Microwave Assisted Facile Synthesis of Zinc-Oxide-Activated Carbon Nanocomposite for Photo-Fenton Degradation of Phenol

Zainab Eniola Ojoro

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Approval of the Institute of Graduate Studies and Research

_____
Prof. Dr. Serhan Çiftçioğlu
Acting Director

I certify that this thesis satisfies the requirements as a thesis for the degree of Master of Science in Chemistry

_____
Assoc. Prof. Dr. Mustafa Halılsoy
Chair, Department of Chemistry

We certify that we have read this thesis and that in our opinion it is fully adequate in scope and quality as a thesis for degree of Master of Science in Chemistry.

_____   _____
Asst. Prof. Dr.Ozan Hayrettin Gülcan   Assoc. Prof. Dr. Mustafa Gazi
Co-Supervisor   Supervisor

Examining Committee
_____

1. Prof. Dr. Fethi Şahin   _____
2. Prof. Dr. Osman Yılmaz   _____
3. Assoc. Prof. Dr. Mustafa Gazi   _____
4. Asst. Prof. Dr. Ozan Hayrettin Gülcan   _____
5. Asst. Prof. Dr. Imge Kunter   _____

ABSTRACT

This work describes simultaneous removal of phenol and photocatalytic experiment to degrade phenol from aqueous solution. Microwave assisted facile synthesis of ZnO-activated carbon nanocomposite for phenol removal employs the use of activated carbon synthesized from waste palm seeds in an easily achievable, cheap and fast method to degrade and remove phenol by depositing ZnO on the activated carbon to produce a rich nanocomposite of Ac-ZnO for subsequent adsorption of phenol onto the activated carbon's surface, followed by photocatalytic degradation of phenol.

Further characterization of the nanocomposite produced was achieved using FTIR, pH point of zero charge and SEM analysis. The following studies were optimized; effect of pH, concentration, adsorbent dosage, effect of contact time and photocatalytic experiment. Based on this experiment, phenol adsorption followed kinetics of the pseudo-first order , maximum phenol adsorption of 39.62mg/g, was recorded at pH 5.0, 0.2g of adsorbent, 400mg/L of phenol under sunlight, this shows an improvement in catalytic activity of phenol aided by sunlight irradiation and introduction of $^\bullet$OH radicals gotten from of H_2O_2 to oxidize and degrade phenol.

Keywords: Activated Carbon, adsorption, Palm seeds, photocatalysis, phenol.

ÖZ

Bu çalışma, sulu bir çözeltiden fenolün giderimi ile aynı anda fotokatalitik yöntemle fenolün parçalanmasını tanımlamaktadır. Mikrodalga destekli olarak ZnO-Aktif karbon nanokompozitik olaylıkla sentezlenerek fenol gideriminde kullanılmıştır. Atık palmiye tohumundan elde edilmiş aktif karbonun ZnO ile zenginleştirilmiş nanokompoziti olan Ac-ZnO, sırasıyla aktif karbon yüzeyinde adsorpsiyon ardından fotokatalitik parçalanma ile fenolü kolay, ucuz ve hızlı bir yöntemle giderimiştir.

FTIR, pH noktası Zero Charge ve SEM analizleri kullanılarak üretilen nanokompozitin ileri karakterizasyonu elde edilmiştir. Aşağıdaki çalışmalar optimize edilmiştir; pH, konsantrasyon, adsorban dozajı, temas süresi ve fotokatalitik deney etkisi etkisi.Bu deneye göre, fenol adsorpsiyonun yalancı birinci mertebe kinetiğine uymaktadır ve 400 mg/L fenole karşın pH 5.0 da 0.2 g adsorbent, güneşışığıaltında H_2O_2 oksidasyonu ile oluşan ·OH radikallerinin fenolü parçalama etkisiyle 39.62 mg/g değerindeki maksimum fenol adsorpsiyonuna ulaşmıştır.

Anahtar Kelimeler: Aktif Karbon, adsorpsiyon, Palmiye tohumu, fotokataliz, fenol.

DEDICATION

This thesis is dedicated to my Family, most especially my precious mum, Mrs. Fausat Oluwatoyin Ojoro who is the pillar that held me throughout my study, to my dad, Mr. Fatai Omotolani Ojoro and elder brother Abdul Azeez Olaseni Ojoro. To my Darling Grandma Alhaja Lawal , my aunt Alhaja A.B Malik, my cousin Dr. Ridwan Lawal, my Teachers, Dr Onwordi, Dr Raimi and Dr Sobola thank you and God bless you for your moral, spiritual and financial support, I also would like to appreciate the best African Researcher I have ever met, Dr Akeem Oladipo who contributed largely to the success of this thesis, God bless you abundantly sir, to my supervisor, Assoc Prof Mustafa Gazi, and co-supervisor, Asst. Professor Ozan Hayrettin Gulcan, God bless and reward you in folds, you are the best. To all my friends especially Kawla Azalok and Halimat Balogun, Vitus and Valentine, Colllins Ogbole, Martins, Kayode, Sadiq, Habib, Nkechi, Abiola and Adeola Adebowale, Dr Biliamin Adeshina, Muftiat Banks Adeshina, God bless you all.

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ZnO-AC   Zinc oxide activated carbon

ZnO   Zinc oxide

AC   Activate carbon

Chapter 1

INTRODUCTION

Efflux of untreated water from the industrial based effluents leads to contamination of underground water due to the release of high amount of toxic compounds (Rajiv et al. 2010).Various industries like the pharmaceutical industries, chemical industries, university laboratories and domestic activities are potential sources of wastewater. These wastewater generated needs to be treated properly before they are released into the environment. Untreated or improperly treated wastewater can cause detrimental effects to the living things.

Wastewater can be categorised based on (1) includes storm water, domestic wastewater, wastewater from research laboratories, leachate, and wastewater from sewage (Henze et al. 2008); (2) application includes from treatment plant-water used to clean equipment (Henze et al. 2008).

1.1 Uses of Phenol

Phenols are valuable starting material for pharmaceutical and chemical, industrial based processes. They are used in the production of drugs, paints, adhesives, cosmetics and resins. Phenol belongs to aromatic organic compounds. It exists as a partially acidic compound with a pKa of 9.95 in water. Phenol is very similar to the alcohol family because it possesses hydroxyl groups. The only distinguishing factor is that the hydroxyl groups present on phenol ring is attached to an aromatic hydrocarbon, unlike the saturated alcohol hydroxyl group which is attached to a

saturated hydrocarbon. As a result of this and resonance in the aromatic ring of benzene, phenol tends to be more acidic than alcohol (Michael and Jerry 2007).
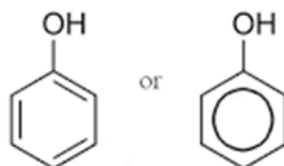
Figure 1: Structure of Phenol with chemical formula C_6H_5OH

Phenol has a reasonable solubility in water with the possibility of forming a miscible clearly dissolved solution of ratio 2.6 by mass (Oskaya et al. 2006). The table below shows the various concentrations of phenol in wastewater from different industrial operation processes (Oskaya et al. 2006).

Table 1: Various concentrations of Phenol from different wastewater

Source of Wastewater	Phenol concentration in mg/L
Coking operations	28 - 3900
Petrochemical Industries	2.8 - 1220
Refineries	6 - 500
Coal Processing Industries	9 - 6800

Phenol occurs naturally in normal excretion of human urine with a reference value of 40 mg/mL (Rehfuss and Urban 2006). It can be degraded by bacteria called *Rhodococcus phenolicus*. At very low concentration phenol can cause extremely high toxicity to humans and other organism and at extremely high concentration it could be carcinogenic and lethal (Oskaya et al. 2006). Also, phenol and its derivatives can wipe out the aquatic organisms at concentrations greater than 5-25 mg/L (Jiang et al. 2002), as well as cause obnoxious taste and poor organoleptic qualities to potable

water at a concentration of about 0.5 mg/L (Jiang et al. 2002). Therefore 0.0005 mg/L of phenol or values lower than this is the maximum tolerable limit of phenol in drinking water. Consequently phenol needs to be eradicated before it is released into water bodies.

1.2 Treatment Methods

The various treatment methods for phenol cannot be overemphasized. Here is an outline of the different types of possible methods that have been applied to eradicate phenol from wastewater.

Table 2: Showing different treatment methods for wastewater

Treatment Methods	References
Electrochemical Oxidation	Jiang et al.(2002), Kujawski et al.(2004), Giraldo et al. (2014)
Ion exchange resin	Jiang et al.(2002), Kujawski et al.(2004), Giraldo et al. (2014)
Ozonation Process	Jiang et al.(2002), Kujawski et al.(2004), Giraldo et al. (2014)
Solvent extraction process	Jiang et al.(2002), Kujawski et al.(2004), Giraldo et al. (2014)
Microbial reduction	Kujawski et al.(2004)
Thermal decomposition	Atieh,(2014)
Adsorption	Kujawski et al.(2004), Giraldo et al. (2014)
Membrane separation	Kujawski et al.(2004)

1.2.1 Thermal decomposition method

Thermal decomposition can effectively treat about 15000 mg/L of phenol contaminated wastewater. As the name portrays, it requires heat as a source of energy for effective treatment to be carried out. Its major disadvantage is that large input of energy is required of up to 300 ºC and also pressure of around 20 M Pa (Atieh et al. 2014). Also, this method is only limited or available for small scale use, consequently, its limitation is that it cannot be applied to treat phenol-contaminated wastewater on a large basis. It is expensive and also not an effective method Kujawski et al. (2004), Giraldo et al. (2014).

1.2.2 Liquid-Liquid Extraction Process

This process is one of the appropriate and adequate ways of treating phenol in wastewater. However, the cost of carrying out this process is extremely high (Atieh et al. 2014). Although, this method can be successfully used to treat phenol concentrations above 300 mg/L in wastewater, it has some shortcomings and the most worrisome one is that during the course of the treatment, the metallic treatment tank can corrode as a result of complex reactions between various types of dissolved acids and salts in solution and the steel tank for example, thereby complicating the whole treatment process.

1.2.3 Treatment by use of Bacteria (Microbial Treatment)

This employs the use of microorganisms, particularly bacteria to mop up the phenol from wastewater. However, the disadvantages are too unpleasant, bacteria cannot withstand high concentrations of phenol, as a result, it may be limited to treatment of wastewater with just low-concentration of phenol or any other contaminant. (Atieh et al. 2014). Further, in wastewater, different types of salts and acids are in the

dissolved state,therefore the bacteria generation might be wiped out before the treatment is completed; therefore, this method is regarded as insufficient.

The above listed methods for treatment of phenol in wastewater have most common disadvantages of either being too expensive or not being efficient enough to eradicate phenol, therefore it is worthwhile to consider a method that will avert both the extremely high cost as well as have more effectiveness in wiping off phenol from wastewater.

1.2.4 Adsorption method

Adsorption is an established and standardized technique used to remove contaminants in wastewater. Some of the materials used in the process of adsorption include fly ash, for example. Alinnor and Nwachukwu (2012) studied the removal of phenol with fly-ash. They revealed that citric acid modified fly-ash had better adsorption properties, and phenol uptake was maximum at higher pH and low temperatures.

Activated carbon is the most common and effective of all these materials. Commercially produced activated carbon is also a very expensive material, however, the past few years have seen various researchers in the world produce activated carbon from either cheap raw materials or even waste materials that are thought to have no significant economic value. Some of the raw materials that have been used to prepare activated carbon include sawdust, date fruit, date seeds, oil palm leaves, seeds, and stems. Myriads of methods have been chosen to remove industrial based effluents, however majority of these methods have one or two limitation which could range from high cost of setting up to ease of carrying out these processes. Adsorption method stands out because of the ease of getting the adsorbents as well as low cost of

setting up and capital investment. Also adsorption produces high result as this method greatly reduce the concentration of the industrial based effluents, it therefore can be said to be a highly efficient method as compared with the likes of filtration, precipitation or coagulation (Rasheed 2013).

1.2.4.1 Adsorption by Activated Carbon

Activated Carbon has high degree of microporosity, 1 gram of activated carbon has surface area of $500m^{2.}$ The use of activated carbon is arguably an alternative to avert the ineffectiveness of the other methods out listed before now, though, the cost of activated carbon can be minimized if produced from waste or cheap materials.. A perfect example is the synthesis of activated carbon from different parts of the palm Trees, which presents advantages such as the presence of the naturally occurring distinct types of functional groups that can be easily modified depending on the type of application in question. The image of an activated Carbon particle is shown below;in figure 2A

Activated Carbon Particle

LARGE DISSOLVED
ORGANIC MOLECULE

SMALL DISSOLVED
ORGANIC MOLECULE

MACROPORE

MICROPORE

ACTIVATED CARBON SUBSTRATE
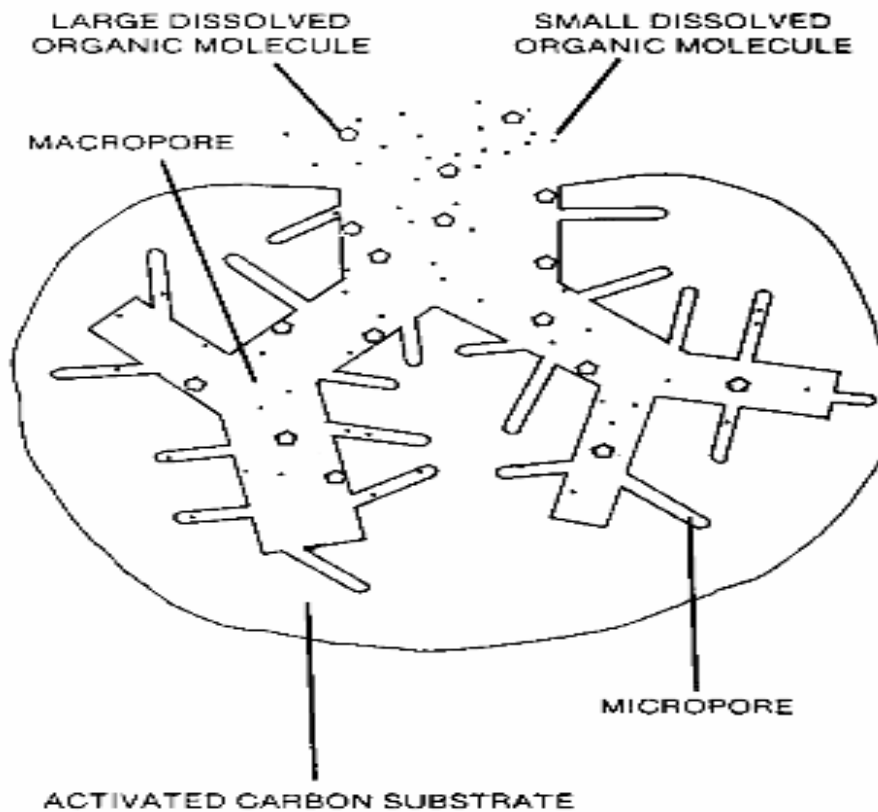
Figure 2A: Diagram of activated carbon particle

The following; H, N_2 and O_2 are bonded to the carbon surface of the activated carbon. Nitrogen in particular presents the major explanation as to why activated carbons are highly effective and complementary materials to remove phenol, because it introduces the alkaline or basic functional group, necessary to react with the slightly positive group on the organic toxins surfaces (Shaarani and Hameed . 2011).

Various research have been carried out with the use of activated carbon as adsorbent, Hameed et al. (2011) studied modification of activated carbon with ammonia, in order to increase the basicity as well as improve adsorption properties of the activated carbon on phenol.

1.2.4.2 Adsorption by Nanocomposites of ZnO-AC

Nanocomposites of ZnO-Ac have been prepared and studied for degradation of various pollutants; one of the notable works was by Chen et al. in 2010 to degrade Rhodamine B.
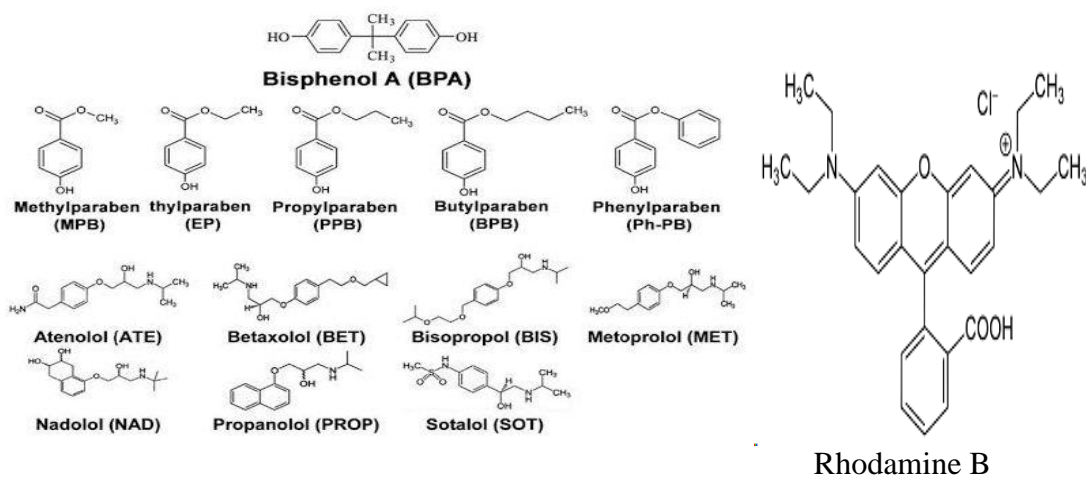
Figure 2B: Structure of different organic pollutants

They were able to degrade Rhodamine B by using this method, by a combination of thermal and micro emulsion method to generate more efficient nanocomposites for degradation of the compound. (Calvante et al. 2015) removed metoprolol using B-doped titanium dioxide, and (Mita et al. 2015) removed Bisphenol A using Pseudomonas Aeruginosa. However, most of these methods are too expensive and the temperatures are too high, also, problems are encountered such as finding suitable particle size and conditions for the appropriate use of these nanocomposites. It is also worthy to note that most of these researchers have not applied this method to degrade phenol (Chen et al. 2010).

1.2.4.3 Adsorption by Nanocomposites

Nanoparticles are materials that have diameters strictly in a range of 1-100 nanometers. They have found usefulness in modern day technology due to their

unique characteristics which includes non-toxicity, cheapness as well as ease of fabrication. There are various types of nanoparticles; including polymeric origin-nanoparticles, metallo-oxide nanoparticles amongst others however, metallo-oxide nanoparticles are considered the best as they are vast materials that are manipulalatable and have wide range of applications in nanotechnology world.

These metallo-nanoparticles include; titanium dioxide, zinc oxides, iron oxides and copper oxides. ZnO is is a multifunctional material due to its multile intrinsic properties a wide range of UV adsorption biodegradability, biocompatibility and high photostability.

ZnO nanoparticle possesses high binding energy and has one of the greatest photosensitivity.

The advantages of ZnO nanoparticle over the others is attributed to its characteristic distinct optical activity which makes it very useful in the process of adsorption of phenol as well as degradation, because it can generate a sufficient electrode potential more than the other nanoparticles, like titanium dioxide .This high electrode potential is fundamental for the treatment of the slightly positively charged phenol to take place (Meshram et al. 2011).

1.3 Objectives of the Research Work

The interest in producing a low-cost and efficient adsorbents to treat the phenolic wastewater has been a major challenge to the modern day scientist. The objective of this work is to produce efficient adsorbents for rapid removal and degradation of phenolic wastewater commonly generated from industries. Here, activated carbon was prepared from a waste material, palm seeds and its efficiency is enhanced with

freshly prepared ZnO nanoparticle via ecofriendly microwave method. This research demonstrated that facile treatment of phenolic wastewater could be achieved using nanocomposites based on activated carbon-ZnO nanoparticles.

Chapter 2

LITERATURE REVIEW

The past decade has seen different researchers dig into a quest for removal as well as degradation of phenol from wastewater. Researchers have explored different materials most especially those of plant origin, like palm parts seeds, trunks, woods, eggshells and all forms of possible low cost materials to produce adsorbent for phenol.

2.1 Phenol Removal by Different Adsorbents

Moyo et al. (2012), removed phenol from wastewater using (yeast) Saccharomyces cerevisiae solution and they gave a result of the maximum adsorption capacity of 26.95 mg/g for phenol. Juajin and Zhu (2014), researched on adsorption of phenol on nitrogen enriched activated carbon produced from wood fiber board, Kumar et al.(2007) removed phenol using activated carbon in basal salt medium, Hameed and Rahman (2008) removed phenol with activated carbon produced from Rattan saw dust, Parker et al. (2013) used starbon prepared from polysaccharides like starch to adsorb phenol, Vasquez et al.(2007) removed phenols from coke wastewater by using activated charcoal. All these methods require various activating agents such as Iron (III) chloride, hydrochloric acid, potassium carbonate, nitric acid amongst others.

Table 3: Different adsorbents and their comparable adsorption potentials

Type of Adsorbents	Q(mg/g) of phenol	Reference
Activated Charcoal	1.48	Vazquez et al. 2007
Activated Carbon (granulated)	165.80	Kumar et al. 2007
Commercial activated carbon	49.72	Ozkaya et al. 2006
Rattan saw dust	149.25	Hameed et al. 2007
Bagasse Fly Ash from Sugarcane	23.83	Srivastava 2006

The aforementioned materials used to prepare activated carbon exhibit various adsorption potential, some input of energy, cost intensive, hard to implement, highly exothermic, have tendency to form more toxic compound with phenol, or even limited to only small scale removal application of phenol.

The previous methods can be sidelined by the production of activated carbon with high adsorption properties with low-cost. We require a carbon-based material, which is reliable, accessible lignocellulosic material capable of yielding more quantity and greater quality activated carbon in order to lower the cost of treatment.

2.2 Preparation of Activated Carbon

Activated carbons are described with a distinct characteristic porous carbon structure. There are different types of activated carbon based on their textural appearance, and listed below.

Table 4: showing different types of activated carbon

ABBREVIATION	FULL NAME OF THE ACTIVATED CARBON
G.A.C	Granular activated carbon
E.A	Extruded activated carbon
P.A.C	Polymer coated activated carbon
B.LA.C	Bead-like activated carbon
I.A.C	Impregnated activated carbon

The individual methods of preparing activated carbon are; incomplete combustion of natural gas, steam activation, acid treatment, and microwave application that is used to pyrolyse the carbonaceous material.

The listed types of activated can be prepared majorly by two different ways that are broadly classified into **PHYSICAL** and **CHEMICAL METHODS**. Another school of thought classified preparation of activated carbon into two other steps that are;

[A] Carbonization also known as charring step that is carried out at high temperature and aimed at removing volatile compounds from the activated carbon being produced. This process occurs, using carbonaceous materials and is first pyrolysed at a temperature between $500-700^0$C, and this process is characterized by pore formation during the activation process- **[B]** Activation process; this process involves a complex reaction between the left over contents of the carbonization step with activating agents, so that pores are formed.

As mentioned earlier, all the methods of producing activated carbon are categorized into the physical or the chemical method

1. **Chemical activation method**; this involves the use of a chemical temperature and operates between 800-1000°C, which results in corrosion of the carbon, consequently producing pores. The common chemicals employed include H_3PO_4, $ZnCl_2$, KOH, etc. (Chen et al. 2013, Mohammed et al. 2002). After the carbon corrodes, and the chemicals are washed out properly so that they can be reused.

2. **Physical activation method**; this is also referred to as gas activation method unlike the chemical method; there is no addition of chemical before carbonization. The material is subject to carbonization directly under an inert atmospheric condition that is followed by application of either of a combination of steam, air or CO_2 to activate the char produced (Ryu et al. 2000). Here, pores are eroded into the char using gasses such as carbon dioxide.

Table 5: Different methods of preparing activated carbon

Method	Temperature	Chemicals	Pretreatment
Chemical activation This produces activated carbon with more open pore structure	➢ Operates at low temperature between 450 – 900 ^{o}C ➢ Shorter time is needed to activate the material	H_3PO_4, NaOH and $ZnCl_2$	Pretreatment is done with chemicals before carbonization
Physical/steam activation This produces activated carbon with fine pore structure.	➢ Higher temperature 600 –1200 ^{o}C	Hot gasses, air	Combination of one or two processes as described below: ➢ **Carbonization:** Involves pyrolysing the material at a temperature between 600-900°C under inert atmosphere e.g. Ar or N_2 gasses. ➢ **Activation/oxidation:**

		15	Involves Carbonization in the presence of CO_2 or steam at a temperature above $250^{\circ}C$

2.3 Surface Characteristics of Activated Carbon

Activated carbon for phenol removal must meet certain requirements. The adsorption

capacity of the activated carbon to be used for removal of aromatic compounds such

as phenol relies deeply on the factors shown in Figure 3 (Thommes et al.2011).
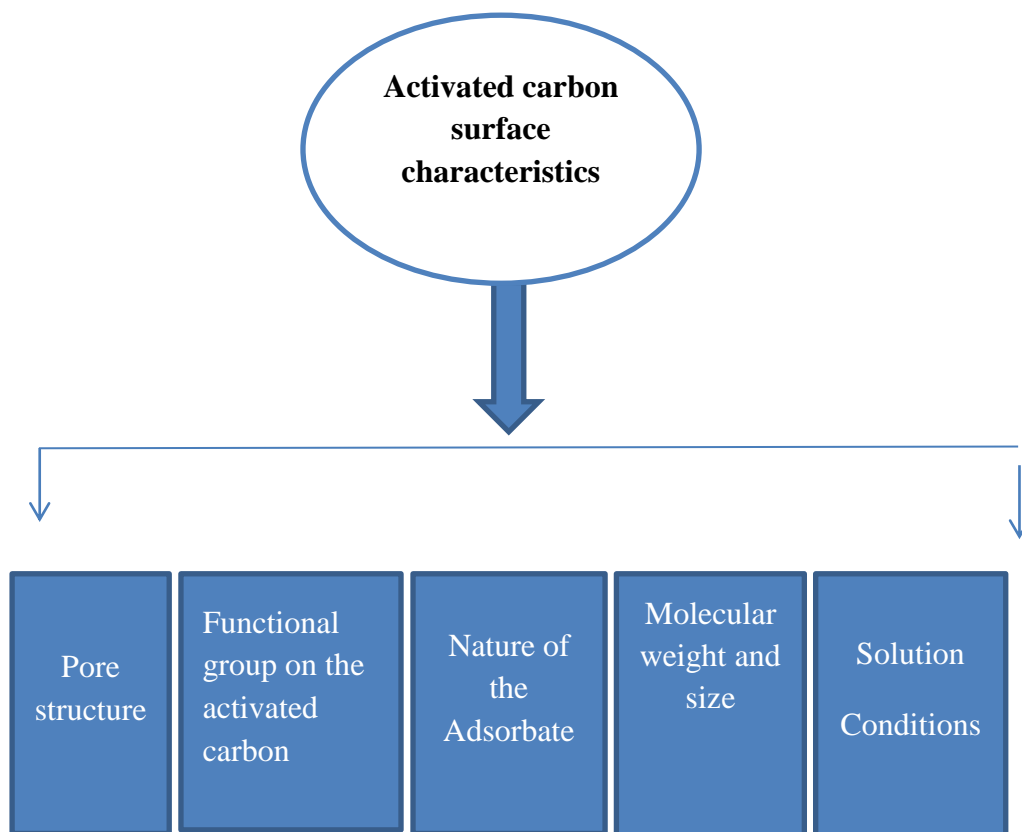
Figure 3: Factors that affects Surface Characteristics of Activated Carbon

The ideal activated carbon surface is endowed with various functional groups and these compliment the adsorption of phenol because the abundance of nitrogen on the activated carbon. The Nitrogen improves the alkalinity of the activated carbon surface and further boosts the adsorption properties of the activated carbon, which makes it a good adsorbent for removal of pollutants in wastewater bodies. As reported the reaction between activated carbon and phenol can occur; in a solution that is un-buffered at partially acidic or close to neutral state. The following reactions may occur between the phenol and activated carbon surface including; close redox interactions between the alkaline surface of O_2 and the phenol ring, ionic driven electrostatic repulsion and attraction and finally the dispersive forces between the pie electrons of the graphite backbone and the phenol structure.

Also, due to the amphoteric nature of carbon, activated carbon also exhibits on its surface the amphoteric nature of carbon, this property greatly affects phenol based on the pH of the solution in question. Phenolates are highly soluble in water, thereby posing a bigger barrier to break as there is formation of a strong bond between the adsorbate and water that is very difficult to break (Busca et al. 2008).

2.4 Adsorption of Phenol by Nanoparticles

Nanoparticles based on semiconductors work by generating electron and creating hole pairs required to degrade pollutants from aqueous media. (Seftel et al. 2014). Different nanoparticles have been employed to remove and degrade phenol, most commonly used ones are, cadmium oxide, titanium dioxide, and Zinc Oxide which. Lots of researches have used titanium dioxide however; Zinc Oxide , interest of this research has been reported to be more efficient than the more commonly used titanium dioxide due to its ability to prevent recombination of electrons or holes and the ease of use in both acidic and basic media (Chen et al. 2010).

ZnO belongs to the class of heterogeneous photocatalyst, has high oxidation capacity, non-toxic, affordable and ease of preparation (Shaari, Tan and Mohammad, 2012). Heterogeneous catalyst work by formation of OH^- in the presence of H_2O_2 or any protonating agent directly on the surface of such heterogeneous photocatalyst, the surface become oxidized to hydroxyl radicals and when an irradiation source is introduced, as a source of energy which must be at least greater than its own band gap (Shaari, Tan and Mohammad ,2012). Also, agglomeration can occur which may result in termination of the whole catalysis process especially this was noticed with titanium di- oxide in particular (Seftel et al. 2014).

Chapter 3

EXPERIMENTAL

3.1 Materials and Methodology

All materials and chemicals used were of analytical grade, no purification before use. The solutions were prepared with pure distilled water. The raw material (palm seeds) was collected from the palm trees found within the Eastern Mediterranean University campus. Reagent grade of phenol, NaOH, zinc sulfate, HCl, H_2O_2, and propanol were obtained from Sigma-Aldrich.

3.2 Pre-treatment of Palm Seeds and Preparation of Activated Carbon

Palm seeds collected were sorted and peeled to get the clean seeds. The seeds were thoroughly cleaned, grinded using a blender, and then an agate mortar to obtain a fine powder. Then the powdered seed was subjected to thermal treatment (400 ºC) using muffle furnace (Nabertherm GmbH model; L 9/11/B180 3N 217398) for 1 hour to obtain activated carbon. The prepared activated carbon was grinded and sieved to a particle size of <100μm and labeled for analysis.

3.3 Preparation of ZnO Nanopowder

A known volume of $ZnSO_4$ (0.2 M) solution was added to 20 mL of 99 percent propanol under constant stirring using (Heidolph heater/electrical stirrer, model EKT hei-Con/ Hei-ConG) for 1 h. To the above solution, 180 mL of NaOH (0.3 M) was added slowly at 70 ºC and stirred continuously for 8 h. The obtained white solid

suspension was filtered, thoroughly washed several times with distilled water and dried at 80 ºC in the conventional oven (Binder model: BD 115 EZ) for 12 h. The dried ZnO nanopowder was then calcined in a muffle furnace (Nabertherm GmbH model; L 9/11/B180 3N 217398) at 500 ºC for 1 h and stored until use.

3.4 Preparation of Ac-ZnO Nanocomposite

After preparation of the precursors, 10 g of activated carbon and 5 g of ZnO nanopowder were dispersed in distilled water and thoroughly stirred to obtain a homogenous mixture. The mixture was then transferred to a 1270 watts microwave and voltage 230V-50 Hz (Arzum model MG820CRK-PM AR 257) and irradiated for 15 min. Finally, the nanocomposite was dried at 100 ºC in the oven (Binder model: BD 115 EZ) for 8 h, and then labeled as Ac-ZnO.

3.5 Adsorption Studies

A stock solution of phenol (500 mg/L) was prepared by dissolving 0.5 g of phenol in 1 L of distilled water. Various working concentrations were prepared from the stock and used for the calibration curve as shown in Fig.4.
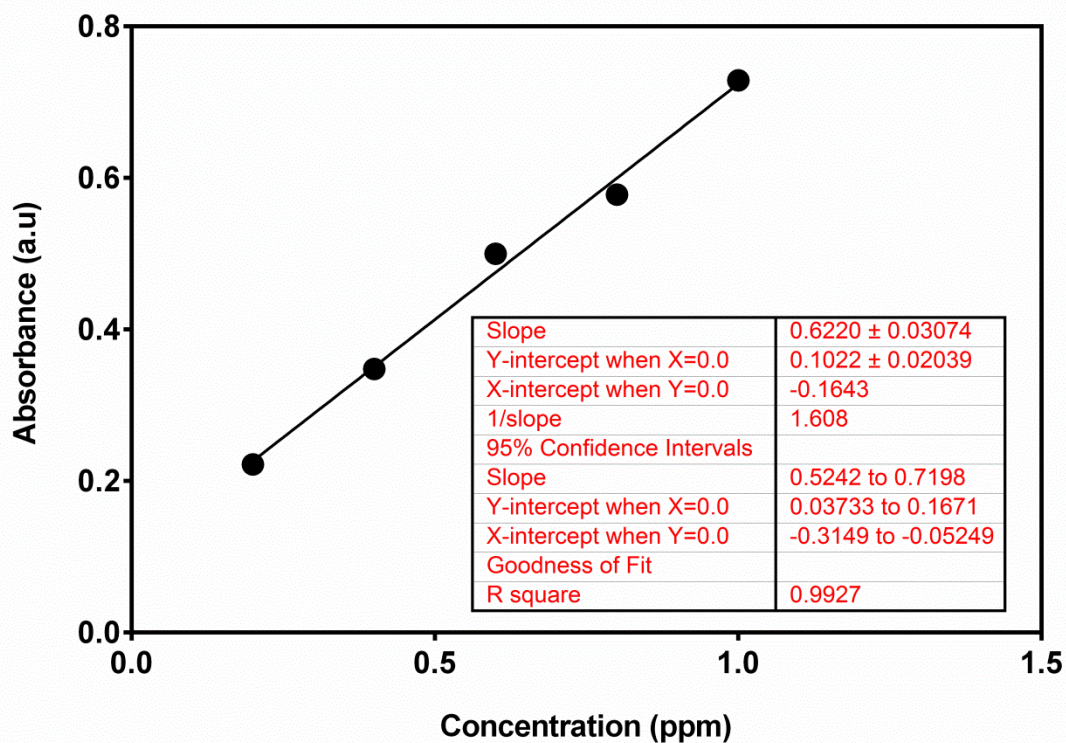
Figure 4: Calibration Curve for Phenol

3.5.1 Effect of Operation Parameters

Various operational parameters were investigated such as effect of pH (3–10), nanocomposite dosage (0.1–0.8 g), initial phenol concentration (50–400 mg/L) and solar irradiation (2–4 h). The initial solution pH was adjusted using 0.1 M Sodium Hydroxide (NaOH) or 0.1 M Hydrochloric Acid (HCl) and fresh dilutions of phenol desired concentration was prepared at the start of each experiment.

3.5.2 Batch Experiments

Adsorption studies were carried out by varying the operation parameters. Phenol solution (20 mL) of desired concentration and pH was taken into 200 mL Erlenmeyer flask and adequately weighted nanocomposite was added under constant mechanical shaker (NUVE, model SL 350) at 200 rpm. Samples were collected after a certain time, filtered and the residual concentration was analyzed using UV–vis spectrometer (UV–Win 5.0, Beijing, T80+) at 270 nm (the phenol maximum absorption

wavelength). The phenol removal percentage by Ac-ZnO nanocomposite was computed by the following equation (Oladipo et al. 2014):

$$Phenol_{R\%} = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \qquad (1)$$

The phenol uptake capacity (mg/g) was also computed using the following equation (Oladipo and Gazi 2015a):

$$q_e = \left(\frac{C_i - C_t}{m_{Ac-ZnO}} \right) \times V \qquad (2)$$

Where C_i, initial phenol concentration

C_f, final phenol concentration and

C_t, residual concentration of phenol at different time, respectively.

All the experimental runs received by Graphpad software were performed in triplicate and average values are reported within.

3.5.3 Photocatalytic Experiments

Prior experiments were performed in the laboratory so as to optimize the degradation process. Ac-ZnO nanocomposite (0.2 g) was added to 200 mg/L phenol solution in an Erlenmeyer flask under constant stirring and exposed to solar irradiation. A known concentration of H_2O_2 (5 mL) was added to the second flask in the presence of nanocomposite and phenol. The experiments were conducted for 4 h under Solar irradition and samples were collected at intervals, filtered and analyzed for residual concentration as previously mentioned.

Chapter 4

RESULTS AND DISCUSSIONS

4.1 Characterization

4.1.1 Scanning Electron Microscopy Analysis

The morphologies of the adsorbents were examined using scanning electron microscopy (SEM model: JEOL JSM-6360 LV) at a voltage of 20 kV. SEM images of AC, ZnO, and Ac-ZnO are depicted in Figure 5.
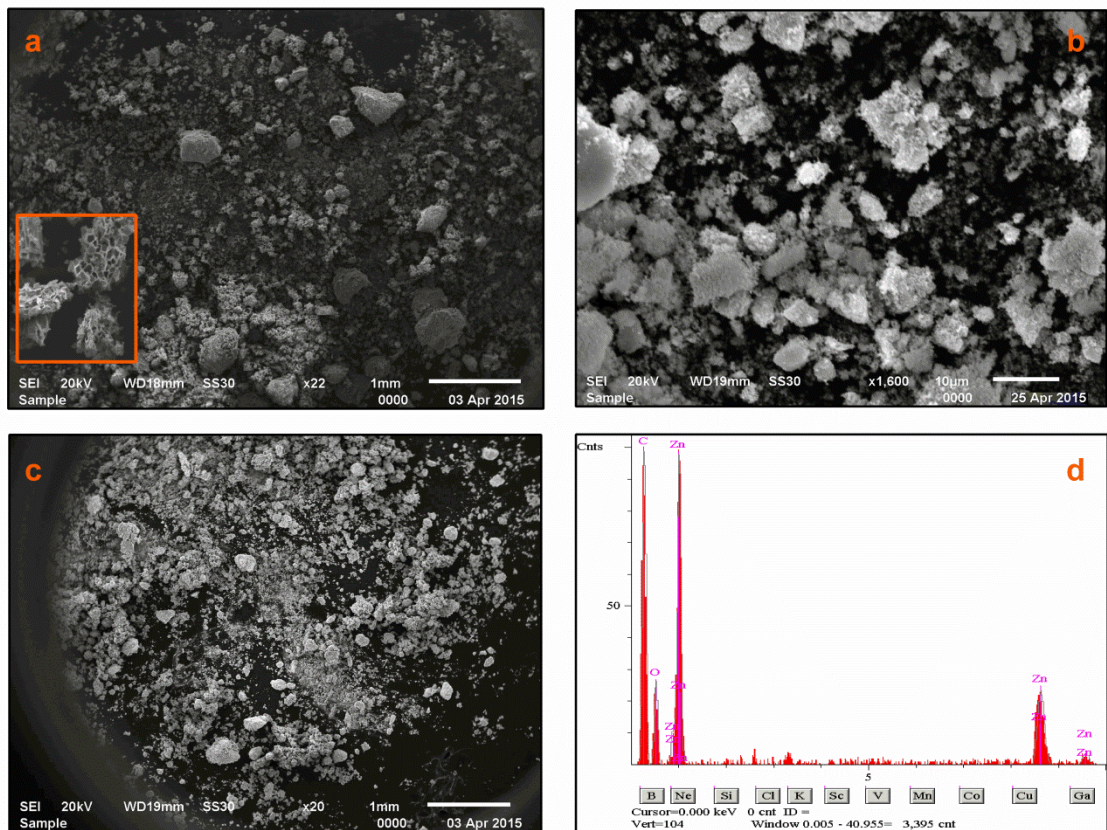

Figure 5: Scanning Electron Microscopy images of (a) AC (b) ZnO (c) AC-ZnO nanocomposite (d) EDS of AC-ZnO

As shown in Fig. 5a, the external surfaces of the prepared activated carbons have cave type openings and pores of different sizes and shapes. From the SEM analysis, the activated carbons have the available surface area for phenol adsorption. The morphology of ZnO nanopowder is shown in Fig. 5b as white crystal-like particles. It is estimated to be within 90−120 nm with irregularly shaped particles via the attachment of several smaller particles. The direct evidence of integration of ZnO nanoparticles onto the prepared activated carbon surface is shown in SEM image Fig. 5c.

Ac-ZnO nanocomposite compared with ZnO and the prepared activated carbon, showed homogenous morphology and well-dispersed ZnO nanoparticles with average particle size less than 100 nm. The energy dispersive spectrum (EDS) of Ac-ZnO in Fig. 5d clearly showed that the synthesized nanocomposite mainly composed of carbon, oxygen and zinc according to the following composition; Zn-22.57, O-12.33 and C-65.09%.

4.1.2 Optical Properties of Adsorbents

The optical characters of the Ac and Ac-ZnO nanocomposite were examined by the use of a UV−vis spectrometer (UV-Win 5.0; Beijing, China) at 300−600 nm. The obtained spectra are shown in Fig. 6. As shown in the spectrum of Ac, no notable peaks were seen within the region investigated. The observation shows that the prepared activated carbon has neither bandgap nor photocatalytic property (Oladipo and Gazi 2015a).

The synthesized ZnO nanopowder showed characteristics peak at 367 nm (3.37 eV). Meanwhile, no broad defect-related peak is observed meaning pure ZnO material was prepared.. Interestingly, a new absorption peak was found in the spectrum of Ac-

ZnO nanocomposite at 380 nm. The peak could be attributed to electron transitions (O $2p \rightarrow$ Zn $3d$) of ZnO particles (Yu et al. 2015). The appearance of new peaks in the Ac-ZnO spectrum confirms the successful integration of ZnO particles on the surface of the prepared activated carbons. The band gap of the nanocomposite (3.26 eV) was observed to be lower than that of ZnO (3.37 eV). This indicates that the nanocomposite photocatalytic efficiency is improved compared to ZnO (Alalm et al. 2014).
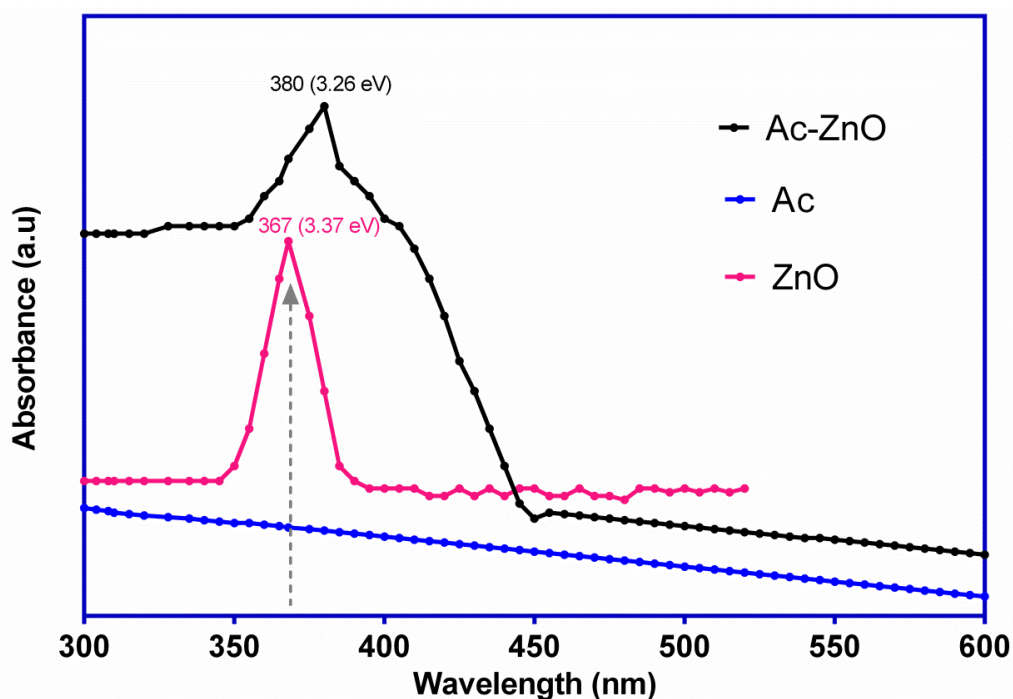
Figure 6: UV−vis spectra of AC, ZnO nanopowder and AC-ZnO nanocomposite

4.2 Surface Area Characteristics and Size Analysis of Adsorbents

The measurements of the surface areas of the adsorbents were performed using surface analyzer (Quantachrome: Nova 2200e) at 77K. The specific surface areas, pore volume and pore sizes of the adsorbents were calculated by Brunauer–Emmett–Teller (BET) method and shown in Fig.7. According to the IUPAC classification, the adsorbents are a combination of type I (microporous materials) and type II, III

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(mesoporous materials). The BET measurement indicates that the surface area of activated carbon, ZnO nanoparticles, and Ac-ZnO nanocomposite is 52.3, 523.5 and 603.5 m^2/g. The result suggests that the existence of ZnO nanoparticles on the activated carbon's surface enhanced the nanocomposite surface area (Oladipo and Gazi 2015b). However, the pore volume of the activated carbon slightly decreased from 0.016 to 0.014 cm^3/g in the presence of ZnO nanoparticles.
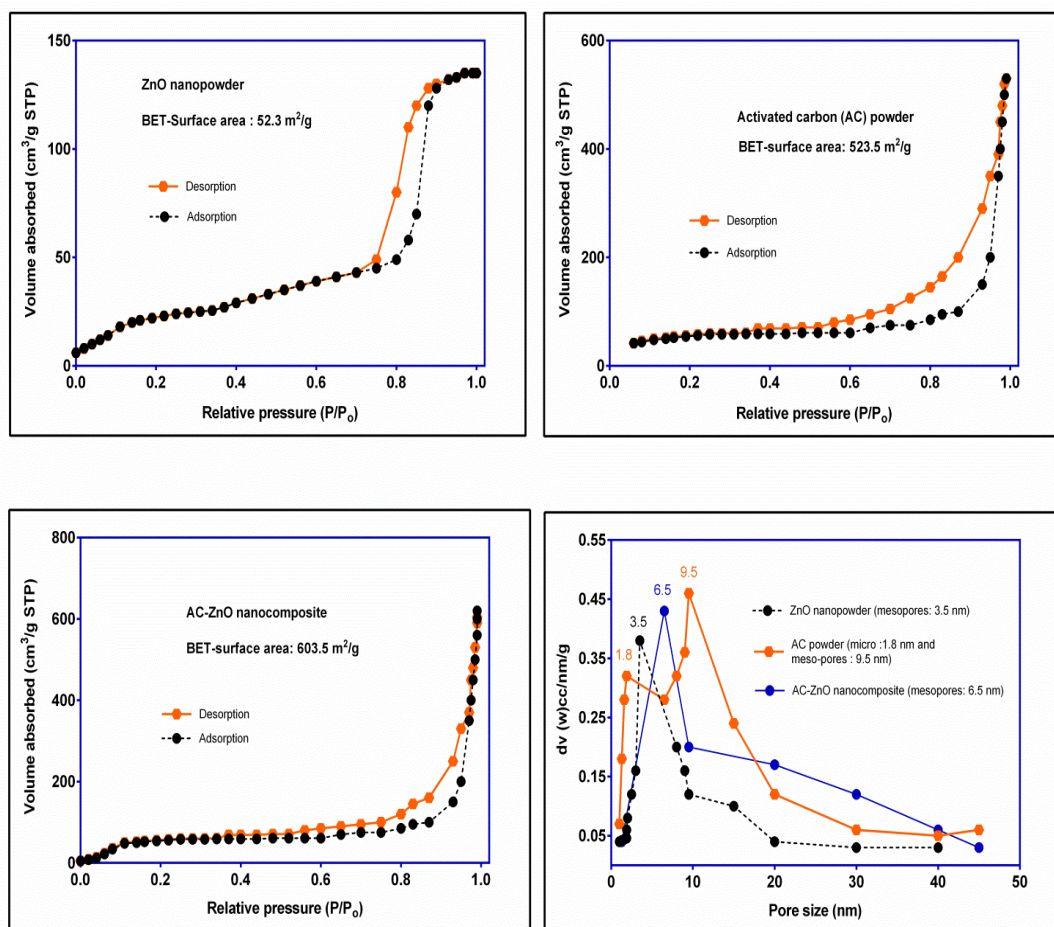

Figure7: Adsorbents pore size distributions for Ac, ZnO, and Ac-ZnO Nanocomposite

As shown in Fig. 7, the ZnO nanoparticles mainly possess mesoporous structure (2−50 nm). However, the activated carbon has minor micropores (< 2nm) and a higher percentage of mesopores (9.5 nm). The mesopore volume of the nanocomposite is lower than those of the activated carbon. Nevertheless, the average pore size of the Ac-ZnO (6.5 nm) is high enough to accommodate the phenolic molecules. This observation confirmed the enhancement in the surface area of Ac-ZnO and similar reports have been given by Oladipo and Gazi (2014a).

4.3 Adsorption studies: Influence of Operation Parameters

4.3.1 Influence of System pH on Phenol Removal

The pH of the system exerts significant influence on the adsorptive and degradative features of the adsorbent. In this study, the effect of initial pH was evaluated in alkaline and acidic conditions. As shown in Fig. 8, maximum removal of phenol was achieved at pH 5. A similar trend of pH influence was reported for the adsorption of phenol by TiO_2/AC and AC-titania catalyst (Alalm et al. 2014; Garcia-Munoz et al. 2014).

The interactions between the nanocomposite and the phenol molecules could be dissociative and electrostatic in nature due the integration of ZnO and Ac. At the optimum pH of 5.0, electrostatic force of attraction between the positively charged nanocomposite and the phenol molecules resulted in maximum removal percentage (99.24%). Thus, led to high adsorption capacity for phenol (9.9 mg/g). Meanwhile, when the solution pH increased beyond 5.0, the uptake capacity decreased. Competition is created between the OH^- ions and phenol ions in the alkaline medium, which resulted in lower removal capacity.
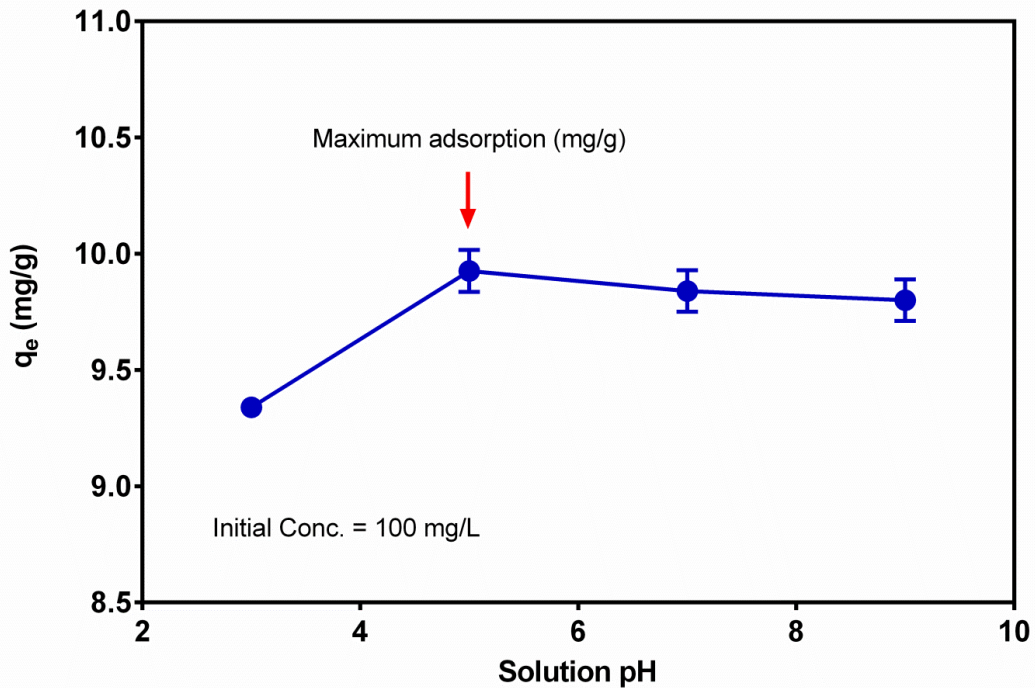
Figure 8: Influence of system pH on the adsorption of phenol by Ac-ZnO at 27±2 °C.

4.3.2 Influence of AC-ZnO Dosage on Phenol Removal

The effect of dosage of Ac-ZnO on phenol removal is shown in Fig. 9. The results indicated that the nanocomposite removal efficiency increased with increasing adsorbent dosage from 5.0 to 40.0 g/L. This can be ascribed to the increase in nanocomposite surface area, and also to the availability of more sorption sites. However, the unit phenol adsorbed decreased with increases in nanocomposite dosage which can be as a result of the reduction in the overall sorption surface area and size available to phenol due to overlapping of the sorption sites (Oladipo et al. 2014).
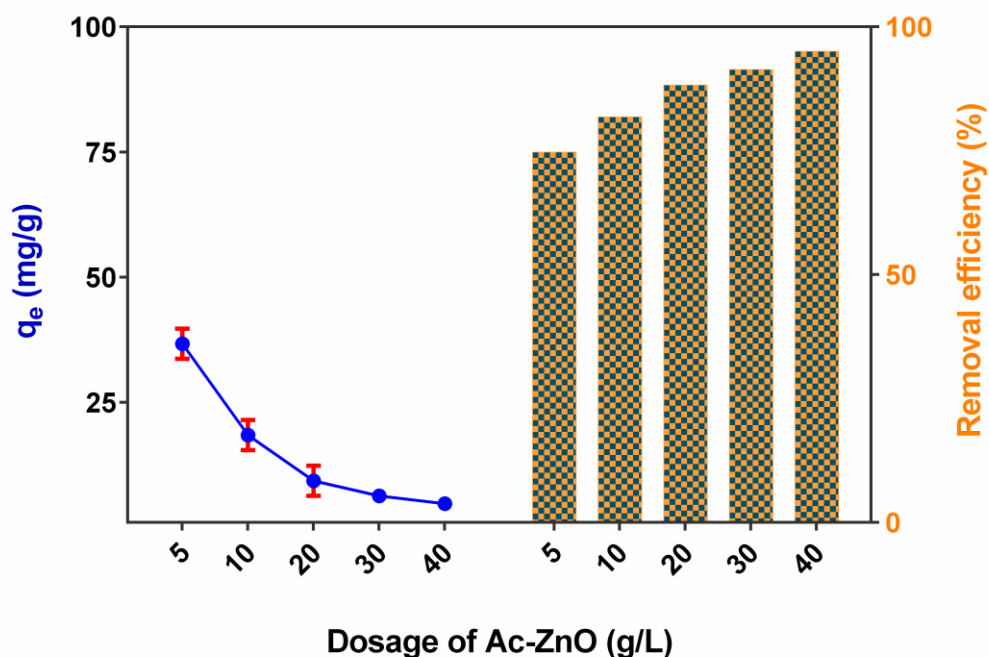
Figure: 9: Effect of adsorbent dosage on phenol removal at Co: 200 mg/L, pH: 5.0.

4.3.3 Influence of initial phenol concentration at fixed adsorbent dosage

The effect of initial phenol concentration was examined by varying the pollutant concentration from 50 mg/L to 400 mg/L at room temperature. The experiments were conducted at fixed adsorbent dosage at pH 5.0. It is evident from Fig. 10 that the uptake capacity increased with the increase in initial phenol concentration. The adsorption capacity increased from 4.85mg/g to 39.62 mg/g when the phenol concentration increased from 50 to 400mg/L. At lower concentrations, the ratio of number of phenol molecules to the available sorption sites on the nanocomposite is low. Therefore, the fractional uptake becomes independent of the concentration (Oladipo and Gazi 2014b). The residual phenol concentration is higher at higher initial concentration, resulting in maximum uptake capacity.

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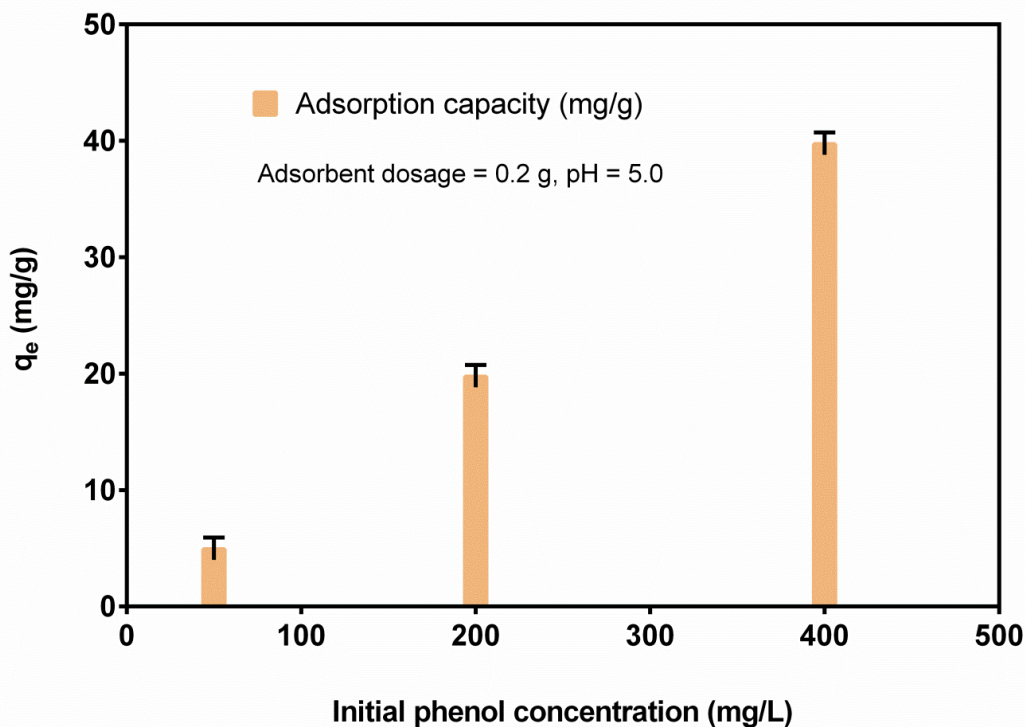
Figure 10: Effect of initial phenol concentration on the removal capacity of Ac-ZnO nanocomposite.

4.4 Photocatalytic studies

4.4.1 Evaluation of Photocatalytic Activity of AC-ZnO Nanocomposite

The photocatalytic activity runs of Ac-ZnO nanocomposite were performed a magnetically stirred volumetric flask in the presence of sunlight. The reactant mixtures consisted of 200 mg/L of Ac-ZnO nanocomposite and 200 mg/L of phenol at pH 5 and were premixed in the dark conditions before exposing to sunlight for degradation. Hydrogen peroxide (2 ppm) was employed as oxidant agent and its effect in the photocatalytic runs is reported in Fig. 11. The activated carbon is seen to play a vital role in the catalytic degradation, and this may be attributed to the existence of various oxygen-containing groups on its surface (Garcia-Munoz et al. 2014). In the absence of sunlight, 75% degradation of phenol was recorded within

120 min and increased up to 83% after 300 min. The decreasing reaction rate was attributed to the depletion of the active sites on the activated carbon.
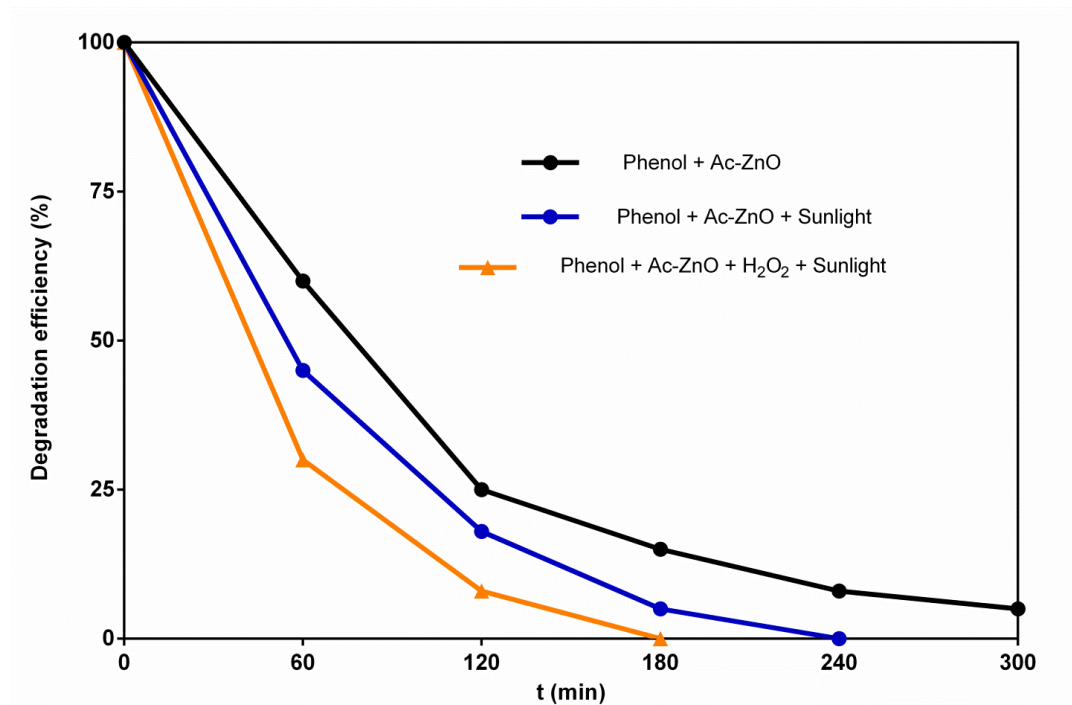
Figure 11: Photocatalytic degradation of phenol

However, higher phenol degradation efficiency was obtained in the presence of sunlight. In the presence of Ac-ZnO nanocomposite and sunlight, 60% phenol degradation was recorded in the first 60 min and complete degradation attained at irradiation time of 240 min. Even though, the activated carbon has no photocatalytic character; the improved degradation was due to increased adsorption of phenol on the surface of Ac, and thus might accelerate photodegradation of the phenol around the ZnO surfaces. Hence, the phenol degradation can be concluded to be a synergistic effect between Ac adsorption and ZnO photocatalysis reaction (Alalm et al. 2014). This was not the case when 2 ppm of H_2O_2 was introduced into the system.

The photocatalytic process was majorly enhanced by the presence of H_2O_2 as it is the sole source of hydroxyl radicals ($^\bullet$OH). Hydroxyl radicals are capable of degrading various pollutants via oxidative pathway (Duran et al. 2008). The results revealed that 84% phenol degradation was achieved in the first 120 min and complete degradation attained after 180 min.

Hence, it can be concluded that photocatalytic oxidation of phenol occurred as result of H_2O_2 present. The enhanced photoefficiency resulted from the combination of a photocatalytic feature of Ac-ZnO and hydroxyl radical generated from the hydrogen peroxide.

4.4.2 Optimization of Degradation Kinetics

The Box-Behnken experimental design was utilized to investigate the effect of different operating variables on the degradation kinetics of phenol in the presence and absence of sunlight. The interaction effects of operating factors (viz: nanocomposite dosage, pH, H_2O_2 and solar irradiation) on the degradation kinetics were obtained.

The three-dimensional surface plots were also constructed using the SigmaXL statistical software (DiscoverSim Ver.: 7.0) to interpret the observations. Three kinetic models (zero, pseudo-first and pseudo-second order) were applied to delineate the phenol degradation process. The kinetic model is expressed as follows; (Oladipo and Gazi 2014c):

$$r = -\frac{dC}{dt} = k_{\text{deg}}C^n \tag{3}$$

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where k_{deg} is the degradation rate constant,

r is the rate of degradation,

C is the concentration of the pollutant (phenol),

t is the reaction time, and

the power n is the reaction order.

The degradation rate constants and R^2 were calculated for each model, and obtained results illustrated in Table 4.1. The results revealed that the phenol degradation process majorly follow pseudo-first order pathway with a high coefficient of correlation ($R^2 = 0.993-0.999$). The degradation kinetic was then simplified in Eq. (4) and observed rate constants (Fig. 12) were utilized to plot response surface plots.

$$\ln\left(\frac{C_o}{C}\right) = k_{\text{deg}}t \tag{4}$$

Table 6: Box Behnken optimization of kinetic rate constants for the degradation of Phenol at different reaction conditions

	Operation parameters				Zero-order		First-order		Second-order	
No	Ac-ZnO (g)	pH	H_2O_2 (ppm)	Solar Irrad. (h)	K_o (mg/l min^{-1})	R^2	K_1 (min^{-1})	R^2	K_2 (l/mg min^{-1})	R^2
1	0.0	3	0	2	7.568	0.452	0.789	0.894	0.023	0.599
2*	0.2	5	2	4	4.677	0.593	0.067	**0.999**	0.043	0.698
3	0.0	5	0	2	8.998	0.465	0.234	0.964	0.002	0.765
4*	0.2	5	0	4	1.456	0.684	0.433	**0.993**	0.001	0.786
5	0.2	3	0	2	3.566	0.573	0.124	0.948	0.003	0.775
6	0.0	5	2	2	3.567	0.532	0.117	0.963	0.003	0.768
7	0.0	3	2	2	7.897	0.592	0.445	0.793	0.012	0.898
8*	0.2	7	0	2	2.876	0.503	0.455	**0.989**	0.076	0.703
9	0.0	3	0	4	1.567	0.596	0.321	0.896	0.089	0.796
10	0.0	7	2	2	5.678	0.495	0.087	0.893	0.023	0.797

*Optimum Experimental Conditions

In Fig. 13a, a pareto chart was constructed under the optimum conditions to graphically display the relative importance of the operation variables. It could be seen that the solution pH is the most important variable followed by the nanocomposite dosage. The surface plots of the degradation rate constants of phenol for the four pairs of variables are shown under our experimental conditions: pH versus Ac-ZnO dosage, AC (Fig. 13b), Ac-ZnO dosage versus solar irradiation, CD (Fig. 13c), and solar irradiation versus H_2O_2, DB (Fig. 12d).
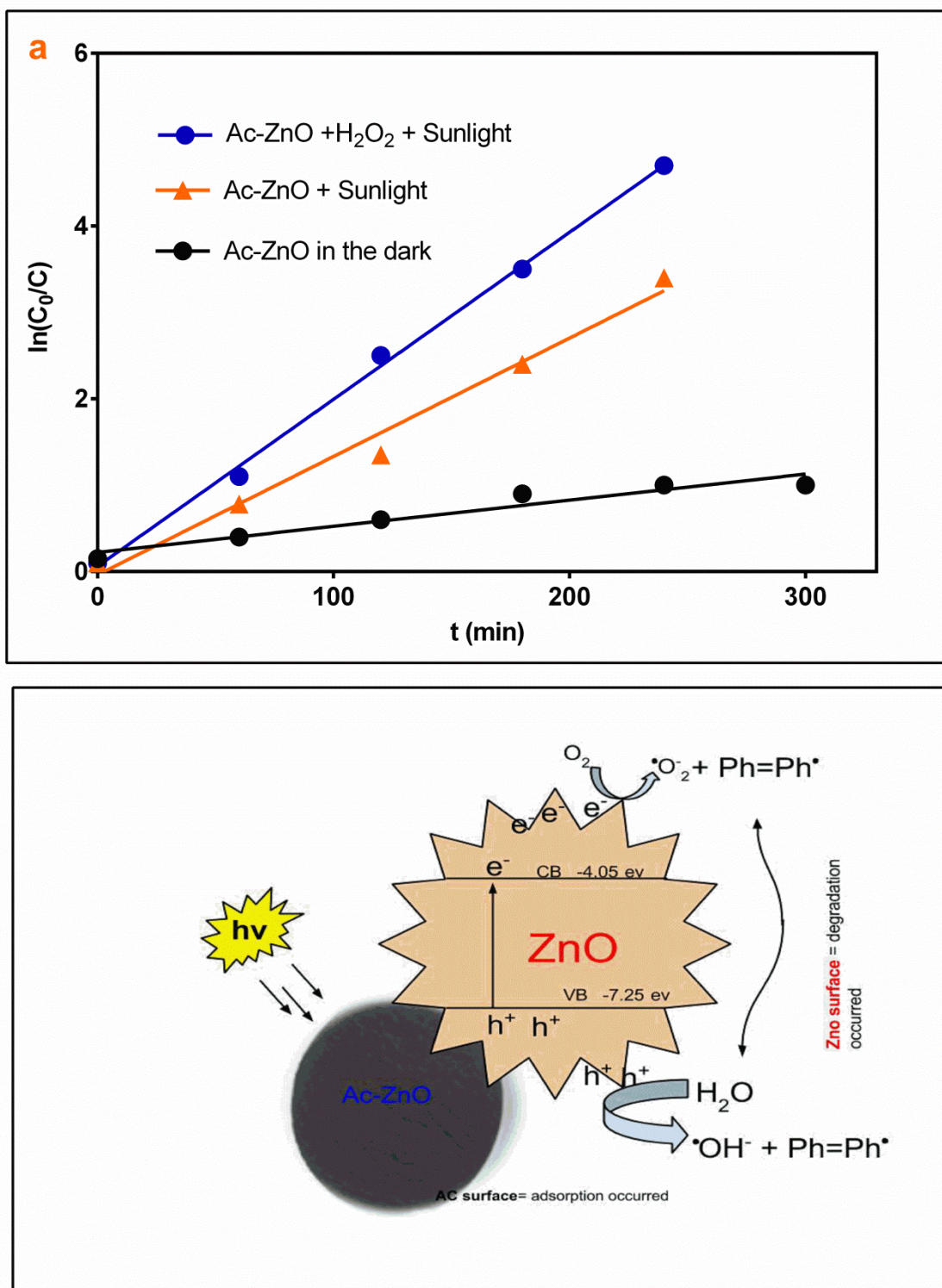
Figure 12: Kinetic analysis of phenol degradation and proposed mechanism

As seen in the surface plots in Fig. 13, the results shows that the rate of phenol degradation decreased with increase in pH of the solution, and increased with

increasing nanocomposite dosage. The **cone** nature of the surface plot confirms that a remarkable interaction exists between these two factors (AC). The degradation was enhanced by the increasing amount of active sites on Ac and increased generation rate of electron/hole pairs by ZnO for mineralization of the phenol. The optimum conditions to have a degradation efficiency of about 99.2% are low pH of 5.0 and nanocomposite dosage of 0.2g (Fig. 13b). By increasing the solution pH above 5.0, lower amount of phenol was degraded and reaction rate decreased. Similar trend was reported and attributed to the competitive reaction between the negatively charged surface of the nanocomposite and the phenol ions.

Photocatalyst in the presence of Sunlight would attack and decompose some organic molecules by bond cleavage and free radical generation; however, usually it occurs at very slow rates. The combination of Sunlight and various oxidants can decompose pollutants very effectively. The decomposition of various organic pollutants using hydrogen peroxide as an oxidant under UV-illumination has been proven to be very effective (Goi and Trapido 2002).

In Fig. 13c, increasing solar irradiation time was noted to enhance the degradation rate irrespective of the nanocomposite dosage. However, as the reaction proceeds, limited amount of active sites are available for the removal of phenol and recombination of electrons and holes may decrease the reaction rate. As shown in Fig. 13d, the phenol degradation rate increased only slightly in the presence of sunlight and H_2O_2. As the reaction proceeds, the generated $^\bullet OH$ radicals are insufficient for the phenol degradation, consequently the rate of phenol degradation decreases. The prepared Ac-ZnO nanocomposite was compared to reported adsorbents as illustrated in Table 7. It can be concluded that Ac-ZnO is fairly suitable

as alternative adsorbents for phenol degradation and its degradation efficiency and removal capacity outperformed many adsorbents.
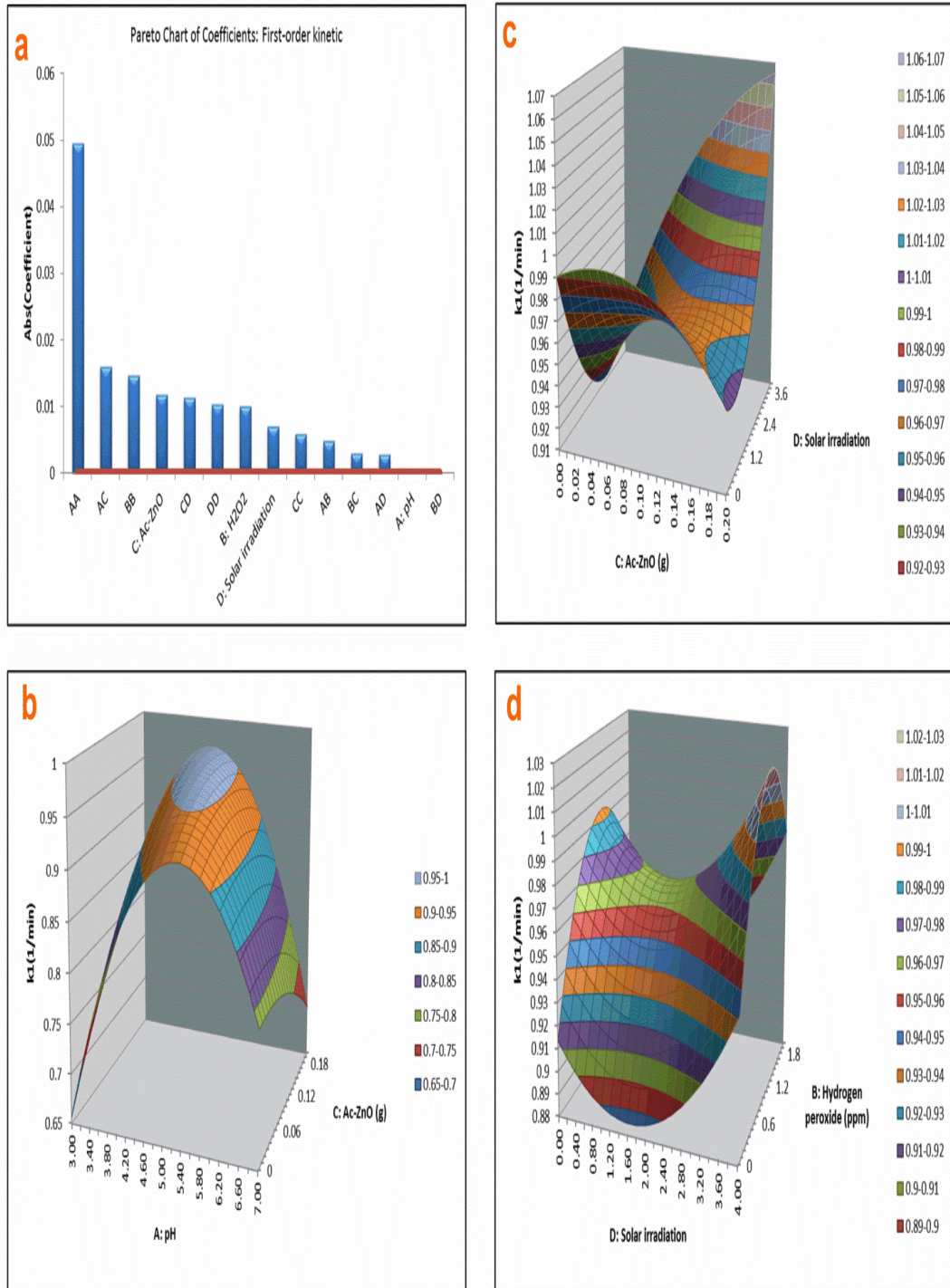
Figure 13: Box Behnken optimization studies of phenol degradation using AC-ZnO Nanocomposite

Table 7: Comparison of AC-ZnO removal capacity with reported adsorbents

Adsorbents	Conc. (mg/L)	pH	Q(mg/g	References)
Ac-ZnO nanocomposite	400	5.0	39.62	**Present work**
Activated charcoal	100	8.4	1.48	Vazquez et al. 2007
Commercial Activated Carbon	100	-	6.193	Ozkaya et al. 2006
Egg shell	800	5.7	192	Giraldo and Moreno-Pirajan. 2014
Rattan saw dust	200	6.5-7	149.25	Hameed and Rahman 2007
Palm Oil mill effluent sludge	300	2-3	12.078	Alam et al. 2006.

Chapter 5

CONCLUSION

This current study explored facile preparation of a cheap nanocomposite, studies of its degradation and adsorption capacity for phenol from aqueous solution was investigated. The ZnO-Ac nanocomposite produced exhibit fairly suitable adsorption and degradation ability for phenol. Based on this current research, adsorption of phenol is solely dependent on solution pH followed by nanocomposite dosage, since optimum condition to have 99.2% degradation efficiency are low pH of 5.0 and 0.2g of nanocomposite.

The results revealed that phenol degradation process majorly followed pseudo first-order kinetics with high R^2 value between 0.993-0.999.Since this process is economical and the nanocomposite is non-toxic, therefore, Ac-ZnO is fairly suitable adsorbent for phenol its degradation and its degradation efficiency and removal capacity outperformed many adsorbents that have been used to remove phenol since value of 39.62mg/g was recorded at pH 5.0, and 400mg/L of phenol.

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