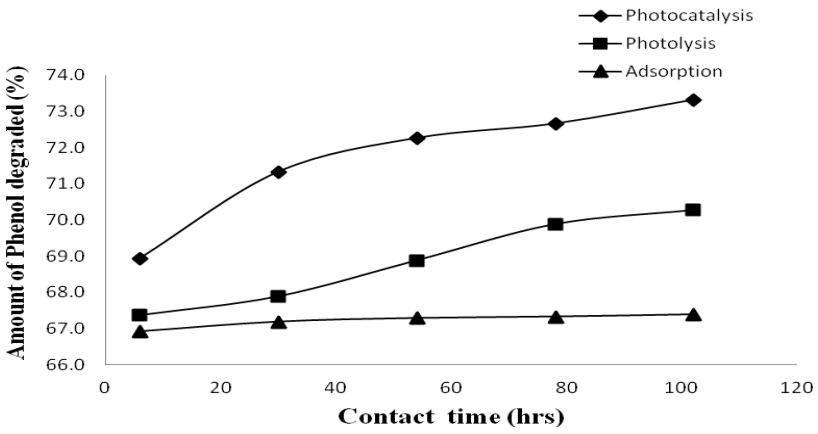

Figure 1: Variation of Amount of Phenol Degraded with Contact time for Solution Containing 75 mg/l of Phenol

Effect of Cocos Nuciferamass on the Degradation of Phenol

For the purpose of analyzing the effect of the mass of the adsorbent on the removal of phenol, photocatalysis experiments were carried out with different concentration of phenol (50, 75, 100 and 150 mg/l) at 4 % TiO_2 loading. Figure 2 shows the variation of amount of phenol degraded with different concentration of phenol at different mass of the adsorbent, *Cocosnucifera* (CN). The results demonstrate that phenol adsorption capacity decreases as adsorbent mass increases. This reveals that more active sites are utilized at lower adsorbent concentration, producing a higher adsorption capacity, while only part of active sites are occupied by phenol at higher adsorbent concentration, leading to a lower adsorption capacity [22]. It is also observed that 1 g of the composite had better removal efficiency as compared to other composite mass.

Effect of TiO_2Loading on the Degradation of Phenol

The uptake of phenol was carried out using 1 g of *Cocosnucifera* at different percent of TiO_2 loading (4, 8, 16 and 20 %) against contact time. The results show that the percentage degradation of phenol increases with increase in the concentration of the catalyst as shown in Figure 3. This can be attributed to the fact that a larger amount of photons are absorbed with increase in TiO_2 loading thus accelerating the process. This result agrees with those reported in the literature [23-25].

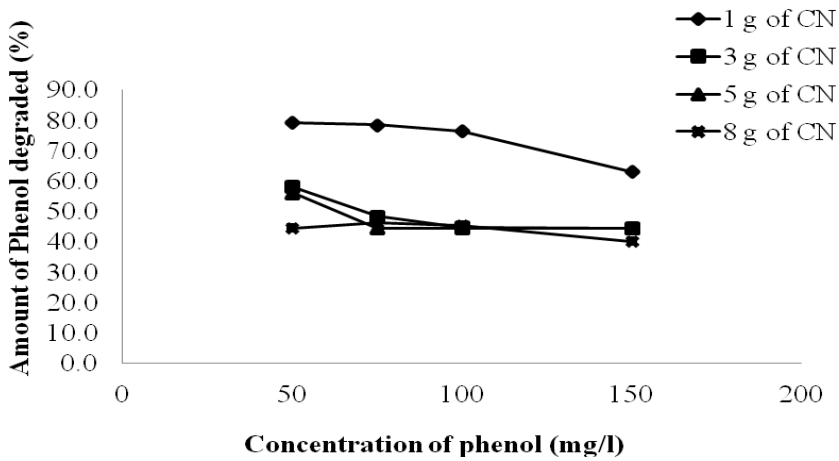

Figure 2: Plot of Different Composite Mass (1, 3, 5 and 8 g) with Initial Phenol Concentrations (50, 75, 100, and 150 mg/l

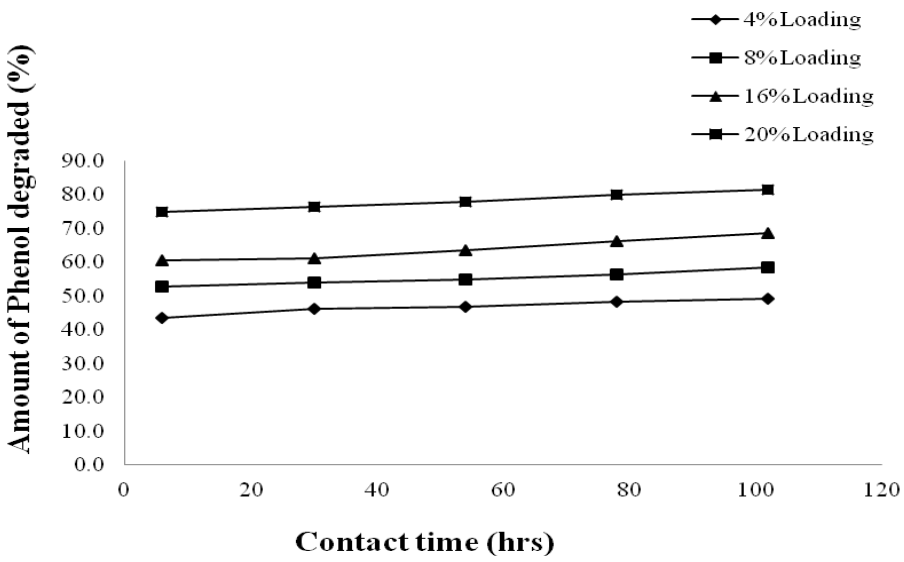

Figure 3: Removal Efficiency of Phenol at Different Percent of TiO_2 Loading with Contact Time for Cocos Nucifera

Effect of Time on the Degradation of Phenol

Effect of contact time plays an important parameter in determining the equilibrium time of adsorption process [26]. The characteristics of adsorbents and its available sites can influence the time needed to reach equilibrium. From experimental results it is observed that the degradation of phenol increases with increasing period of contact. Large amount of phenol was degraded at 102 hours and the equilibrium was attained in the fifth day.

3.5 Kinetics

In order to investigate the mechanism of adsorption, kinetic models such as the pseudo-second order, and Langmuir isotherm model were applied to study the adsorption dynamics. Photocatalysis has often been modeled with Langmuir isotherm by many researchers. This model covers the adsorption properties of the substrate on the photocatalyst surface as reported by Jain and Shalini [27] and Joshi and Shrivastata [28]. Langmuir theory is based on the assumption that adsorption is a type of chemical combination or process characterized with unimolecular.

For adherence to the Langmuir isotherm a linear plot of Ce/q_e against Ce must be linear [4, 27]. q_e is the initial concentration of phenol (mg/l) and Ce is the equilibrium concentration of phenol (mg/l). Figure 4 and 5 shows the Langmuir plots for data from the photocatalysis and adsorption experiments, respectively. The values of the adsorption parameters (Q_o and b) determined from the intercept and slope of the linear plots are given in Table 1.

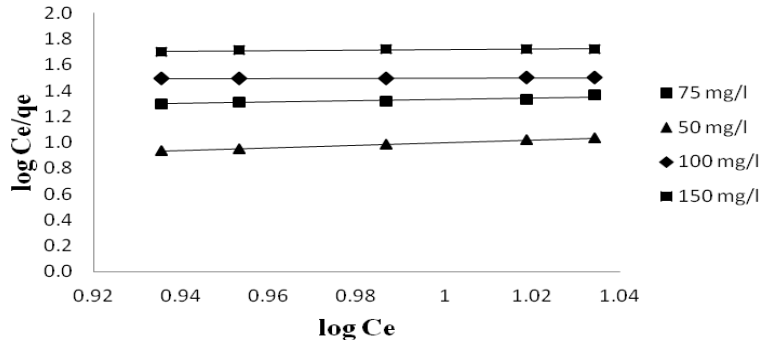

Figure 4: Langmuir isotherm for the Degradation of Phenol Using Photocatalysis Experiment

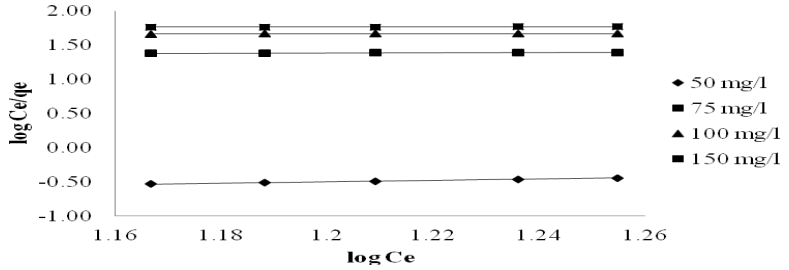

Figure 5: Langmuir isotherm for the Degradation of Phenol Using Adsorption Experiment

Table 1: Parameters for Langmuir isotherm for Phenol Degradation

Concentration	Photocatalysis			Adsorption		
(mg/l)	R^2	b	q_0	R^2	b	q_0
50	0.988	1.000	1.000	1.000	1.00	-1.699
75	0.831	0.559	0.774	0.957	0.15	1.206
100	0.987	0.051	1.447	0.957	0.52	1.603
150	0.733	0.197	1.523	0.980	0.05	1.711

The pseudo-second-order kinetic model is used in the following linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad 2$$

where k_2 is the adsorption rate constant of pseudo-second-order kinetic model, q_t is the adsorption uptake at time *t*. Figure 6 (for photocatalysis) and Figure 7 (for adsorption process) show adherence to the Pseudo-second-order kinetic model. This suggests that phenol degradation on the adsorbent appeared to be controlled by a chemisorptions process [29].

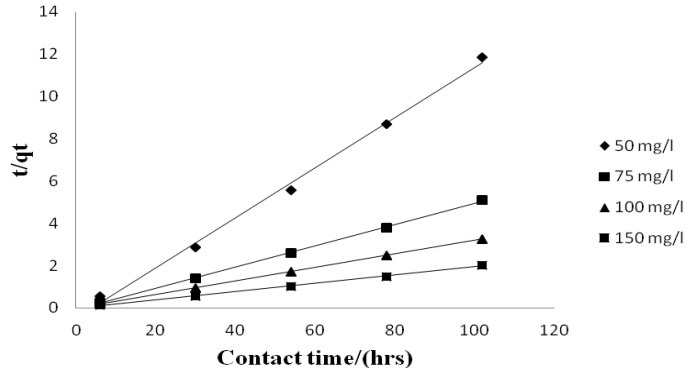

Figure 6: Pseudo-Second-Order Plot for the Degradation of Phenol by *Cocos* Nucifera Using Photocatalysis Process

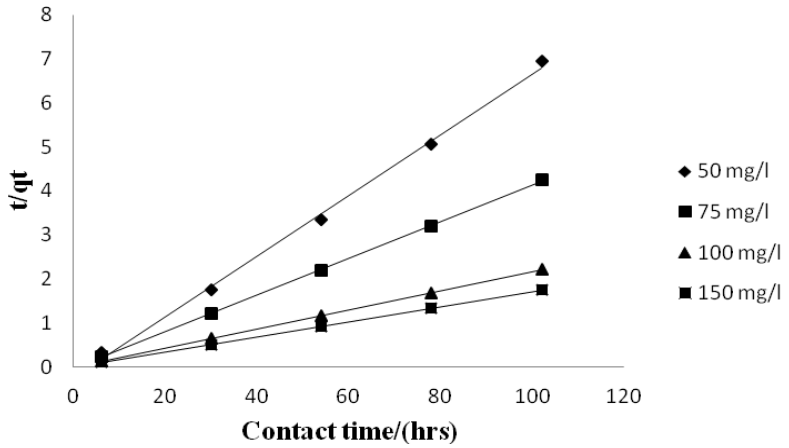

Figure 7: Pseudo-Second-Order Plot for the Degradation of Phenol by Cocos Nucifera Using Adsorption Process

Conclusions

The following conclusions have been drawn from the presents study –

(i) The developed technique of phenol removal using coconut shell appears to be low cost and practically viable for application in industry.
(ii) The degradation of phenol is dependent on the initial phenol concentration, contact time, TiO_2 loading and mass for *Cocosnucifera*.
(iii) The percentage removal of phenol was found to increase with decrease in the initial concentration of phenol.
(iv) The degradation process for phenol in aqueous follows the trend, photocatalysis> photolysis > adsorption. Maximum removal efficiency were obtained using 1 g of the adsorbent with a TiO_2 loading of 20 %.
(v) Kinetic studies using Langmuir isotherm and pseudo-second-order model fitted well with the experimental data.

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