

# Degradation of Phenol in Aqueous System by Solar Photocatalysis, Photolysis and Adsorption Processes

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## Abstract

Phenol degradation in aqueous solutions using chitosan prepared from *Crassostrea gigas* (Sea oyster) shells as adsorbent was investigated using photocatalysis and adsorption processes at ambient temperature. Photolysis was carried out 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<sub>2</sub> loading (4, 8, 16 and 20 %), and composite mass (adsorbent + TiO<sub>2</sub>) (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<sub>2</sub>) and decreases with increase in initial concentration of phenol and composite mass. Combination of UV irradiation with TiO<sub>2</sub> loading gave a degradation efficiency ranging from 98.13 - 98.92 % while UV irradiation with composite mass gave a degradation efficiency ranging from 84.80 - 98.51 %. The efficiency of the processes of degradation of phenol followed the trend: photocatalysis>photolysis> adsorption. The kinetics of the degradation fitted the Langmuir and pseudo-second-order models.

**Keywords:** Adsorption, *Crassostrea gigas*, Photocatalysis, Photolysis, Titanium dioxide

## 1. Introduction

Environmental pollution has been a major issue affecting our coastal regions. A broad range of organic pollutants are introduced into the water environment from various sources such as industrial effluents, agricultural runoff and chemical spills (Barni *et al.*, 1992). Marine environment are polluted by different organic pollutants from these sources, like chlorinated and non chlorinated aliphatic and aromatic compounds (example phenols), dyes, detergents and surfactants, agro wastes like insecticides, pesticides and herbicides, disinfection byproducts, volatile organic compounds, plastics, inorganic compounds like heavy metals, noxious gases like NO<sub>x</sub>, SO<sub>x</sub>, CO and NH<sub>3</sub>, and pathogens like bacteria, fungi and viruses (Vinu and Madras, 2010). Phenol and its derivatives are widely used in many petrochemical industries and petroleum refineries as well as chemical and pharmaceutical industries and are considered one of the priority pollutants in wastewater, because they are harmful to organisms even at low concentrations (Uddin *et al.*, 2007; Ahmaruzzaman, 2008; Yamasaki *et al.*, 2008; Jian-Mei *et al.*, 2009; Okasha and Ibrahim, 2010). The concentration of phenols in waste waters varies from 10 to 3000 mg/l. They impact taste and odour to water and are highly toxic to aquatic life, animal and human beings (Mahadewswamy *et al.*, 1997 Annadurai *et al.*, 2007). Therefore, several treatment processes have been used to eliminate phenolic compounds from waste waters. Some of these processes include: photo-fenton degradation (Achak *et al.*, 2008; Mohd *et al.*, 2009; Zhao *et al.*, 2010), adsorption (Segura *et al.*, 2009; Parida and Prahan, 2010; Babuponnusami and Muthukumar, 2011), photocatalysis (Laoufi and Bentahar, 2008; Devipriya and Yesodharan, 2010; Etim *et al.*, 2015) and biodegradation (Agarry and Solomon, 2008; Agarry *et al.*, 2009).

The present research shows systematic laboratory investigations of the removal of phenol from aqueous solutions using chitosan prepared from *Crassostrea gigas* (sea oyster) shells as adsorbent and TiO<sub>2</sub> (as catalyst). The main objective of this research is to investigate the efficiency of phenol degradation from wastewater by applying photocatalysis and adsorption processes.

## 2. Experimental

The various chemicals used for analysis were sourced within Nigeria. Phenol was obtained from Med-lab Scientific Enterprise, Port Harcourt with molecular weight 94.11 and 99.5 % purity. Wastewaters of different concentrations of phenol were synthetically prepared (in mg/l) using distilled water. Minimum assay of 98 % TiO<sub>2</sub> and 96.096 % NaOH was used. The chitosan used was prepared from the Oyster exoskeleton shell. All other chemicals were of Analar grade and all weighing were done with Mettler P 1210 digital analytical balance.

### **2.1. Oyster shell preparation**

Oysters of commercial size measuring 14–17 cm in length was purchased from a local supplier. The shell was scrubbed under running water to remove fouling organisms, mud and other debris adhering to the shell and allowed to drain and subsequently dried under the sun. All experimental oysters and controls were processed within 36 hours of harvesting.

### **2.2. Extraction of chitin and chitosan**

Chitosan was prepared from oyster waste (shell). To obtain a uniform size product, the dried shell was ground into coarse particles using a centrifugal grinding mill. Dried ground shell was placed in opaque plastic bottles and stored at ambient temperature until used. The dried oyster shell (1 g) was demineralized with 10 percent hydrochloric acid at ambient temperature with a solid-to- solvent ratio of 1:10 (w/v), in an acid resistant vessel and stirred for 22 hours. This was to help remove the calcium carbonate.

The demineralized shells were deproteinized with 10 % sodium hydroxide solution for 24 hours at 70°C at a solid to solvent ratio of 1:15 (w/v) to remove acetylic groupings. This enables the shells to dissolve during preparation forming chitosan. The chitosan was washed with tap water and decolorized with acetone, dried under vacuum for 2-3 hours until the powder was crispy. The chemical reactions were carried out at ambient temperature. In this study, TiO<sub>2</sub> was supported on chitosan using a modified procedure in which 25 g of TiO<sub>2</sub> was mixed with a solution of 5 g of chitosan dissolved in 100 ml of 3 % acetic acid. The mixture was then introduced dropwise into a 1 M solution of NaOH. Finally they were crosslinked using a 2.5 % glutaraldehyde solution for 24 hours. The resultant Chitosan-TiO<sub>2</sub> photocatalyst (CTP) were then stored under de-ionized water until use (Akach *et al.*, 2012).

### **2.3. Photocatalysis experiment**

For photocatalysis experiment, phenol solutions of different concentration (50, 75, 100, and 150 mg/l) were treated with known weight of chitosan adsorbents. All experiments were carried out using 150 ml conical flask to ensure maximum penetration of solar UV rays (Malato, 2009). The adsorbent with different TiO<sub>2</sub> 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 to 15:00 hours for a period of 5 days at ambient temperature (27±1 °C).

After illumination for the specified period, the suspension was centrifuged and the supernatant was analyzed for its phenol content by spectrophotometric techniques (APHA, 2005) using Varian UV-VIS spectrophotometer at a wavelength of 270 nm, and the amount of phenol degraded in (percent) was calculated using the equation (Omar, 2012):

$$\text{Percentage degradation} = \frac{C_i - C_f}{C_i} \times 100 \quad 1$$

where C<sub>i</sub> is the initial concentration before degradation and C<sub>f</sub> is the concentration after degradation.

### **2.4. Photolysis experiments**

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.

### **2.5. 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.

## **3. Results and Discussion**

### **3.1. Effect of phenol concentration on the degradation of phenol**

Series of photocatalysis, adsorption and photolysis experiments were carried out at various concentrations of phenol (50, 75, 100 and 150 mg/l) in order to investigate the effect of phenol concentration on the degradation of phenol.

Figure 1 shows the variation of amount of phenol degraded with contact time for solution containing 50 mg/l of

phenol. It is observed that the degradation of phenol was at maximum using photocatalysis experiment as compared to photolysis and adsorption. Similar trend (not shown) was also observed for solutions containing 75, 100 and 150 mg/l of phenol. This observation is similar to result obtained by Rahmani *et al.* (2008), and the trend is due to the present of more hydroxyl radicals from illumination of sun rays and catalyst.

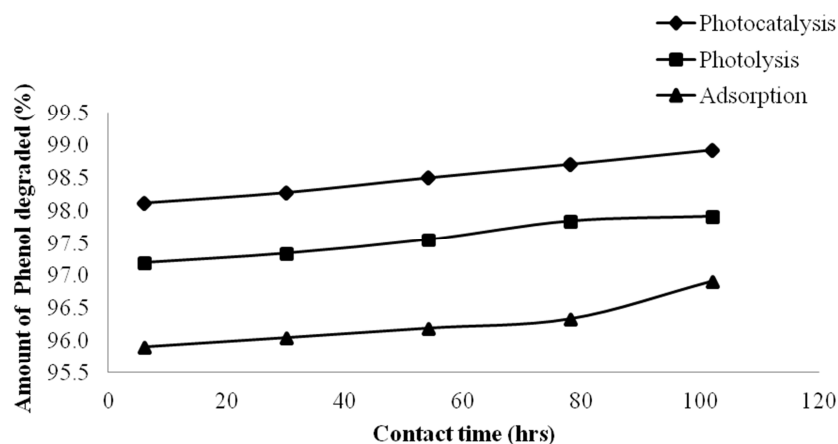


Figure 1. Variation of amount of phenol degraded with contact time for solution containing 50 mg/l of phenol

### 3.2. Effect of composite mass on the degradation of phenol

In order to investigate the effect of adsorbent mass on the removal of phenol, a series of photocatalytic experiments were carried out with different adsorbent masses (1, 3, 5 and 8 g) and at initial phenol concentration (50, 75, 100 and 150 mg/l).

Figure 2 shows the variation of amount of phenol degraded (%) with contact time for solution containing different concentration of phenol using 1 g of the chitosan prepared from *Crassostrea gigas*. It was observed that percentage removal of phenol was at maximum at initial phenol concentration of using 50 mg/l while at 150 mg/l concentration of phenol, the degradation rate decreased. This can be attributed to decrease in adsorbent surface area and of less adsorption sites. Similar trend was also observed when other masses of the adsorbent were used. This observation is similar to that reported by Akach *et al.* (2012). Figure 3 show the summary of different composite masses (1, 3, 5 and 8 g) with initial phenol concentrations (50, 75, 100, and 150 mg/l). It was observed that the effective degradation of phenol occurred with 1 g of composite mass. Increase in mass of adsorbent with time shows reduction in the rate of degradation.

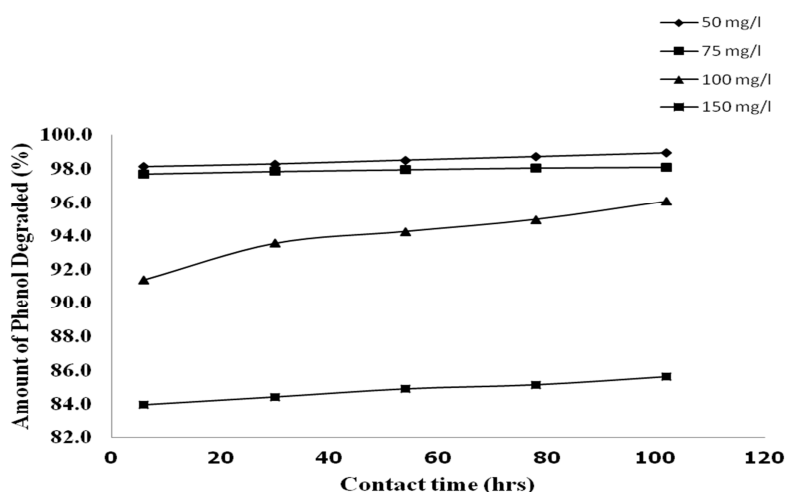


Figure 2. Variation of amount of phenol degraded with contact time for solution containing different concentration of phenol using 1 g of composite mass

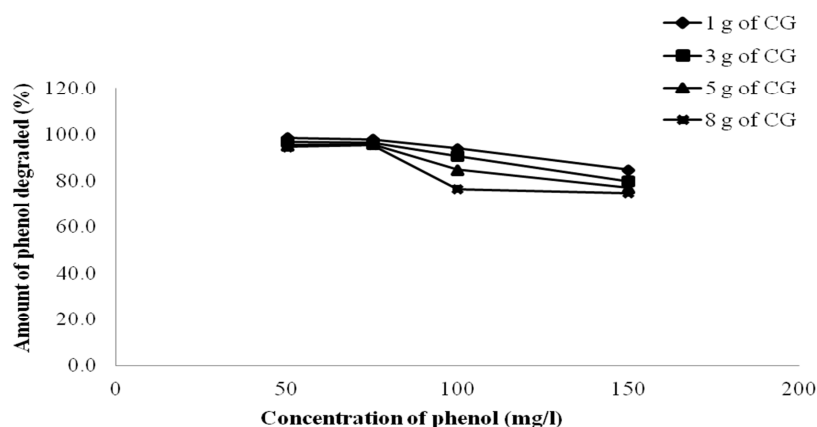


Figure 3. Variation of amount of phenol degraded with initial concentration of phenol for different composite mass

### 3.3. Effect of $TiO_2$ loading on the degradation of phenol

Removal efficiency of phenol was carried out using 1 g of chitosan at different percent of  $TiO_2$  loading (4, 8, 16 and 20 %). The results indicate that the percentage degradation increase with increase in the concentration of the catalyst as shown in Figure 4. 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 well with those previously reported in the literature (Wu *et al.*, 2008; Pinki *et al.*, 2008; Anju *et al.*, 2012; Etim *et al.*, 2015).

### 3.4. Effect of time on the degradation of phenol

Contact time is an important parameter to determine the equilibrium time of adsorption process (Kilic *et al.*, 2011). The characteristics of adsorbents and its available sites can influence the time needed to reach equilibrium. From experimental results showing the contact time duration (6, 30, 54 and 102 hours), it is evident that the degradation of phenol increase with increasing period of contact. Large amounts of phenol were degraded at 102 hours and the equilibrium was attained in the fifth day.

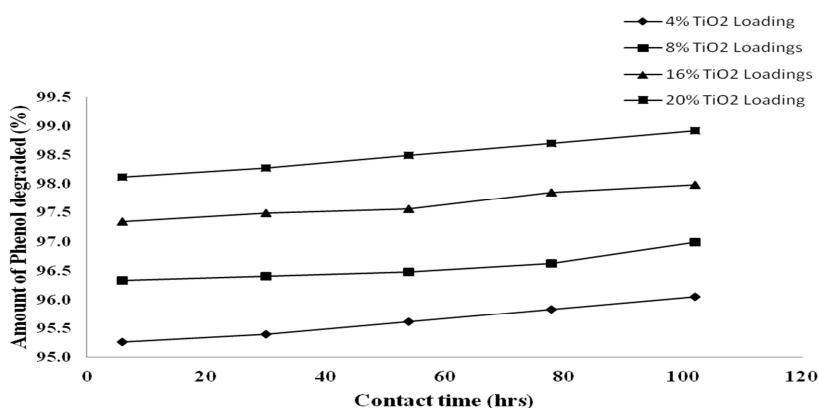


Figure 4. Removal efficiency of phenol with time for different percent of  $TiO_2$  loading

### 3.5. Kinetics

The experimental data were analysed for its fitness to adsorption isotherms and the Pseudo-second-order kinetic model. It was observed that the adsorption process obeys Langmuir isotherm model (Jain and Shalini, 2006; Chengwen *et al.*, 2014) for photocatalysis and adsorption experiments as shown in Figures 5 and 6. The values of the adsorption parameters ( $Q_0$  and  $b$ ) determined from the intercept and slope of the linear plots are given in Table 1.

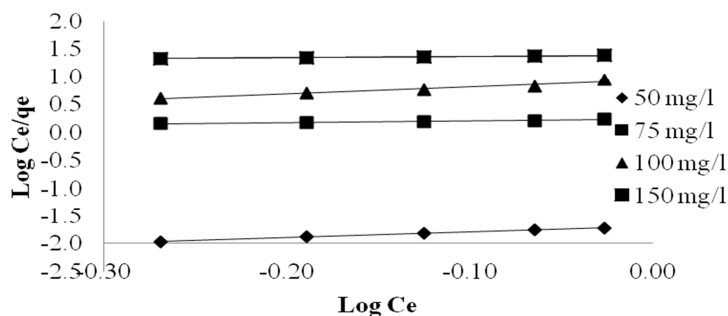


Figure 5. Langmuir isotherm for the degradation of phenol (photocatalysis experiments)

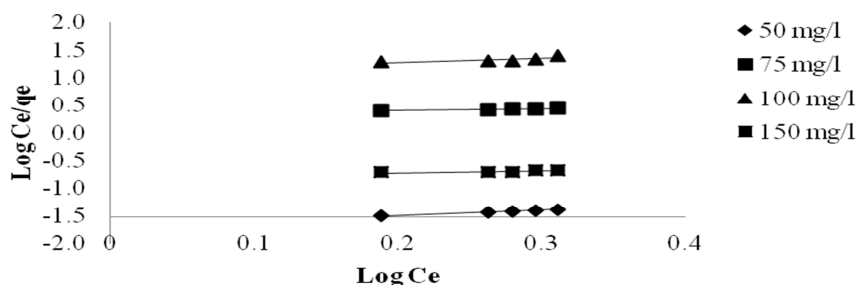


Figure 6. Langmuir isotherm for the degradation of phenol (adsorption experiments)

Table 1. Parameters for Langmuir isotherm for phenol degradation

Concentration (mg/l)	Photocatalysis			Adsorption		
	R <sup>2</sup>	b	q <sub>0</sub>	R <sup>2</sup>	b	q <sub>0</sub>
50	1.000	1.000	1.699	1.000	1.002	1.699
75	0.929	0.314	0.234	0.798	0.267	0.345
100	0.948	1.261	0.930	0.657	0.762	1.119
150	0.969	0.187	1.382	0.643	0.345	0.787

Figure 7 (for photocatalysis) and Figure 8 (for adsorption process) show adherence to the Pseudo-second-order kinetic model using photocatalysis process. The pseudo-second-order kinetic model can be written in the linear form:

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

where  $k_2$  is the adsorption rate constant of pseudo-second-order kinetic model,  $q_t$  is adsorption uptake at time  $t$ . This suggests that phenol degradation on the adsorbent appeared to be controlled by a chemisorptions process (Chengwen *et al.*, 2014).

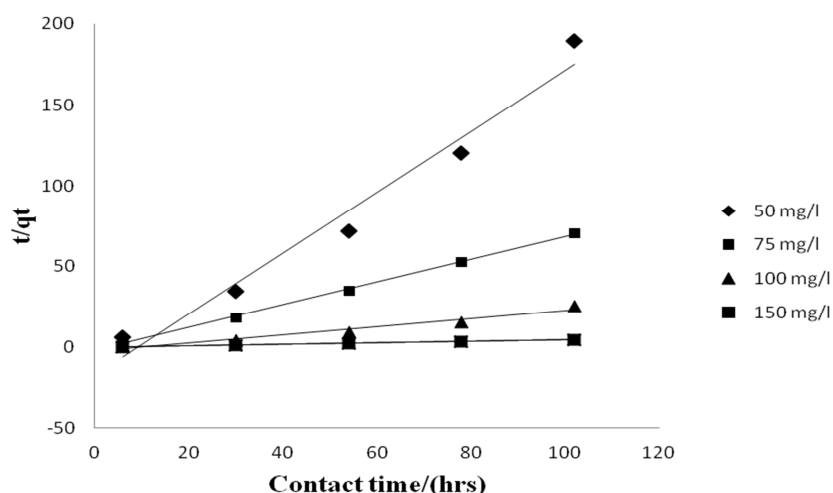


Figure 7. Pseudo-second-order plot for the degradation of phenol using photocatalysis process

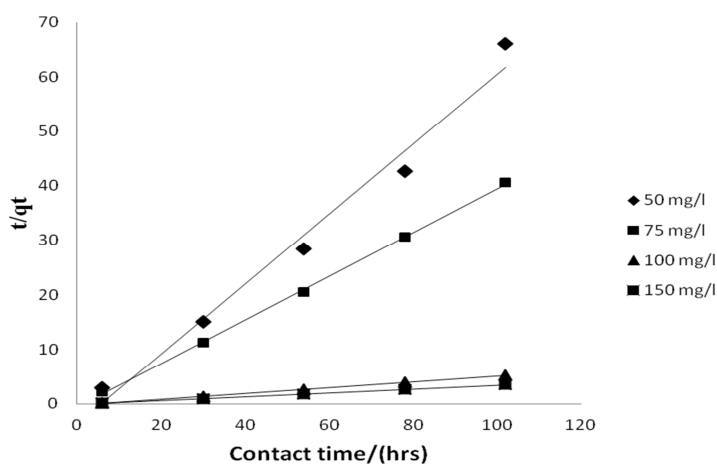


Figure 8. Pseudo-second-order plot for the degradation of phenol using adsorption process

## Conclusions

The treatment of waste water by photocatalysis, photolysis and adsorption processes is an important topic of environmental research and a versatile technique for pollutant degradation. From the results obtained, the following conclusions can be deduced.

- i) The degradation process for phenol in aqueous system follows the trend, photocatalysis > photolysis > adsorption. The highest degradation was obtained using 1 g of the composite photocatalyst with a TiO<sub>2</sub> loading of 20 %.
- ii) The degradation of phenol is dependent on the initial phenol concentration, contact time, TiO<sub>2</sub> loading and composite mass.
- iii) Kinetic studies using Langmuir isotherm and pseudo-second-order model fitted well with the experimental data.

## References

Achak, M., Hafidi, A., Ouazzani, N., Sayadi, S. & Mandi, L. (2008), "Low-cost Biosorbent "Banana Peel" for the Removal of Phenolic Compounds from Olive Mill Waste Water: Kinetic and Equilibrium Studies", *Journal of Hazard Materials*, 166, 117 – 125.

Agarry, S. E. & Solomon, B.O. (2008), "Inhibition Kinetics of Phenol Degradation by *Pseudomonas Aeruginosa* from Continuous Culture and Washout Data", *Bioremediation Journal*, 12(1), 12 – 20.

Agarry, S. E., Audu, T.O. & Solomon, B.O. (2009), "Substrate Inhibition Kinetics of Phenol Degradation by *Pseudomonas* Fluorescence from Steady State and Washout Data", *International Journal of Environmental Science Technology*, 6(3), 443 – 450.

Akach, J., Onyango, M.S. & Ochieng, A. (2012), "Solar Photocatalytic Degradation of Biorecalcitrant Wastes", *Applied Catalysis B: Environmental*, 12: 1- 4.

Ahmaruzzaman M. (2008), "Adsorption of Phenolic Compounds on Low-cost Adsorbents: a Review", *Colloid Interface Science*, 143, 48-67.

American Public Health Association (APHA) (2005), "Standard Methods for Examination of Water and Wastewater" 21<sup>st</sup> Edition, Washington DC, APHA.

Anju, S.G., Jyothi K.P., Sindhu, J., Suguna, Y. & Yesodharan, E.P. (2012), "Ultrasound Assisted Semiconductor Mediated Catalytic Degradation of Organic Pollutants in Water: Comparative Efficacy of ZnO, TiO<sub>2</sub> and ZnO-TiO<sub>2</sub>", *Research Journal of Recent Sciences*, 1, 191-201.

Annadurai, A., Ling, L. Y. & Lee, J. F. (2007), "Biodegradation of Phenol by *Pseudomonas pictorum* on Immobilized with Chitin", *African Journal of Biotechnology*, 6(3), 296 - 303.

Babuponnusami, A. & Muthukumar, K. (2011), "Degradation of Phenol in Aqueous Solution by Fenton, Sono-fenton and Sono-photo Fenton Methods", *Clean-Soil, Air, Water*, 39, 142-147.

Barni, B., Cavicchioli, A., Riva, E., Zanoni, L., Bignoli, F. & Castellano, L. (1992), "Pilot Plant – Scale Photodegradation of Phenol in Aqueous Solution by Photocatalytic Membranes Immobilizing Titanium Dioxide", *Chemosphere*, 30, 1861 – 1874.

Chengwen, S., Shuaihua, W., Murong C., Ping, T., Mihua, S & Guangrui, G. (2014), "Adsorption Studies of Coconut Shell Carbons Prepared by KOH Activation For Removal of Lead (II) from Aqueous Solutions", *Sustainability*, 6, 86-98.

Devipriya, S.P. & Yesodharan, S. (2010), "Photo Catalytic Degradation of Phenol in Water using TiO<sub>2</sub> and ZnO", *Journal of Environmental Biology*, 31, 247-249.

Etim, I. N., Okafor, P. C., Etiuma, R. A. & Obadimu, C. O. (2015), "Solar Photocatalytic Degradation of Phenol Using *Cocos nucifera* (Coconut) Shells as Adsorbent", *Journal of Chemistry and Biochemistry*, 3(1), 01-24

Jain, R & Shalini, S. (2006), "Photocatalytic and Adsorption Studies on the Removal of Dye Congo red from Wastewater", *International Journal of Environmental and Pollution*. 27, 1-3.

Jian- Mei L., Xiang- Guang, M., Chang-Wei, H & Juan, D. (2009), "Adsorption of Phenol, p-chlorophenol and p-nitrophenol onto Functional Chitosan", *Bioresource Technology*, 100, 1168-1173.

Kilic M, Apaydin-Varol, E. & Putin A E. (2011), "Adsorptive Removal of Phenol from Aqueous Solutions on Activated Carbon Prepared from Tobacco Residues: Equilibrium, Kinetics and Thermodynamics", *Journal of Hazardous Materials*, 189, 397-403.

Laoufi, N.A., Tassalit, D. & Bentahar, F. (2008), "The Degradation of Phenol in Water Solution by TiO<sub>2</sub> Photocatalysis in a Helical Reactor", *Global Nest Journal*, 10, 404 - 419.

Mahadewswamy, M., Mall, I.D., Prasad, B. & Mishra, I.M. (1997), "Removal of Phenol by Adsorption on Coal Fly Ash and Activated Carbon", *Pollution Resource*, 16, 107-175.

Malato, S (2009), "Decontamination and Disinfection of Water by Solar Photocatalysis", *Catalysis Today*, 147,

1-4.

Mohd, A.T., Hameed, B.H. & Ahmad, A.L. (2009), "Batch Adsorption of Phenol onto Physiochemical-activated Coconut Shell", *Journal Hazard Materials*, 161, 1522 – 1529.

Okasha, A.Y. & Ibrahim, G.H. (2010), "Phenol Removal from Aqueous Systems by Sorption of using some Local Waste Materials", *EJEAF Che*, 9(4), 796-807.

Omar, H. A. (2012), "Adsorptive Removal of Phenol from Aqueous Solution using Natural and Immobilized Chitin by Dithiazone". *New York Science Journal*, 5(8), 47- 48.

Parida, K.M. & Prahan, A.C. (2010), "Fe/Meso-Al<sub>2</sub>O<sub>3</sub>: An Efficient Photo-fenton Catalyst for the Adsorptive Degradation of Phenol", *Industrial and Engineering Chemical Resource*, 49, 8310-8318.

Pinki, B. P., Rakshit, A., Anil, K & Madhu, J. (2008), "Visible Light Induced Photocatalytic Degradation of some Xanthene Dyes using Immobilized Anthracene", *Bulletin of Chemical Society of Ethiopia*, 22(3), 361-368.

Rahmani, A.R., Samadi, M.T & Enayati, M. (2008), "Investigation of Photocatalytic Degradation of Phenol by UV/TiO<sub>2</sub> Process in Aquatic Solutions", *Journal of Resource Health Science*, 8 (2), 55-60.

Segura, Y., Molina, R., Martinez, F. & Melero, J.A. (2009), "Integrated Heterogeneous Sonophotofenton Procedure for the Degradation of Phenolic Aqueous Solution", *Ultrasonic Sonochemistry*, 16, 417-424.

Uddin, M .T, Islam, M S & Abedin, M. Z. (2007), "Adsorption of Phenol from Aqueous Solution by Water Hyacinth Ash", *Journal Engineering and Applied Science*, 2(2), 11-15.

Vinu, R., & Madras, G. (2010), "Environmental Remediation by Photocatalysis", *Journal of the Indian Institute of Science*, 90, 2-6.

Wu, R., Chen, C., Chen, M. & Lu, C. (2008), "Titanium Dioxide-mediated Heterogeneous Photocatalytic Degradation of Terbufos: Parameter Study and Reaction Pathways", *Journal of hazardous materials*, 162, 945-953.

Yamasaki, H., Makihatal, Y. & Fukunaga, K (2008), "Preparation of Crosslinked  $\beta$ -cyclodextrin Polymer Beads and their Application as a Sorbent for Removal of Phenol from Wastewater", *Journal Chemistry Technology Biotechnology*, 83, 991-997.

Zhao, G.H., Li, Y.F., Liu, X.X. & Liu, X.L. (2010), "Preparation of Capsules Containing 1- nonanol for Rapidly Removing High Concentration Phenol from Aqueous Solution", *Journal Hazard Material*, 175, 715 – 725.