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Preparation, Characterization and Application of Coffee Husk Based Activated Carbon for Adsorption of Cr(VI) From Aqueous Solution

BY;

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Abstract

This research proposed coffee husk as a low-cost material for production of activated carbon and investigated its application for adsorption of Cr(VI) from aqueous solution. The initial work involved, the optimization of process parameters involved in preparation of activated carbon by chemical activation using H_3PO_4. Four parameters such as concentration of H_3PO_4, impregnation ratio, carbonization temperature and holding time were optimized by Response Surface Method (RSM) using Box-Behnken design technique and the produced activated carbon applied for Cr(VI) adsorption. RSM revealed that the effect of on operational parameters on Iodine number and yield of coffee husk activated carbon was best described by quadratic polynomial model. Analysis of variance (ANOVA) revealed a good agreement between experimental and predicted value. The characterization result showed that the coffee husk activated carbon has good properties and compared favourably with other reference activated carbons. FTIR test and point of zero charge pH, showed the presence of acidic functional groups on surface. Cr(VI) adsorption shows that the system was pH dependent. The linear regression analysis of kinetic data confirmed that pseudo-second order rate expression best fitted for all temperature. Langmuir equation was found to fit the equilibrium data for Cr(VI) adsorption with monolayer capacity of 78.74, 84.03 and 92.59 mg/g at 25, 35 and 45^oC respectively. Thermodynamic analysis asserted endothermic and spontaneous nature of the system with involvement of chemical adsorption process.

Key word; ***Activated carbon, Coffee husk, process optimization, Cr(VI) adsorption***

List of Acronyms and Abbreviations

AC	Activated Carbon
ANOVA	Analysis of Variance
APHA	American Public Health Association
ASTM	American Society for Testing Materials
AWWA	American Water Works Association
AWWA	American Water works association
BBD	Box Behnken Design
C.V	Coefficient of Variation
Df	Degree of Freedom
FTIR	Fourier Transform Infrared spectrometry
IN	Iodine Number
MB	Methylene Blue
MBN	Methylene Blue Number
MC	Moisture Content
PZC	Point of Zero Charge
RSM	Response Surface Methodology
VC	Volatile Content
WHO	World Health Organization

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1. Introduction

1.1 Background

Literatures defined activated carbon stating that it is an excellent adsorbent which is produced in such a way that it exhibits high specific surface area and porosity. It is a porous material with large specific surface area, large pore volume, and various oxygen-containing functional groups on the surface. These characteristics, along with the surface's chemical nature (which depends on the raw materials and the activation used in its preparation process), allow it to attract and retain certain compounds in a preferential way, either in liquid or gaseous phase (Peláez-Cid and Teutli-León, 2012).

Activated carbon is used in a number of industrial applications including separation and purification technologies, catalytic processes, biomedical engineering, and energy storage, among others (Gonzalez-Serrano *et al*., 2004, Guo *et al*., 2005, Luo *et al*., 2008). The extensive application of activated carbon is mainly due to its wide availability, high performance in adsorption processes, surface reactivity and the versatility to modify its physical and chemical properties for synthesizing adsorbents with very specific characteristics (Durán-Valle, 2012, Joao Valente Nabais *et al*., 2008).

Activated carbon is commonly considered an expensive material because of the chemical and physical treatments used in its synthesis, its low yield, its production's high energy consumption, or the thermal treatments used for its regeneration and the losses generated meanwhile (Dias *et al*., 2007). The search for the appropriate mechanism for its production process and optimization of operation conditions is an important factor for tackling production costs. This includes identifying new row material with high carbon content and low cost. Researchers proposed number of lignocellulosic industrial and agricultural wastes. Those lignocellulosic wastes not only lessen its cost of production, but also diminish environmental impact of agricultural and industrial wastes and avoid additional cost for waste management (Peláez-Cid and Teutli-León, 2012). Optimization of process parameter and the way to enhance the qualities of the carbons produced is also being studied to make its production more profitable, and, hence, solve specific environmental issues.

Sooner or later mass production of activated carbon from agricultural residue is inevitable, for its increased need for adsorption of pollutant from industrial wastewater. With this regard designing ways for the production of activated carbon through economic ways is the need of the hour. Optimizing application of activated carbon in adsorption process through its proper design in the way to enhance the adsorptive efficiency of produced activated carbon is the other knowledge gap to be addressed, in making its application economically feasible and environmentally sustainable.

With this regard, not fully investigated yet, coffee husk is one of those lignocellulosic precursor proposed for preparation of AC and shown promising result (Waleska E. Oliveira *et al*., 2008). It is the major solid waste residue from the handling and processing of coffee. Since Ethiopia is one of major coffee producing countries in the world, large amount of coffee husk is produced as waste. In addition to its low-cost, coffee husk has shown better adsorptive capacity, property of high carbon contents and low inorganic compound levels (Waleska E. Oliveira *et al*., 2008, Namane *et al*., 2005, Joao Valente Nabais *et al*., 2008). But research lack on how process parameters in preparation of coffee husk activated carbon interact and affect surface characteristic and yield. The behaviour of adsorption system such as equilibrium isotherm, kinetic model and thermodynamic parameters were not reported yet.

1.2 Statement of Problem

The demand for activated carbon is increasing owing to the increased utility of the carbon materials in pollution control. As the applications of activated carbon are immense, the gap between demand and supply is ever widening. As a result, cost of activated carbon is increasing. This is due to the use of non-renewable and relatively expensive starting material such as either coal based or petroleum pitch based which are prone to exhaustion and unjustified in pollution control applications (Tan *et al*., 2007). Their global distribution is also non uniform. This may in due course result in scarcity of the material in addition to becoming expensive. This situation necessitates the need for the exploration of new sources of carbon materials with desired physico chemical properties namely, high specific surface area, micro or meso porosity or both, depending on the end application, surface functionality, thermal stability, carbon purity, adsorptive capacity and chemical composition.

In their literature review of the last two decades (1992–2011) Peláez-Cid and Teutli-León (2012) indicated that worldwide researchers had proposed number of agricultural and industrial wastes as low cost sources to obtain raw materials for the production of activated carbon. These researchers have in mind not only to lessen its cost of production, but also to diminish environmental impact of agricultural and industrial wastes and to avoid cost of associated cost of solid waste handling (Peláez-Cid and Teutli-León, 2012).

This research presented coffee husk as new low-cost, locally abundant material for production of activated carbon and investigated its application for adsorption of Cr(VI) from aqueous solution. In this endeavor, initially process parameters involved in preparation of coffee husk activated carbon by chemical activation using H_3PO_4, were optimized aiming at the reduction of its production cost. Then the characteristics of activated carbon prepared at predicted optimum operational parameters were analyzed. Finally, application of coffee husk activated carbon for Cr(VI) adsorption from aqueous solution was investigated, and adsorption process is properly designed through accurate description of equilibrium isotherm, kinetic model and determination of thermodynamic parameters.

1.3 Objectives

1.3.1 General Objective

To investigate optimum coffee husk based activated carbon preparation process, its characteristic and application in batch adsorption of Cr(VI) from aqueous solution.

1.3.2 Specific Objectives

Specific objectives of the study are:

- Optimization of process parameters in preparation activated carbon from coffee husk by chemical activation using H_3PO_4.
- Characterization of coffee husk based activated carbon produced at predicted optimum process conditions.
- Investigation of the application of coffee husk based activated carbon for adsorption of Cr(VI) from aqueous solution.

2. Literature Review

2.1 Introduction

Mankind is dependent upon ecosystem services such as air, water, food, and for provision of materials for development and construction. While the importance of ecosystems and their services cannot be underestimated, a wide range of human and natural processes have altered the way they function, eroding their capacity to deliver these vital ecosystem services for human well-being. According to Corcoran *et al*. (2010) the quality of our environment is deteriorating day by day with the largest cities reaching saturation points and unable to cope with the increasing pressure on their infrastructure. Much of industrial wastewater is discharged without treatment to open watercourses, reducing the quality of larger volumes of water and sometimes infiltrating aquifers and contaminating groundwater resources. Worldwide, it is estimated that industry is responsible for dumping 300-400 million tons of heavy metals, solvents, toxic sludge, and other waste into waters each year (UNEP, 2010).

Aquatic ecosystems have long been used as a medium for transporting and disposing of human, agricultural, and industrial wastes, discharged directly or indirectly into the water courses. More than 80 per cent of sewage in developing countries is discharged untreated, polluting rivers, lakes and coastal areas (WWAP, 2009) and remains far from satisfactory even in some developed countries. Pollutants including microbes, nutrients, heavy metals, organic chemicals, oil and sediments; heat, which raises the temperature of the receiving water, are typically the cause of major water quality degradation around the world.

While significant progress has been made in many developed nations to reduce direct discharges of pollutants into water bodies, more than 70 percent of industrial wastes in developing countries are dumped untreated into waters (UN-water). Industrial pollutants often alter broad water quality characteristics, such as temperature, acidity, salinity, or turbidity of receiving waters, leading to altered ecosystems and higher incidence of water-borne diseases. Impacts can be heightened by the synergistic combination of contaminants affecting species communities and structures, wildlife habitats, biodiversity, degradation of other environmental services, and in decreased productivity and simplification of trophic webs (UNEP, 2010).

A wide range of physical and chemical processes are available for the removal of pollutants from effluents. A major drawback with those treatment systems is sludge production, and, high operational cost and some of them are complicated for management. This actually makes the application of these technologies to be limited only in developed countries. In response to this challenge a different attempt were undertaken to produce a media which was feasible and cost effective to use by the majority (Alebel Abebe Belay, 2010). With this regard, the prevalence of adsorption separation in the environmental chemistry remains an aesthetic attention and consideration abroad the nations, owning to simplicity of design, ease of operation, insensitivity to toxic substances and complete removal of pollutants even from dilute solutions (Foo and Hameed, 2010). Despite its prolific use in adsorption processes, the biggest barrier of its application by the industries is the cost-prohibitive adsorbent and difficulties associated with regeneration (Foo and Hameed, 2009). Realizing the complication, a growing exploitation to evaluate the feasibility and suitability of natural, renewable and low-cost materials as alternative adsorbents has been exerted. With this regard, activated carbon is the most promising adsorbent in environmental application.

2.2 Activated Carbon

Activated carbon is broadly defined to include a wide range of amorphous carbon based materials prepared in such a way that they exhibit a high degree of porosity and an extended surface area (Bansal and Goyal, 2005). Moreover, all non-carbon impurities are removed and the surface is oxidized. Although today the term ‘activated carbon’ is taken for granted, a long time elapsed before it became generally adopted. These characteristics, along with the surface's chemical nature (which depends on the raw materials and the activation used in its preparation process), allow it to attract and retain certain compounds in a preferential way, either in liquid or gaseous phase (Peláez-Cid and Teutli-León, 2012).

Activated carbons are used in a number of industrial applications including separation and purification technologies, catalytic processes, biomedical engineering, and energy storage, among others. Activated carbon is one of the most commonly used adsorbents in the removal process of industrial pollutants, organic compounds, heavy metals, herbicides, and dyes, among many others toxic and hazardous compounds (Peláez-Cid and Teutli-León, 2012).The extensive

application of activated carbon is mainly due to its relatively low cost with respect to other adsorbents, wide availability, high performance in adsorption processes, surface reactivity and the versatility to modify its physical and chemical properties for synthesizing adsorbents with very specific characteristics (Haro *et al*., 2011). Recently, the demand of activated carbons has increased significantly as a water-purifying agent to reduce the environmental risks caused by the water pollution worldwide (Altenor *et al*., 2009, Bello-Huitle *et al*., 2010).

2.3 Activated Carbon Application as Low-Cost Adsorbent

Nowadays, activated carbon finds wide application in many areas, but especially in the environmental field. Aside from environmental pollution control, activated carbon is mainly used in industry in various liquid and gas phase adsorptions (Bansal and Goyal, 2005). Among liquid phase applications one can list food processing, preparation of alcoholic beverages, decolorization of oils and fats, product purification in sugar refining, purification of chemicals (acids, amines, gylcerin, glycol, etc.), enzyme purification, decaffeination of coffee, gold recovery, refining of liquid fuels, purification in electroplating operations, purification in the clothing, textile, personal care, cosmetics, and pharmaceutical industries, and applications in the chemical and petrochemical industries. Gas phase applications include recovery of organic solvents, removal of sulfur-containing toxic components from exhaust gases and recovery of sulfur, biogas purification, use in gas masks, among others. Activated carbon is also used in medical and veterinary applications, soil improvement, removal of pesticide residues, and nuclear and vacuum technologies (Cecen, 2011).

Activated carbon adsorption is most commonly applied in industrial wastewater treatment to meet stringent regulations for discharge into receiving waters. In industrial wastewater treatment, activated carbon adsorption can be utilized as a separate unit process. It may be placed after various physicochemical treatment steps such as coagulation/clarification, filtration, and dissolved air flotation. Another alternative is to use activated carbon adsorption prior to biological treatment to remove compounds which might be toxic to a biological system. However, the most widely adopted procedure is to place activated carbon adsorption as a tertiary or advanced treatment step subsequent to biological treatment for removal of refractory organics. To some extent this procedure may also be effective in the removal of inorganics (Cecen, 2011).

Nowadays, activated carbon finds wide application in the treatment of wastewaters generated from industries such as food, textile, chemical, pharmaceutical, pesticides and herbicides production, coke plant, munitions factories, petroleum refineries and storage installations, organic pigments and dyes, mineral processing plants, insecticides, pesticides, resins, detergents, explosives, and dyestuffs. It is also employed in the treatment of sanitary and hazardous landfill leachates (Cecen, 2011).

The demand for activated carbon is increasing owing to the increased utility of the carbon materials in pollution control. As a result, cost of activated carbon is also growing depending on the application. Designing ways for the production of activated carbon through economic ways is the need of the hour. A range of low cost, easily available, carbon rich and low ash precursors and sources are being explored for the production of carbon materials.

Most of the commercial activated carbons are either coal based or petroleum pitch based which are prone to exhaustion. Their global distribution is non uniform. As the applications of activated carbon are immense, the gap between demand and supply is ever widening. This may in due course result in scarcity of the material in addition to becoming expensive. This situation necessitates the need for the exploration of new sources of carbon materials with desired physico chemical properties namely, high specific surface area, micro or meso porosity or both, depending on the end application, surface functionality, thermal stability, carbon purity, adsorptive capacity and chemical composition (inherent or induced presence of hetero atoms like B, N, S and P).

Traditionally, the activated carbons used in wastewater treatment are obtained from coal/lignite, wood or animal bones but, recently, there is a growing interest in the use of alternative and low-cost precursors for their production (Elizalde-González and Hernández-Montoya, 2007, Altenor *et al*., 2009, Mohamed *et al*., 2010).

The production of activated carbons from agricultural and industrial wastes is usually justified by two factors: the unique properties of these precursors and the possibility of mass production at an affordable cost. Several studies reported in literature indicate that it is possible to produce high quality activated carbons from raw agricultural and industrial lignocellulosic waste

materials. These carbons are suitable for different applications including the removal of various pollutants from both drinking water and wastewaters. These pollutants include dyes, heavy metals, fluorides, phenols and other organic and inorganic toxic compounds, which are considered as priority substances for wastewater treatment in several countries (Altenor *et al*., 2009).

Lignocellulosic materials have been and will be with mankind forever and they hold a promise of renewable and inexhaustible supply of carbon materials provided suitable methods of production are developed. In addition they are more evenly distributed throughout the globe relative to either coal or petroleum (Durán-Valle, 2012). Thus the lignocellulosic material, a regenerable natural resource, is a viable option for the generation of carbon materials rather than fossil fuels.
Preparation of Activated Carbon

According to Hernández-Montoya *et al*. (2012), the preparation of ACs from lignocellulosic materials involved two processes, the carbonization and the activation, which can be performed in one or two steps depending on the activation method (physical or chemical, respectively). The carbonization consists of a thermal decomposition of raw materials, eliminating non-carbon species and producing a fixed carbon mass with a rudimentary pore structure (very small and closed pores are created during this step). On the other hand, the purpose of activation is to enlarge the diameters of the small pores and to create new pores.

Specifically, when the carbonization is carried out in an inert atmosphere the process is called pyrolysis. According to the literature, the pyrolysis of lignocellulosic materials as coconut shells, coffee husk, olive stones, walnut shells, etc., gives rise to three phases: the char, oils (tars) and gases. The relative amount of each phase is a function of parameters such as temperature of pyrolysis, nitrogen flow rate and heating rate. For example, slow heating rates promote high yields of the carbon residue while flash pyrolysis is recommended for high liquid (oil) ratios (Mohamed *et al*., 2010).

During the pyrolysis of lignocellulosic precursors, a rudimentary porosity is obtained on the char fraction as a consequence of the release of most of the non-carbon elements such as hydrogen,

oxygen and nitrogen in form of gases and tars, leaving a rigid carbon skeleton formed by aromatic structures (Hernández-Montoya *et al*., 2012).

All the available methods of activation can be classified in to two types, namely, physical activation or chemical activation depending on whether a gaseous or solid activating agent is used. Each of these methods has its own merits and demerits.

During physical activation, the agricultural and industrial waste (lignocellulosic) material as such or the previously carbonized materials can undergo gasification with water vapor, carbon dioxide, or the same combustion gases produced during the carbonization. Ammonium persulfate, nitric acid, and hydrogen peroxide have also been used as oxidizing agents (Salame and Bandosz, 2001). Chemical activation consists of impregnating the agricultural and industrial waste (lignocellulosic) or carbonaceous raw materials with chemicals such as $ZnCl_2$, H_3PO_4, HNO_3, H_2SO_4, NaOH, or KOH. The carbonization step and the activation step simultaneously progress in the chemical activation (Hayashi *et al*., 2002). Then, they are carbonized (a process now called "pyrolysis") and, finally, washed to eliminate the activating agent. The application of a gaseous stream such as air, nitrogen, or argon is a common practice during pyrolysis which generates a better development of the material's porosity. (Elizalde-González and Hernández-Montoya, 2007, Girgis *et al*., 2002).

According to Hernández-Montoya *et al*. (2012) review chemical activation is the most used method for the preparation of ACs (~60%) from agricultural and industrial waste (lignocellulosic) precursors. Physical activation methods is used in 28% of the studies and a low quantity of studies combine both methods (i.e., physicochemical) to produce ACs. H_3PO_4 and $ZnCl_2$ are the two more employed activating agents in the impregnation of agricultural and industrial waste (lignocellulosic) materials (30% and 24 %, respectively), whereas alkaline reagents such as KOH, NaOH and K_2CO_3 have been considered because ACs with high specific surface can be obtained (1500-2500m^2g^{-1}). Physical activation of agricultural and industrial waste (lignocellulosic) precursors normally renders carbons with lower specific surface area. However, when compared with chemical activation, this method is not corrosive and does not require a washing step (Hernández-Montoya *et al*., 2012).

2.3.1 Parameters for Activated Carbon Preparation

Research has shown that carbon properties such as specific surface area, porosity, density and mechanical resistance depend greatly on the raw material used. However, it may be possible to modify these parameters changing the conditions in the pyrolysis process of the agricultural and industrial waste (lignocellulosic) materials. The pore size distribution and surface area are determined by the ratio between the mass of the chemical agent and the raw material. Besides, activation time, carbonization temperature and heating rate are important preparation variables for obtaining ACs with specific characteristics (Mohamed *et al*., 2010). The effects of all these parameters in the textural characteristics of ACs employing different activating agents are discussed in the following sections.

In particular, the most important parameters to be considered while preparing activated carbons from agricultural and industrial waste (lignocellulosic) materials are described below.

2.3.1.1 Activating Agent

A multitude of activating agents has been extensively employed for the production of activated carbon materials with desired pore structure. The purpose of activation is to create and develop (volume and size) porosity in the carbon material and thereby increase the adsorptive capacity.

In preparation of activated carbon, the lignocellulosic precursor is treated primarily with a chemical agent, such as H_3PO_4, H_2SO_4, HNO_3, NaOH, KOH or $ZnCl_2$ by impregnation or physical mixture and the resulting precursor is carbonized at temperatures between 400 and 800ºC under a controlled atmosphere.

H_3PO_4 is the most commonly used chemical agent for synthesis of activated carbon. The use of $ZnCl_2$ has declined because of the environmental pollution problems with zinc disposal (Girgis *et al*., 2002). KOH also have been used as activation reagents in the preparation of activated carbons with high specific surface.

According to Hernández-Montoya *et al*. (2012) and references therein, in the last 20 years, the activation of lignocellulosic materials with H_3PO_4 has become an increasingly used method for the large-scale manufacture of ACs because the use of this reagent has some environmental

advantages such as ease of recovery, low energy cost and high carbon yield. H_3PO_4 plays two roles during the preparation of ACs:

- H_3PO_4 acts as an acid catalyst to promote bond cleavage, hydrolysis, dehydration and condensation, accompanied by cross-linking reactions between phosphoric acid and biopolymers;
- H_3PO_4 may function as a template because the volume occupied by phosphoric acid in the interior of the activated precursor is coincident with the micropore volume of the activated carbon obtained (Zuo *et al*., 2009).

The chemical and physical properties of ACs obtained by chemical activation with H_3PO_4 are affected by the experimental conditions of preparation such as acid concentration, time of activation, impregnation ratio, carbonization temperature and heating rate. Also some recent works have shown that the atmosphere used in the carbonization process has an obvious effect on the physicochemical properties of ACs (Zuo *et al*., 2009).

In the review of Hernández-Montoya *et al*. (2012) most literatures show the concentration of acid is greater than 50% (w/w) and the activation temperature for 75 % of these studies is between 350 and 600 ºC. Carbons obtained with the highest phosphoric impregnation ratio (China Fir and avocado kernel seeds) are the materials with the largest S_{BET}(1785 and 1802 m^2g^{-1}). Additionally, the carbon obtained from Oil palm shell and activated using a rather low impregnation ratio (0.09) was one of the materials with a lower specific surface area (356 m^2g^{-1}).

2.3.1.2 Carbonizing Temperature

It has the most influence over the activated carbon's quality during the activating process. It must be at least 400 °C to ensure the complete transformation of organic compounds (present in agricultural and industrial waste (lignocellulosic) precursors) into graphene structures. The degree of specific surface area development and porosity is incremented on par with the carbonizing temperature (Olivares-Marín *et al*., 2006b). During physical activation, carbonization temperatures are greater than those needed for chemical activation (Lussier *et al*., 1994). However, carbonization temperatures used in activated carbon production are generally greater than 400°C and temperatures ranging from 120 to 1000°C have been used. (Salame and

Bandosz, 2001, Elizalde-González and Hernández-Montoya, 2008, Elizalde-González and Hernández-Montoya, 2007, Rajeshwarisivaraj *et al*., 2001). It has been reported that carbon obtained from peach pits with temperatures below 700 °C still have a high content of hydrogen and oxygen (MacDonald and Quinn, 1996).

2.3.1.3 Carbonizing Time

This parameter must be optimized to obtain the maximum porosity development while still minimizing the material's loss due to an excessive combustion. Bouchelta *et al*. (2008) have shown that the yield percentage decreases with increase of activation temperature and hold time. Carbonization times ranging from 1 h (Rajeshwarisivaraj *et al*., 2001, Wu *et al*., 1999) up to 14 h (Rajeshwarisivaraj *et al*., 2001) have been used in charcoal production.

2.3.1.4 Mass Ratio of Precursor and Activating Agent

The complete saturation of agricultural and industrial waste (lignocellulosic) precursor must be ensured to develop the adsorbent porosity with the minimum activating agent consumption. This leads a minor consumption of chemical compounds and a better elimination of the excess during the carbon washing process. The effect of the increase in proportion of the impregnation over the carbon porous structure is greater than the one obtained with the increase of carbonizing temperature (Olivares-Marín *et al*., 2006a).

2.3.1.5 Heating Speed

Regularly, heating ramps with a low speed are used for preparation of activated carbon. This approach allows the complete combustion of material precursor and favors a better porosity development. Rapid heating during pyrolysis produces macroporous residue (Heschel and Klose, 1995).

2.4 Characteristics and Technique of Characterization

Properties such as specific surface area, pore size, and pore size distribution are important material characteristics not only for AC but also in many processing applications, including those for catalysts, sintered materials, pharmaceutical products, and chromatographic carriers.

Gas adsorption measurements are widely used for the characterization of a variety of porous solids. Of particular importance is the application of physisorption (physical adsorption) for the determination of the surface area and pore size distribution. Nitrogen (at 77 K) is the recommended adsorptive for determining the surface area and mesopore size distribution, but it is necessary to employ a range of probe molecules to obtain a reliable assessment of the micropore size distribution. An alternative technique to gas adsorption is mercury porosimetry used for macropore size analysis. For operational reasons, krypton adsorption (at 77 K) is usually adopted for the determination of relatively low specific surface areas ($<2 m^2 g^{-1}$), but this technique cannot be employed for the study of porosity (Durán-Valle, 2012).

The iodine number is the amount of iodine, in milligrams, adsorbed per gram of carbon when the equilibrium concentration (C_e) of iodine is 0.02 M. It is the most fundamental parameter used to characterize activated carbon performance. It is a measure of activity level (higher number indicates higher degree of activation), often reported in mg/g (typical range 500–1200 mg/g). It is a measure of the micropore content of the activated carbon (0 to 20 Å, or up to 2 nm) by adsorption of iodine from solution. It is equivalent to surface area of carbon between 900 m^2/g and 1100 m^2/g (Baseri *et al*., 2012, Sivakumar *et al*., 2012) The micropores are responsible for the large surface area of activated carbon particles and are created during the activation process. It is in the micropores that adsorption largely takes place (Ekpete O.A. and Horsfall M.JNR, 2011).

It has been established that the iodine umber in mg/g gives an estimate of the surface area in m^2/g (Gergova *et al*., 1994) and measures the porosity for pores with dimensions between 1.0 - 1.5nm (Collin *et al*., 2006). The removal of iodine by the activated carbons is related to their porosity characteristics which determine the degree of accessibility of these molecules. A lower iodine number can be ascribed to the presence of pores narrower than 1.0 nm, which make up most of the structure of these carbons (Khadija *et al*., 2008). For carbons prepared by physical activation, the mass of iodine absorbed was generally low (92 to 261 mg/g), whereas carbons prepared by chemical activation exhibited a higher iodine adsorption capacity (240-268 mg/g) indicating improved porosity. These carbons contain mostly micro pores with a small contribution of mesoporosity. AC recommended for water treatment, are to show iodine values ranging from 600 to 1100 mg/g (American Water Works Association, 1991).

2.5 Cr(VI) Adsorption on Low Cost Activated Carbon

The element chromium can exist in six valency states, 0, II, III, IV, V and VI, which represent the number of bonds an atom is capable of making. Metallic chromium Cr(0) does not occur naturally in the environment and Cr(II) is unstable and converted quickly to Cr(III). Cr(IV) and Cr(V) are also unstable and occur briefly as intermediates of conversions between Cr(III) and Cr(VI). Cr(III) and Cr(VI) are the environmentally important chromium species (Zayed and Terry, 2003). Chromium is most commonly found in nature as Cr(III), which is the most stable species. Most Cr(III) compounds are insoluble in water and Cr(III) is considered to be an essential trace element for human diets, although ingestion of large amounts can cause toxic effects (Zayed and Terry, 2003). The second most common and stable form of chromium in the environment is Cr(VI) compounds which are more toxic than Cr(III) due to their high water solubility and mobility (Mohan *et al*., 2006a).

Chromium is one of toxic pollutants discharge from industrial wastewater with concentration varying from 5.2 to 208,000 mg/L (Miretzky and Cirelli, 2010). Industrial sources of Cr(VI) include leather tanning, cooling tower blow down, plating, electroplating, anodizing baths, rinse waters, etc (Mohan and Pittman Jr, 2006, Mohan *et al*., 2006b). Exposure to Cr(VI) may cause repository problems (asthma), internal hemorrhage, dermatitis, kidney and liver damage, dermatitis, and nausea. Skin and eye contact may cause nasal septum, ulceration, irritation, severe burn and permanent damage to eye (Kara and Demirbel, 2012). The maximum allowable level for chromium discharge onto land surfaces is 0.1 and 0.05 mg/L for drinking water (WHO, 2011).

A wide range of physical and chemical processes are available for the removal of Cr(VI) from effluents. A major drawback with those treatment systems is sludge production, and, high operational cost and some of them are complicated for management. This actually makes the application of these technologies to be limited only in developed countries. In response to this challenge a different attempt were undertaken to produce a media which was feasible and cost effective to use by the majority (Alebel Abebe Belay, 2010). With this regard, the prevalence of adsorption separation in the environmental chemistry remains an aesthetic attention and consideration abroad the nations, owning to simplicity of design, ease of operation, insensitivity

to toxic substances and complete removal of pollutants even from dilute solutions(Foo and Hameed, 2010). Despite its prolific use in adsorption processes, the biggest barrier of its application by the industries is the cost-prohibitive adsorbent and difficulties associated with regeneration (Foo and Hameed, 2009). Realizing the complication, a growing exploitation to evaluate the feasibility and suitability of natural, renewable and low-cost materials as alternative adsorbents has been exerted.Regarding Cr(VI) adsorption a number of low cost materials such as olive bagasse (Demiral *et al*., 2008), modified tannery waste (Anandkumar and Mandal, 2011), sugar industrial waste (Fahim *et al*., 2006), maize bran (Hasan *et al*., 2008), olive stones(Attia *et al*., 2010), sugar beet tailing (Dong *et al*., 2011), sawdust (Hamadi *et al*., 2001), Rubber wood sawdust (Karthikeyan *et al*., 2005), biomass sorbent (Anuradha Jabasingh and Pavithra, 2010) has been reported.

3. Material and Method

3.1 Optimization Study (specific objective -1)

3.1.1 Chemical Reagents

All chemical reagents in this study were analytical grade. Potassium dichromate ($K_2Cr_2O_7$) was used as the source for chromium stock solution. All the required solutions are prepared with analytical reagents and distilled water.

Sodium thiosulfate (0.100N) was prepared by dissolving 24.820g sodium thiosulfate in 75mL of freshly boiled distilled water and 0.1g of sodium carbonate was added to minimize bacterial decomposition of the thiosulfate solution. Finally the solution was diluted to the mark and allowed to stand for 4 days before standardized using Potassium Iodate Solution. Standard Iodine Solution was prepared by mixing 12.7g of iodine and 19.1g of potassium iodide (KI) in a beaker. Small amount of water was added while stirring until the total volume was 50 to 60mL. Then solution was allowed to stand for 4h to ensure that all crystals are thoroughly dissolved. Finally quantitatively transfer to a 1-L volumetric flask, filled to the mark with distilled water and stored in an amber bottle.

3.1.2 Experimental Design for Preparation Activated Carbon

For determination of independent process variables involved in preparation of coffee husk based activated carbon and their interaction affecting the characteristic of AC prepared, RSM method based on Box-Behnken design was applied. The effect of activating agent concentration, impregnation ratio (weight of activating agent to weight of coffee husk), carbonization temperature and holding time were analyzed as main factor variable. Independent process variables involved in activation/carbonization process and their experimental levels were presented in Table 2. In RSM for response IN and Yield, a model was defined that can predict the individual and interaction effect of different parameters. The coded values of independent variables were found from equation:

$$\chi_i = \frac{X_i - X_0}{\Delta X}, \qquad i = 1, 2, 3, \dots, k \qquad \textbf{Eq. 1}$$

Where χ_i is the dimensionless value of an independent variable; X_i is the real value of an independent variable; X_0 is the value of X_i at the center point; and ΔX is the step change. \

In RSM for response IN and yield, a model was defined that can predict the individual and interaction effect of different parameters. General form of a quadratic model for four variables as presented below was used.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j + \varepsilon \qquad \textbf{Eq. 2}$$

Where Y = predicted response, β_0= constant coefficient, β_i = linear effect coefficients, β_{ii}= quadratic effect coefficients, β_{ij} =interaction effect coefficients, x_i= independent variables

The optimum values of the factors were obtained by solving the regression equation, analyzing the surface of the three-dimensional response surface plot, and also by the setting up of constraints for the levels of the variables. The goal fixed for the degradation was to produce coffee husk activated carbon process for a minimum concentration of activating agent, impregnation ratio, holding time, and carbonization temperature, so as to maximize IN and Yield to be cost effective.

Table 1: Independent variables range and level

Variable		Unit	Range and Level		
			-1	0	+1
Concentration of activating agent (H_3PO_4)	A	M (mole)	3	5	7
Impregnation Ratio	B	-	1	2	3
Temperature	C	^oC	500	600	700
Holding Time	D	min	30	60	90

Coffee husk was collected from Arba Minch local coffee processing unit. It was washed thoroughly many times with distilled water and boiled at 105°C in dry oven for 1hr to remove dirt and color. Dried coffee husk was grounded to 750µm, sieved by 500µm. Then of 100g prepared coffee husk was taken and impregnated in flask with H_3PO_4, at given concentration and impregnation ratio for 24. After the reaction subsided, the materials were dried in 105ºC for a

period of 24 hours. The dried masses were washed with excess of distilled water to remove the free acid residues. Then the masses were dried at 105ºC, and finally carbonized at respective carbonization temperature and holding time in a horizontal cylindrical furnace with continuous Nitrogen flow of 10 mL/min and heating rate of 10^{o}C/min.

3.2 Characterization study (specific objective-2)

3.2.1 Iodine Number

The iodine number determination was according to the ASTM D4607-94 method. Sample of AC was treated with 10.0mL of 5% HCl, and then the mixture was boiled for 30s and cooled. Then 100.0mL of 0.1N iodine solution was added to the mixture and stirred for 30s. The resulting solution was filtered and 50.0mL of filtrate was titrated with 0.1N sodium thiosulfate using starch as indicator. The Iodine amount adsorbed per gram of carbon (X/M) was plotted against the iodine concentration in the filtrate (C), using logarithmic axes. If the residual iodine concentration (C) was not in range of 0.008 to 0.04, the whole procedure was repeated using different carbon masses. The iodine number is the X/M value when the residual concentration is 0.002N. The X/M and C value were calculated equation 1 and 2 respectively.

$$X/M = \frac{(N_1 * 126.93 * v_1) - \left[(v_1 + v_{HCl})/v_F\right]}{M_c} * \frac{(N_{Na_2S_2O_3} * 126.93) * v_{Na_2S_2O_3}}{M_c} \quad \textbf{Eq. 3}$$

$$C = \left(N_{Na_2S_2O_3} * V_{Na_2S_2O_3}\right) \quad \textbf{Eq. 4}$$

Where; N_1 is the iodine solution normality, V_1 is the added volume of iodine solution, V_{HCl} is the added volume of 5% HCl, V_F is the filtrate volume used in titration, $N_{Na_2S_2O_2}$ is the sodium thiosulfate solution normality, $V_{Na_2s_2O_3}$is the consumed volume of sodium thiosulfate solution and M_c is the mass of activated carbon.

3.2.2 Methylene Blue Number

The procedure described by ASTM D2330 was applied for MB number determination (American Society for Testing Materials, 2000). MB (0.15g) was weighed and dissolved in 100ml de-ionized water. The activated carbon samples (0.1g) each were weighed and transferred into 50ml

stoppered flask. 10ml MB solution was added from a burette and the mixture shaken for 5 minutes. Once the 10ml solution was decolorized, MB solution was added 1ml at a time until there was no further decolorization. The end point was considered to be reached when the blue color persisted for 5 minutes. The amount of MB adsorbed was calculated as follows:

$$\text{MB number } \left(\frac{\text{mg}}{\text{g}}\right) = \frac{15 \times \text{V}}{10 \times \text{m}} \qquad \textbf{Eq. 5}$$

Where, V= Volume of the methylene blue solution consumed (ml) m= Mass of activated carbon sample used for the test (g)

3.2.3 Carbon Yield

The total yields were determined after sample processing in terms of raw material mass. The dried weight, W_o of each pre-treated sample was determined using Metler balance and the carbon yield calculated as;

$$Y_{ch} = \frac{w_f}{w_o} * 100\% \qquad \textbf{Eq. 6}$$

Where: w_o is dry weight before chemical impregnation and w_f is dry weight of produced coffee husk activated carbon.

3.2.4 Proximate Analysis

Moisture content; Moisture content was determined according to ASTM 2867-99. Each AC sample (2g) was weighed and dried in a furnace continuously. The drying sample was constantly reweighed at a 10 mins interval until a constant weight (W_p) was obtained. The crucible and its content was retrieved and cooled in desiccators. The difference in weight (∂W) was recorded and the moisture content (MC) calculated from Eq. (1) as loss in weight on drying divided by initial weight of carbon multiplied by 100.

$$\text{MC} = \frac{\text{W}_\text{o} - \text{W}_\text{p}}{\text{W}_\text{o}} * 100\% \qquad \textbf{Eq. 7}$$

Where W_p= weight of Carbon retrieved from the furnace and W_o= initial dry weight of the AC sample.

Volatile content and Ash content: The volatile ash content of activated carbon is the non combustible residue left after burning samples at 750-800°c for 0.5h in muffle furnace. Ash content determination was done according to the ASTM D2866-94 method. Dry AC sample (1.0g) was placed in to a porcelain crucible and transferred into a preheated muffle furnace set at a temperature of 1000^{o}C. The furnace was left on for one hour after which the crucible and its content was transferred to desiccators and allowed to cool. The crucible and content was reweighed and the weight lost was recorded as the ash content of the AC sample (W_{ash}). Then the % ash content (dry basis) was calculated from the equation;

$$\text{Ash cont.} = \frac{W_{ash}}{W_o} * 100\% \qquad \textbf{Eq. 8}$$

$$\text{Volatile Content}(\%) = \frac{W_o - W_{ash}}{W_o} * 100\% \qquad \textbf{Eq. 9}$$

Where W_o is the dry weight of carbon sample before ashing.

Fixed Carbon: Fixed Carbon was determined by assuming that the sulphur content was negligible in all cases the fixed carbon content (FC) was given as:

$$\text{FC} = 100\% - \text{MC} - \text{VC} \qquad \textbf{Eq. 10}$$

Where; Y_{ch}= carbon yield (%), MC= Moisture Content (%), VC=Volatile Content (%), Ash= ash content (%)

3.2.5 pH and Conductivity

The pH and conductivity were determined according to the method of ASTM D3838-80 with slight modification as follows; 1.0 g of carbon activated carbon sample was weighed and transferred into a 250 mL beaker and 100 mL of distilled water was added and stirred for1 hour. Samples were allowed to stabilize and then pH measured using an electronic pH/Conductivity meter, Jenway 430 Model. The same samples were further used for electrical conductivity (EC) of the ACS and results read off in mS.

3.2.6 Pore Volume

Each AC sample (1g) was immersed in water and boiled for 15 minutes in order to displace air from the pores. The samples were superficially dried and reweighed. The pore volume was calculated as increase in weight (∂w) divided by the density (ℓ) of water at 20^{o}C using equation

$$\text{Pore Volume} = \frac{\partial w}{\iota_{t20}} \qquad \textbf{Eq. 11}$$

3.2.7 Bulk Density and Porosity

A cylinder and an aluminium plate were each weighed. A sample of activated carbon was placed into the cylinder, reweighed and transferred into the aluminium plate and then oven dried to a constant weight at a temperature of 105^{o}C for 60 mins. The weight of dry sample was recorded after drying. A cleaned, dried well-cooked density bottle was weighed. A small quantity of sample of activated carbon was taken and ground to powder; sieved using 110 µm mesh size, and gradually put into the density bottle with a little amount of water added and weighed. The volume of void (V_v) was obtained by first determining the total volume of the cylinder used for the experiment and also determining the volume of the AC used:

The volume of void (V_v) was obtained as;

$$V_v = V_{\text{cylinder}} - V_{\text{activated carbon used}} \qquad \textbf{Eq. 12}$$

The bulk density and porosity were calculated as;

$$\text{Bulk density} = \frac{\text{mass of carbon sample}}{\text{volume}} \qquad \textbf{Eq. 13}$$

$$\text{porosity}(\eta) = \frac{\text{volume of void}}{\text{total volume}} \qquad \textbf{Eq. 14}$$

3.2.8 Zero point charge (P^{H}_{zpc})

The Isoelectric point or Zero point charge (P^{H}_{zpc}) of the carbon samples were measured by using the method described by Durán-Valle (2012). A known quantity of a series of 13 $NaNO_3$ solutions having the initial pH values ranging from 1 to 7 with 0.5 increment were prepared in duplicate using dilute HCl and dilute NaOH. While in one duplicate 0.5g of coffee husk activated carbon was added and mixed for a specified period of time. Then the solutions were

filtered off and the activated carbon was separated. The final pH values of the ten solutions were measured and thereby calculation of ΔpH was made by subtracting the initial pH values from final pH values. The graph was drawn by plotting the final pH values against ΔpH. From the graphs plotted, the pH_{zpc} (point of zero charge) of the Nanoporous activated carbon was determined.

3.2.9 FT- IR (Fourier Transform Infrared spectrometry)

The FTIR study was conducted on activated adsorbent sample to determine the various organic and inorganic groups on the surface before adsorption. Then FTIR was also conducted after adsorption so that the organic and in organic group which participate in the adsorption process was determined by watching the change in frequency occurred due to adsorption of chrome on adsorbent.

3.3 Bach Adsorption Study (specific objective-3)

Bach adsorption experiments were conducted by to investigate parametric effect of pH, contact time, and initial Cr(VI) concentration. The effect of pH on the Cr(VI) adsorption onto coffee husk activated carbon was studied at pH range of 1 to 8. For this study 100mL of Cr(VI) solution with initial concentration of 100mg/L, was taken in 250mL Erlenmeyer flasks and pH was adjusted to pH of 1-8 using required quantity of 1 N HCl (or) 1 N NaOH before mixing the adsorbent. Then 0.5g of coffee husk activated carbon was added to the solution and agitated at 200rpm in a thermostat water bath shaker at 35^{o}C of temperature. To examine effect of contact time and initial Cr(VI) concentration, 200ml of Cr(VI) solution with different initial Cr(VI) concentration, (100, 200, and 300mg/L) was taken in 250mL conical flask and pH was adjusted to 2. Then 0.5g of coffee husk activated carbon was added and the solution was agitated at rate of 200rpm in thermostatic shaker set at 35^{o}C. Cr(VI) was determined from the sample taken from the solution at time interval of 1, 2, 3, 4, 6, and 8 hours.

3.3.1 Kinetic Study

Kinetic study was conducted by taking 200mL of Cr(VI) solution with initial concentration of 100mg/L in 250mL Erlenmeyer flasks and adjusting the pH to 2. Then 0.5g of coffee husk

activated carbon was added and the solution was agitated at 200rpm in thermostat shaker at 25, 35 and 45^{o}C. Solution was sampled at time interval of (1, 2, 3, 5, and 8h) and analyzed. Experimental data were analyzed against kinetic models, which explain the mechanism of the adsorption processes. The kinetics of Cr(VI) adsorption on coffee husk activated carbon were analyzed using pseudo first-order (Lagergren, 1898), pseudo second-order (Ho *et al*., 2000), Elovich (Chien and Clayton, 1980, Sparks, 1986), and intraparticle diffusion (Weber and Morris, 1963, Srivastava *et al*., 1989) kinetic models.

3.3.2 Isotherm Study

Equilibrium isotherms were studied by taking 100mL of Cr(VI) solution (50 - 500mg/L) in 250mL Erlenmeyer flasks and solution pH was adjusted to 2. The 0.5g of coffee husk activated carbon was added to the solution and agitated at 200rpm for 8 h (equilibrium time) in thermostat shaker at temperature of 25, 35, and 45^{o}C. To establish the adsorption capacity of coffee husk activated carbon experimental data was fitted against two parameter isotherm equations such as Langmuir, Freundlich,, Tempkin, and Dubinin–Radushkevich (D-R) isotherm equations.

3.3.3 Analysis of Cr(VI) and Statistics

After predetermined contact time adsorbent was decanted and separated from the solution using filter paper (using 0.45mm membrane filter) and the filtrate analyzed. For this purpose a 0.25% (w/v) solution of 1,5-diphenylcarbazide was prepared in acetone. Each sample solutions (15mL) containing various concentrations of Cr(VI) were pipette out into 25mL standard flasks. To this 2mL of 3 M H_2SO_4 was added followed by 1 mL of 1-5 diphenylcarbazide and total volume was made up to 25mL using distilled water. Cr(VI) concentrations estimated by the intensity of the brownish-red color complex formed, was measured using UV -spectrophotometer (Perkin-Elmer lambda 950 UV/VIS Spectrometer) at 540nm (APHA *et al*., 1998).

The amount of Cr(VI) adsorbed on the carbon surface was determined by mass balance equation.

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad \textbf{Eq. 15}$$

Percentage adsorption was calculated according to the expressions:

$$\%\ \text{Adsoption} = \frac{(C_0 - C_t)}{C_0} \qquad \textbf{Eq. 16}$$

Where q_t (mg/g) is the amount of chromium adsorbed per unit mass of adsorbent; C_t and $C_0(\text{mgL}^{-1})$ are the liquid phase and initial concentration of concentrations of metal ion respectively. V the volume of solution (L), m is the mass of the carbon material (g).

In isotherm, and kinetic studies, the conformity between experimental data and the model predicted values was expressed by the correlation coefficients (r^2) and Chi-square analysis. The advantage of using Chi-square test was comparing all isotherms on the same abscissa and ordinate. The equivalent mathematical statement was;

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \qquad \textbf{Eq. 17}$$

Where $q_{e,m}$ equilibrium capacity obtained by calculated from model (mg/g) and q_e was the equilibrium capacity (mg/g) from the experimental data. If data from model were similar to the experimental data, χ^2 would be a small number and vice versa.

4. Result and Discussion

Result and discussion is presented in three consecutive parts based on the stated specific objectives as follows;

First, it was found to be important to prepare AC with good adsorptive property and reasonable yield. However these two properties depend on level and combination of operational parameters involved in production of activated carbon. Thus the first objective of this research addresses this issue by identifying process parameters which result optimum adsorptive capacity which is indicated by Iodine Number of prepared activated carbon and yield. This is carried out by the application of Response Surface Methodology to model and optimize the process parameters involved in preparation of coffee husk activated carbon by chemical activation using H_3PO_4.

Second, it is important to characterize activated carbon prepared. Activated carbon characteristics, Iodine Number and yield which are used in optimization study are not enough to fully understand the activated carbon produced. The standard method of characterization of surface area and pore volume are important. Thus, second objective of this research is intended to fully characterize activated carbon produced at optimized operational conditions.

Third, as engineering (applied) research, this study address application of produced activated carbon for adsorptive removal model environmental pollutant. Cr (VI) is selected as model environmental pollutant. Thus, objective three is intended to address potential application of produced activated carbon for adsorptive treatment of Cr (VI) through batch adsorption isotherm study.

4.1 Optimization Process

The effect of concentration of H_3PO_4, impregnation ratio, carbonization temperature and holding time on IN and yield of coffee husk activated carbon was analyzed. RSM was applied to model and optimize different process parameters in the preparation of coffee husk activated carbon. Operational parameters with optimum IN and yield were predicted using developed model. Accordingly, first, model development and evaluation was discussed. Second, the effect of

independent variables on response variables was examined. Then finally using the model optimum points of operational parameters were predicted.

4.1.1 Development and Evolution of Prediction Model

Twenty five unique experimental conditions and five central replicate, total of twenty nine experimental runs were carried out. Each of experimental runs was conducted according to procedure described above in methodology part. For each of the experimental runs IN and Yield was determined using the methodology described. Experimental result of IN and yield were fed to design expert soft ware for multiple regression fitting. Quadratic polynomial model was fitted with backward elimination regression with alpha to exit = 0.10.

Table 2: Sequential Model Sum of Squares [Type I] for IN and MBN

	Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Iodine Number	Mean vs Total	7096818	1	7096818			
	Linear vs Mean	223227.5	4	55806.88	65.25623	< 0.0001	
	2FI vs Linear	5711.5	6	951.9167	1.156704	0.3713	
	Quadratic vs 2FI	**11448.92**	**4**	**2862.231**	**11.91078**	**0.0002**	**Suggested**
	Cubic vs Quadratic	2181.5	8	272.6875	1.383284	0.3561	Aliased
	Residual	1182.783	6	197.1306			
	Total	7340570	29	253123.1			
Yield	Mean vs. Total	5.561724	1	5.561724			
	Linear vs. Mean	0.149983	4	0.037496	45.23809	< 0.0001	
	2FI vs. Linear	0.00285	6	0.000475	0.501686	0.7990	
	Quadratic vs. 2FI	**0.012648**	**4**	**0.003162**	**10.07198**	**0.0005**	**Suggested**
	Cubic vs. Quadratic	0.003517	8	0.00044	3.002846	0.0987	Aliased
	Residual	0.000878	6	0.000146			
	Total	5.7316	29	0.197641			

The sequential model sum of squares is presented in Table 3. Model summary statistics is presented in Table 4. The Box-Behnken experimental matrix, experimental and predicted values of IN and yield obtained under different experimental conditions are presented in Table 5. Analysis of variance is presented in Table 6. Residual plots and 3D and contour plots are presented in Fig 1-6.

Sequential Model Sum of Square (Type I) selected the highest order polynomial where the additional terms are significant and the model is not aliased. From sequential model sum of squares (Table 3) it was found that quadratic model was the most suitable model to describe effect of selected process condition in preparation of coffee husk activated carbon on both IN and yield of produced coffee husk activated carbon. The final obtained equation for prediction of both response variables based on coded factor was as follows;

$$IN\left(\frac{mg}{g}\right) = +485.27 + 46.08 * A + 57.00 * B + 101.33 * C + 54.42 * D + 20.25 * A * B - 24.75 * B * D + 18.00 * C * D - 21.79 * B^2 + 21.71 * C^2 + 22.84 * D^2 \quad \text{Eq. 18}$$

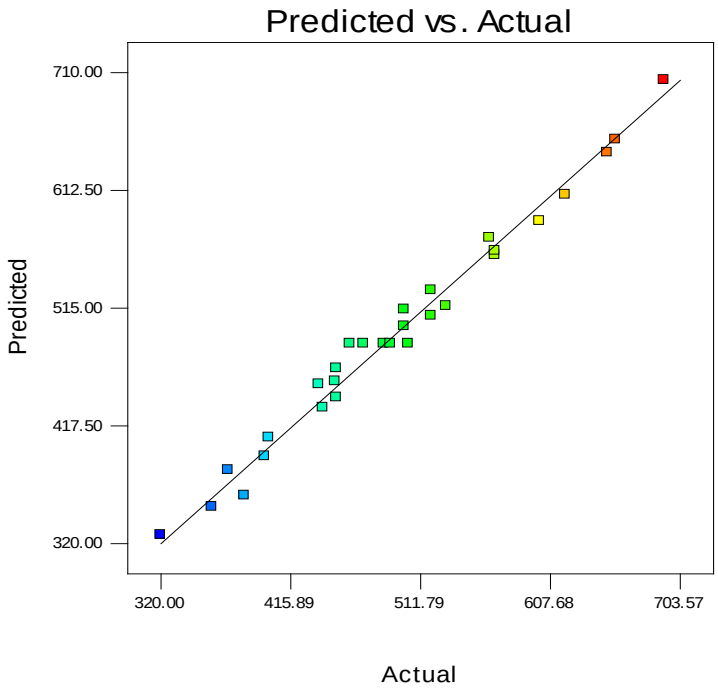
$$Yield(\%) = 0.45 + 0.02 * B - 0.07 * C - 0.085 * D + 0.02 * C * D + 0.02 * B^2 - 0.033 * C^2 - 0.0 \quad \text{Eq. 19}$$

Table 3: Model Summary Statistics of both general and reduced model

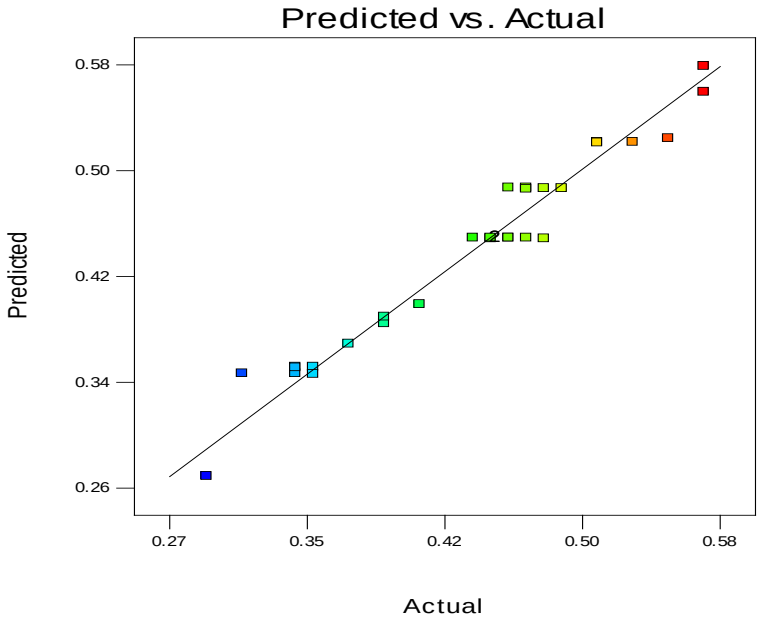
	General model		Reduced model	
	IN	Yield	IN	Yield
R-Squared	0.98	0.96	0.98	0.97
Adj R-Squared	0.97	0.94	0.97	0.94
Pred R-Squared	0.95	0.92	0.94	0.86
Adeq Precision	41.57	33.56	33.78	24.32
Mean	494.68	0.43	494.68	0.43
Std. Dev.	14.71	0.01	15.50	0.01
C.V. %	2.97	4.01	3.13	4.04
PRESS	11227.65	0.01	14588.09	0.02

Table 4: The Box-Behnken design of experimental matrix with experimental and predicted value

Std. no	Coded Factor				Actual Factor				IN (mg/g)			Yield		
	A	B	C	D	CA (M)	IR (w/w)	CT (^{o}C)	HT (Min)	Exp. Value	Prd. value	Residual	Exp. Value	Prd. valu	Residual
1	-1	-1	0	0	3	1	600	60	370	380	-10.65	0.47	0.47	0.00
2	1	-1	0	0	7	1	600	60	440	432	7.68	0.5	0.47	0.03
3	-1	1	0	0	3	3	600	60	449	454	-5.15	0.43	0.44	-0.02
4	1	1	0	0	7	3	600	60	600	586	13.18	0.42	0.44	-0.03
5	0	0	-1	-1	5	2	500	30	397	392	4.93	0.57	0.58	-0.01
6	0	0	1	-1	5	2	700	30	567	559	8.26	0.41	0.4	0.01
7	0	0	-1	1	5	2	500	90	450	465	-14.90	0.37	0.37	0.00
8	0	0	1	1	5	2	700	90	692	704	-11.57	0.29	0.27	0.02
9	-1	0	0	-1	3	2	600	30	400	407	-7.61	0.53	0.52	0.01
10	1	0	0	-1	7	2	600	30	500	499	0.23	0.51	0.52	-0.01
11	-1	0	0	1	3	2	600	90	531	516	14.56	0.35	0.35	0.00
12	1	0	0	1	7	2	600	90	619	608	10.39	0.34	0.35	-0.01
13	0	-1	-1	0	5	1	500	60	320	327	-6.86	0.49	0.5	-0.02
14	0	1	-1	0	5	3	500	60	450	441	9.14	0.5	0.47	0.03
15	0	-1	1	0	5	1	700	60	520	530	-9.53	0.37	0.37	0.00
16	0	1	1	0	5	3	700	60	650	644	6.47	0.35	0.34	0.01
17	-1	0	-1	0	3	2	500	60	382	359	22.43	0.48	0.49	-0.01
18	1	0	-1	0	7	2	500	60	437	451	-14.73	0.49	0.49	0.00
19	-1	0	1	0	3	2	700	60	567	562	4.77	0.34	0.35	-0.01
20	1	0	1	0	7	2	700	60	656	654	1.60	0.31	0.35	-0.04
21	0	-1	0	-1	5	1	600	30	358	350	7.85	0.54	0.54	-0.01
22	0	1	0	-1	5	3	600	30	500	514	-13.65	0.52	0.51	0.01
23	0	-1	0	1	5	1	600	90	520	509	11.51	0.36	0.37	-0.01
24	0	1	0	1	5	3	600	90	563	573	-9.99	0.33	0.34	0.00
25	0	0	0	0	5	2	600	60	480	484	-25.27	0.46	0.45	0.01



(a)



(b)

Figure 1: Predicted Vs. Actual plot of for response variables iodine number (a) and yield (b)

To assess the adequacy of a model, the coefficient of determination (R^2) and the lack of fit test were commonly used. Coefficient of determination (R^2) refers to the changes described by the model to the overall changes. Therefore, whatever R^2 is closer to 1, the power of fitted model is greater to describe the response changes as a function of the independent variables.

From the Model Summary Statistics (Table 4) it can be seen that the regression coefficient of the quadratic model developed for IN is 0.984 which shows that the model adequately explains 98.4% of the variation and also the R^2 adj. of 0.975 is in reasonable agreement with the pred. R^2 of 0.953 for the quadratic model. Similarly the value of R^2 (0.961) of yield model is significant explaining 96.17 % of variability in yield. Also the "Pred R-Squared" of 0.9210 is in reasonable agreement with the "Adj R-Squared" of 0.94 for yield.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. As can be seen from model summary statistics (Table 4), this ratio is 41.57 and 33.56 for IN model and yield model respectively indicating an adequacy of signal. Which in turn asserts that both models can be used to navigate the design space.

The ANOVA result (Table 5) shows that the Model F-value of 110.78 (IN) and 75.48 (yield) implies both models are significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. The associated p value is used to estimate whether F is large enough to indicate statistical significance. The values of p > F, less than 0.05 indicates that the model is considered to be statistically significant whereas values greater than 0.05 indicate the model terms are not significant.variable.

Regarding this, both models are statistically significant at level of p-value <0.0001. The ANOVA result also presented p- values of individual model terms. According to the result all four linear terms, interaction of acid concentration and impregnation ratio, impregnation ratio and holding time, carbonization temprature and holding time and second order terms of acid concentration, carbonization temprature, and holding time (A, B, C, D, AB, BD, CD, B^2, C^2, D^2) are significant model terms in IN medel. Whereas linier terms of impregnation ratio, carbonization temprature and holding time, interaction between carbonization temprature and

holding time and second order terms of impregnation ratio and carbonization temprature (B, C, D, CD, B^2, C^2) are significant model terms in yield model.

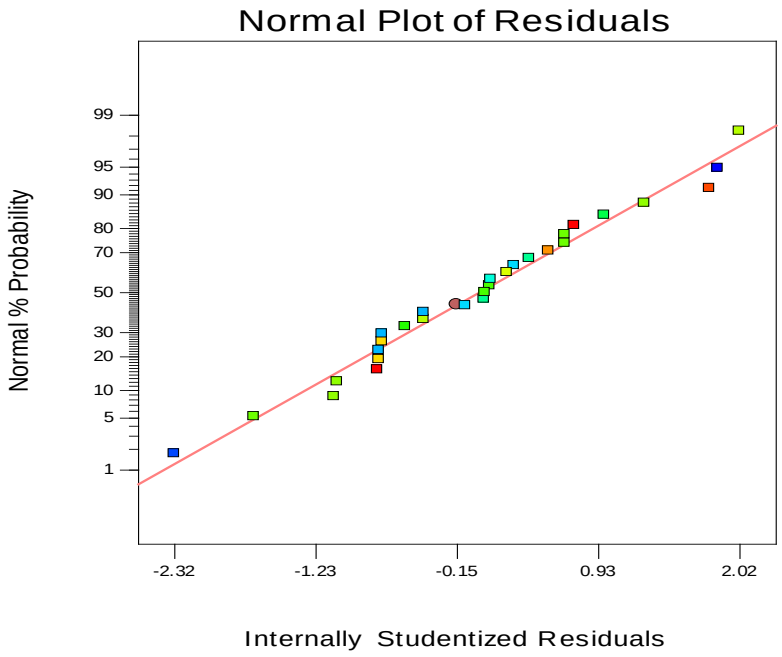
Table 5: Analysis of variance (ANOVA) table for IN and Yield

	Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Iodine Number	**Model**	**239855.2**	**10**	**23985.52**	**110.7888**	**< 0.0001**	**Significant**
	A-Concentration of H_3PO_4	25484.08	1	25484.08	117.7106	< 0.0001	
	B-Impregnation Ratio	38988	1	38988	180.085	< 0.0001	
	C-Carbonization Temp.	123221.3	1	123221.3	569.1576	< 0.0001	
	D- Holding Time	35534.08	1	35534.08	164.1314	< 0.0001	
	AB	1640.25	1	1640.25	7.576291	0.0131	
	BD	2450.25	1	2450.25	11.31767	0.0035	
	CD	1296	1	1296	5.986205	0.0249	
	B^2	3193.305	1	3193.305	14.74983	0.0012	
	C^2	3171.555	1	3171.555	14.64937	0.0012	
	D^2	3508.722	1	3508.722	16.20674	0.0008	
	Residual	3896.959	18	216.4977			
	Lack of Fit	**2755.759**	**14**	**196.84**	**0.68994**	**0.7303**	**not significant**
	Pure Error	1141.2	4	285.3			
	Cor Total	243752.2	28				
Yield	**Model**	**0.163383**	**7**	**0.02334**	**75.48855**	**< 0.0001**	**Significant**
	B-Impregnation ratio	0.004408	1	0.004408	14.25762	0.0011	
	C- Carbonization Temp.	0.0588	1	0.0588	190.1735	< 0.0001	
	D- Holding Time	0.0867	1	0.0867	280.4089	< 0.0001	
	CD	0.0016	1	0.0016	5.174789	0.0335	
	B^2	0.00234	1	0.00234	7.566699	0.0120	
	C^2	0.00715	1	0.00715	23.12506	< 0.0001	
	D^2	0.001068	1	0.001068	3.454983	0.0771	
	Residual	0.006493	21	0.000309			
	Lack of Fit	**0.005973**	**17**	**0.000351**	**2.702723**	**0.1733**	**not significant**
	Pure Error	0.00052	4	0.00013			
	Cor Total	0.169876	28				

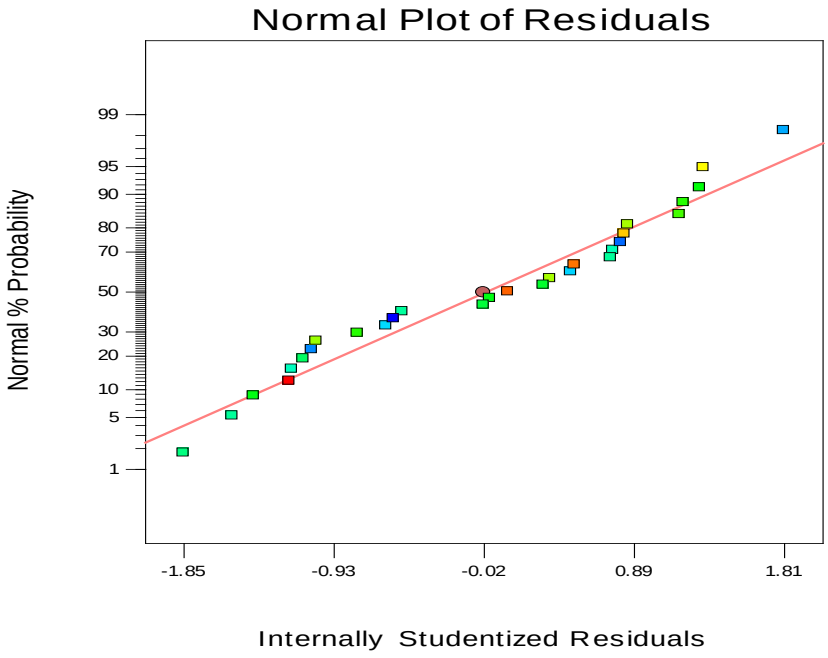
The ANOVA table also shows a term for residual error, which measures the amount of variation in the response data left unexplained by the model. Lack of Fit test showes that the "Lack of Fit F-value" of 0.69 (for IN) and 2.70 (for yield) which implies the Lack of Fit is not significant

relative to the pure error. There is a 73.03% (for IN) and 17.33% (for yield) chance that a "Lack of Fit F-value" this large could occur due to noise.

Model diagnosis was also conducted by cheking assumptions of normal distribution of error, abcense of constant error and outliers. Graphs of Normal probability plot of the studentized residuals to check for normality of residuals, Studentized residuals versus predicted values to check for constant error, and Externally Studentized Residuals to look for outliers were ploted.

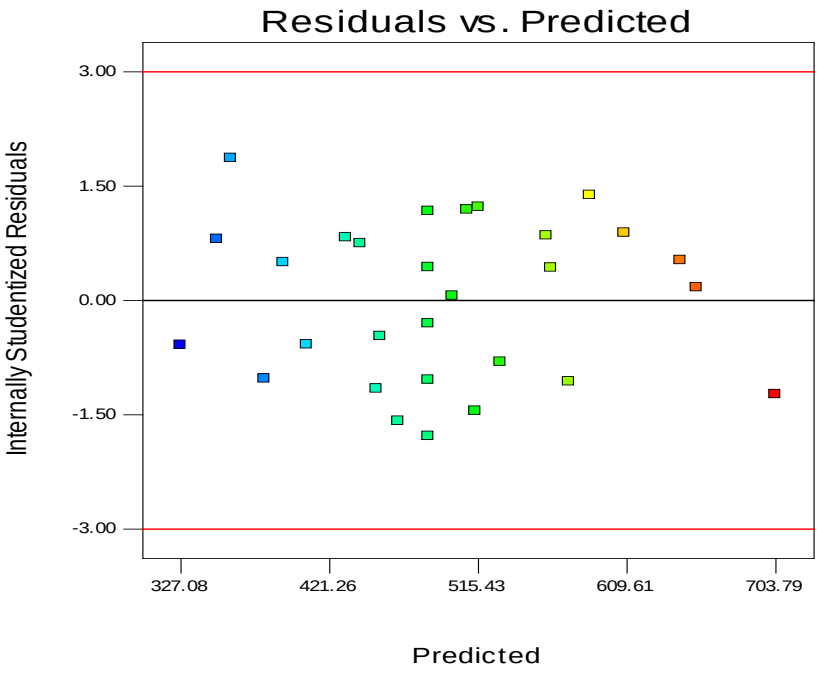


(a)

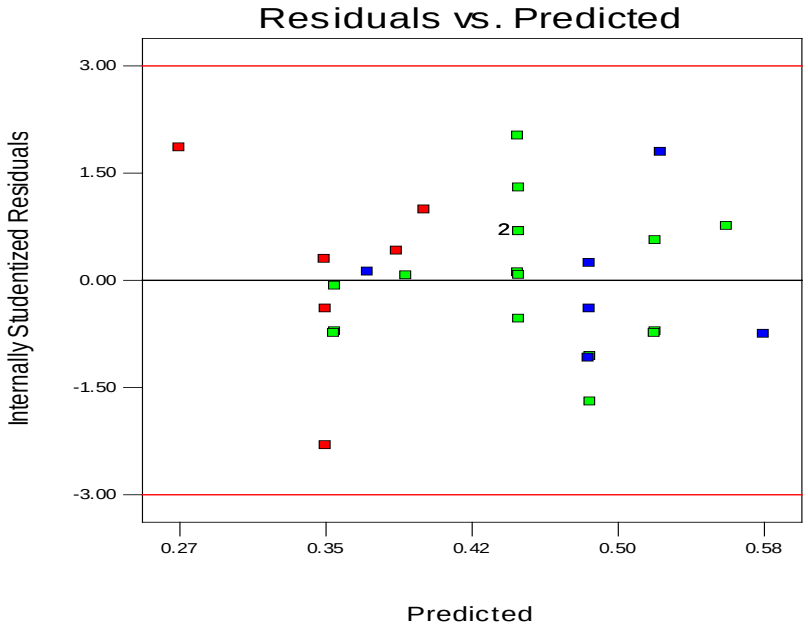


(b)

Figure 2: Normal probability plot for IN model (a) and Yield model (b), indicating meeting of normality assumption

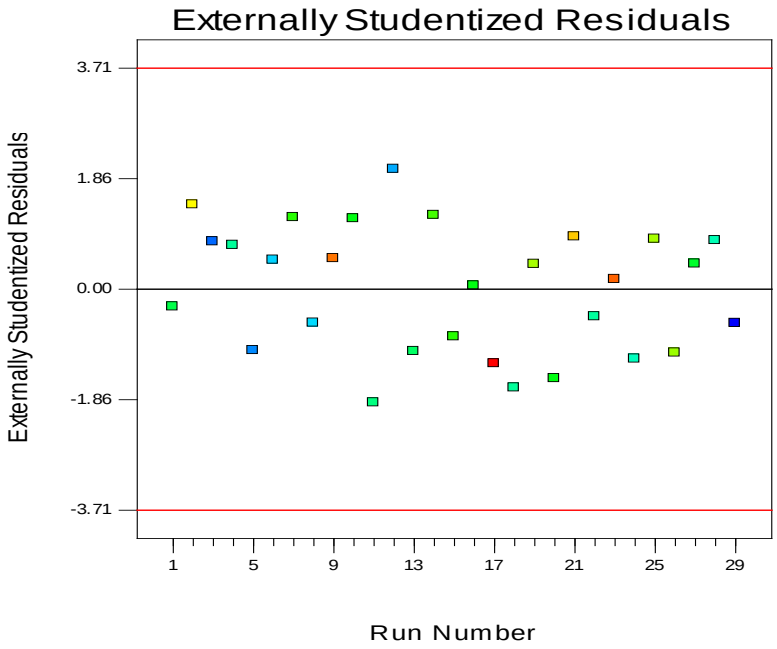


(a)

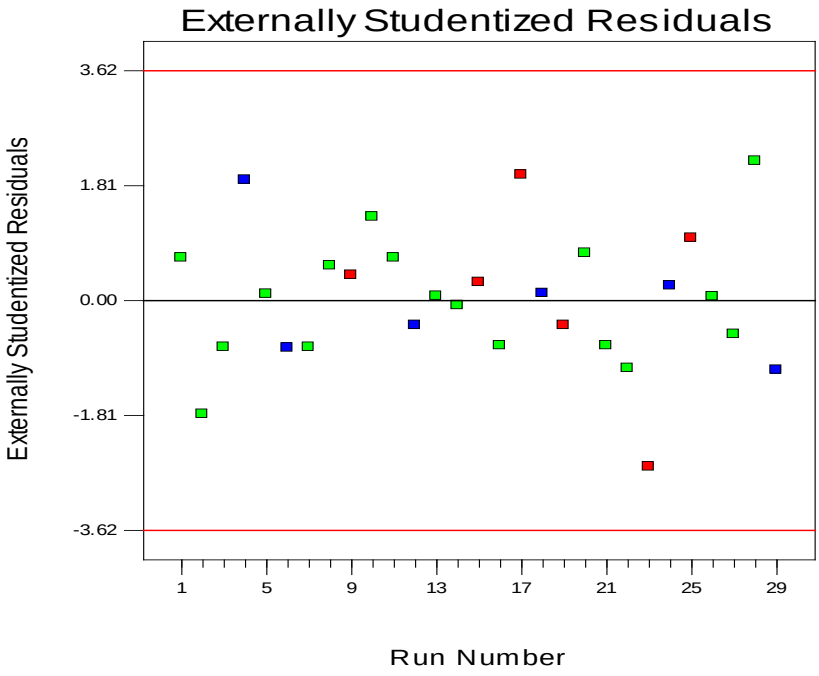


(b)

Figure 3: Residuals vs Predicted plot for IN model (a) and Yield model (b), assert absence of constant error



(a)



(b)

Figure 4: Externally Studentized Residuals plot for IN model (a) and Yield model (b) absence influential outlier outlier

4.1.2 Effect of Independent Variables on IN

According to Table 7, the linear effects of all four independent variables are significant (P< 0.**0001**). Thus, each variable in turn can effect the quality of coffee husk activated carbon. In the investigated experimental region IN increase with increase in all of the variables i.e all four indipendent variables have posetive effect on IN of the coffee husk activated carbon. Taking IN as direct indicator of surface area and pore volume, this result is suported by other researchs (Joao Valente Nabais *et al*., 2008).

Preturbation plot in Figure 4 is an important diagramatic representation to compare all effects of all factor at particular point in design space. The response is ploted by changing only one factor over its range while holding other factors constant. Steepy slope or curvature for a factor shows that response variable is sensitive to that factor. A relatively flat line shows insensetivity of response for that particular factor.

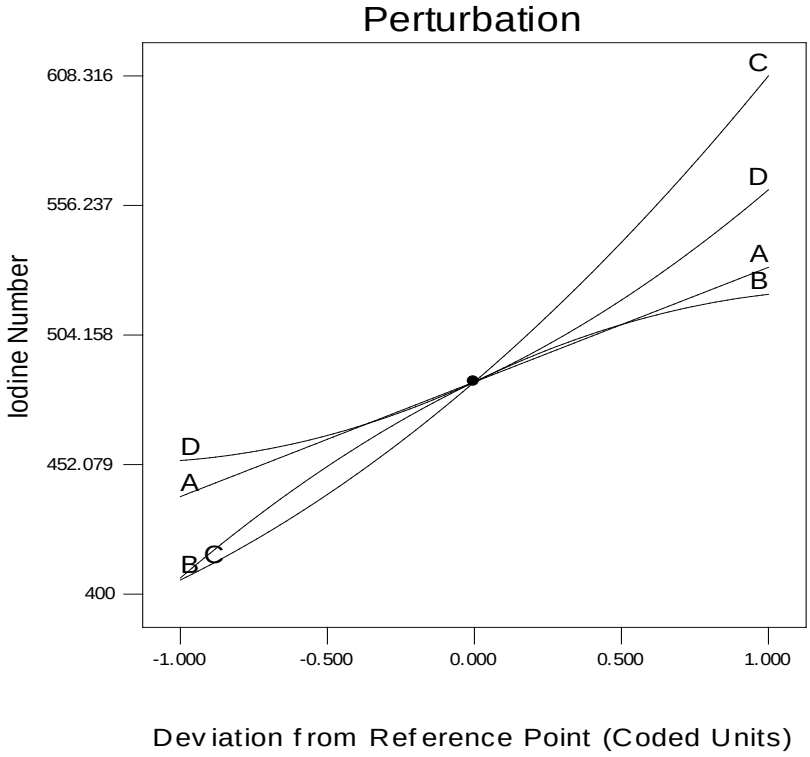
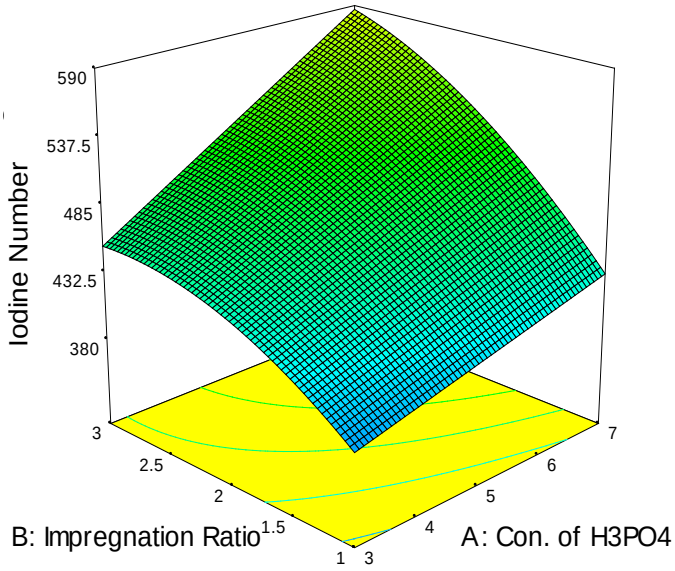


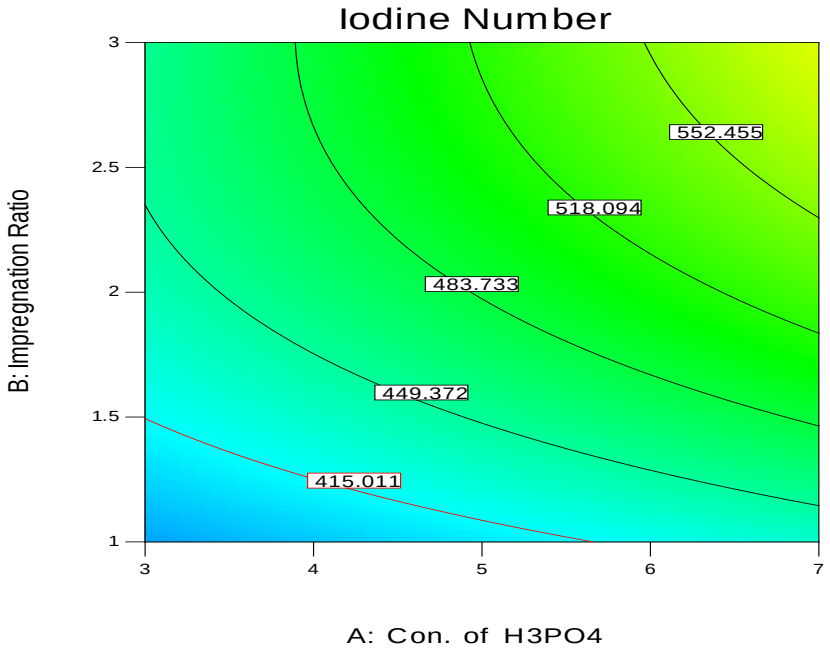
Figure 5: Perturbation plot depicting the effect of operational parameters for preparation of activated carbon on Iodine number of coffee husk activated carbon

The plot in Figure 4 depicted that all factores have positive effect on IN. It can be also seen that response variable is most sensetive to carbonization temprature followed by impregnation ratio. This can be also evidenced by ANOVA result. According to ANOVA result, the effect of impregnation ratio (F= 183.77, P-value < 0.0001) and carbonization temprature (F=580.83 P-value < 0.0001) is much more influontial than that of concentration of activating agent (F= 120.12) and holding time (F=167.49). The change in carbonizing temprature from 500^{o}C to 700^{o}C, changes IN from 404.8 mg/g to 608.5mg/g.

Second-degree effects of impregnation ratio and carbonization temprature are also significant. Factor interaction terms of carbonization temprature with concentration of H_3PO_4 and with impregnation ratio are also significant. Effect of factor interactions on IN is presented by three-dimensional and contour response surface plot as shown in Figure 5-7.

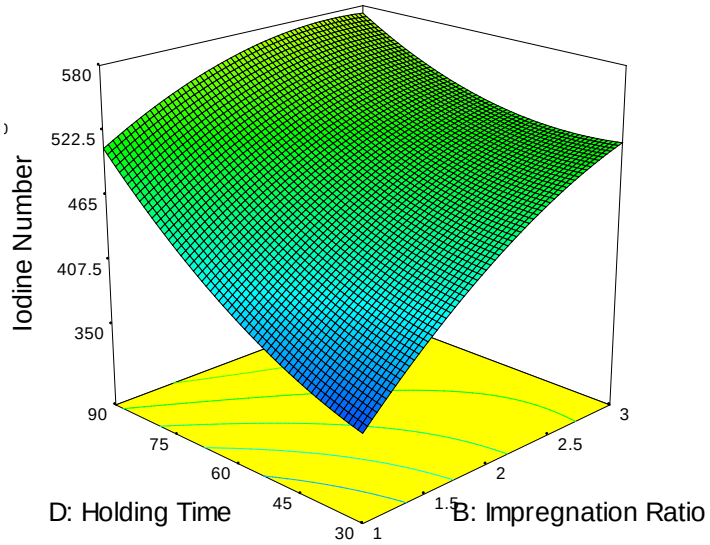


a

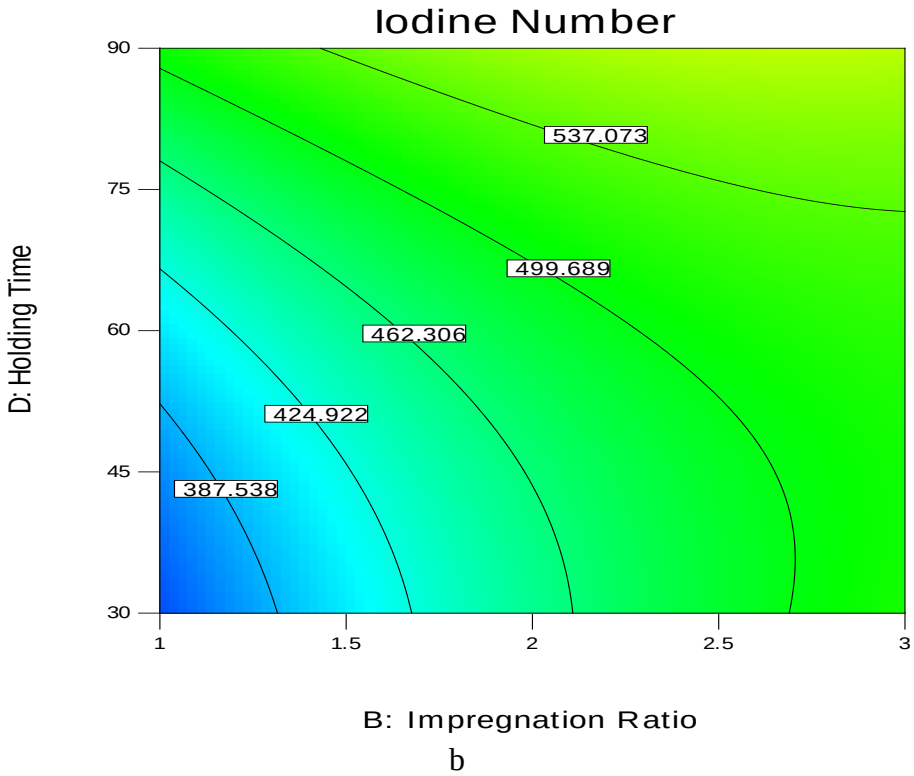


b

Figure 6: 3D (a) and contour (b) plot showing interaction effect of impregnation ratio and concentration of H_3PO_4 on IN of produced coffee husk activated carbon

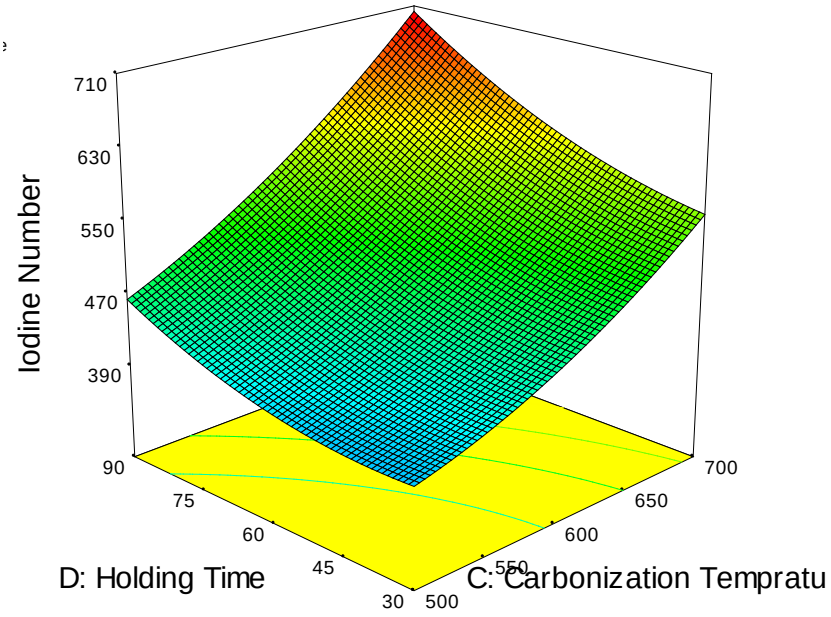


a

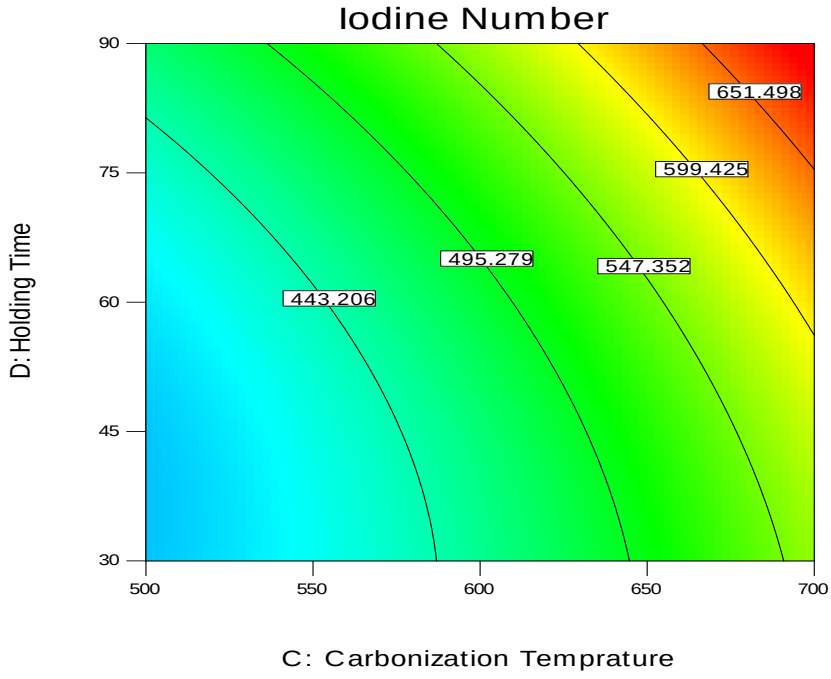


b

Figure 7: 3D (a) and contour (b) plot showing interaction effect of holding time and impregnation ratio on IN of produced coffee husk activated carbon



a



b

Figure 8: 3D (a) and contour (b) plot showing interaction effect of impregnation ratio and concentration of H_3PO_4 on IN of produced coffee husk activated carbon

4.1.3 Effect of Independent Variables on Yield

The ANOVA result presented in Table 6 shows impregnation ratio, carbonization temprature and holding time were significant (p-value <0.0001) linear terms affecting yield of coffee husk activated carbon. The second order effect of impregnation ratio and holding time was also significant at level of p value <0.001. This later two variables also exibit interaction effect (p-value= 0.033).

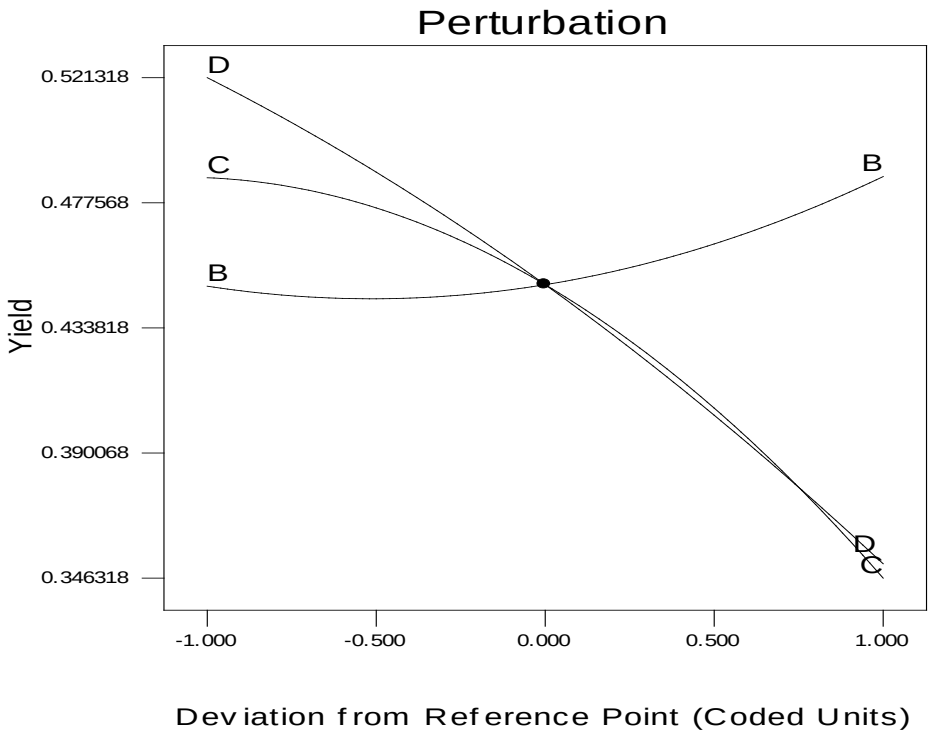
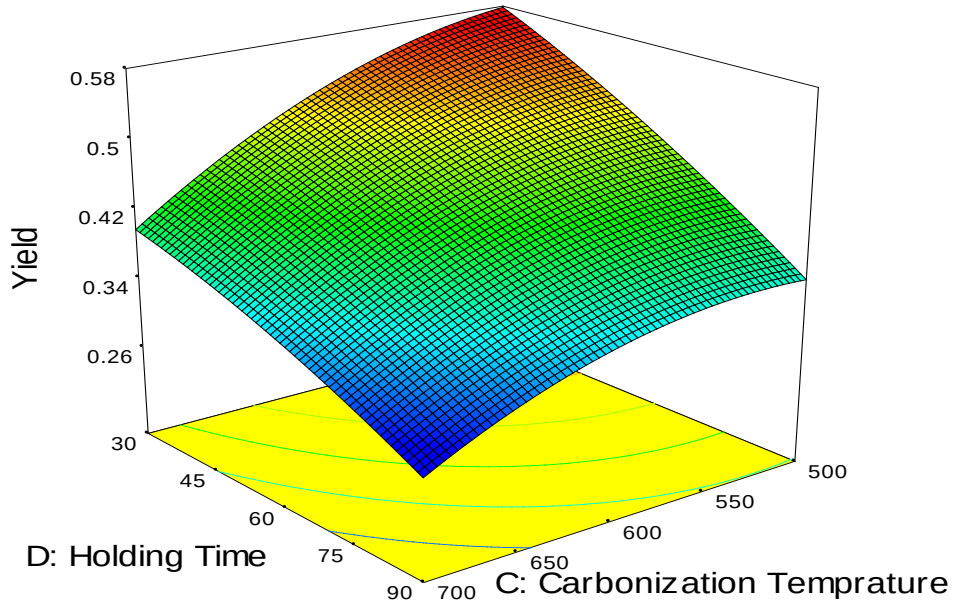
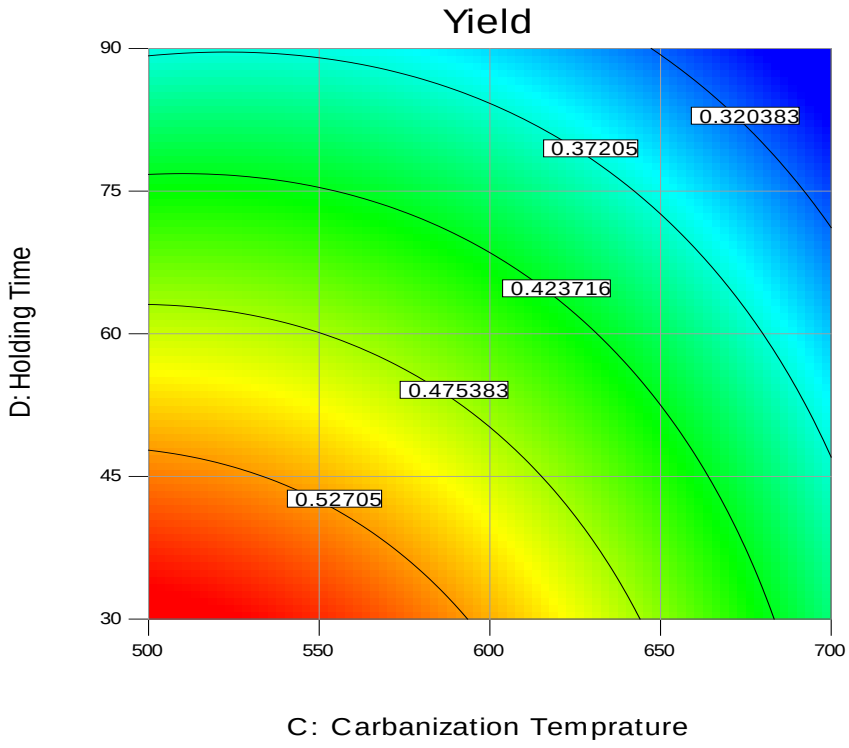


Figure 9: Perturbation plot depicting the effect of operational parameters for preparation of activated carbon on yield of coffee husk activated carbon

Perturbation plot shows that carbonization temprature and holding time exhibit negative effect while impregnation ratio had slightly positive effect on yield. This result is supported by findings of other research (Bouchelta *et al*., 2008, Xian-Fa Li *et al*., 2014, Metin Açıkyıldıza *et al*., 2014, Guo *et al*., 2005). At lower level, yield is sensitive to holding time than carbonization temperature but at higher level yield shows similar sensetivity for both holding time and carbonization temperature. For impregnation ratio yield shows insignificant sensitivity at lower level and sensitivity gradually increase as impregnation ratio increases. Interaction effect of carbonization temprature and holding time is presented in 3D and contour plot in Figure 9.



a



b

Figure 10: 3D (a) and contour (b) plot of interaction effect of carbonization temperature holding time on Yield

4.1.4 Process Optimization and Evaluation

One of the main objectives of RSM is the determination of the optimum settings of the control variables that result in a maximum (or a minimum) response over a certain region of interest (Khuri and Mukhopadhyay, 2010 , Anuradha Jabasingh and Pavithra, 2010).

Process parameters were optimized to IN and yield while minimizing consumption of activating agent which is attained at minimum concentration of the acid and impregnation ratio and power consumption for thermal treatment attained at minimum carbonization temperature and holding time. Predicted optimum values of process variables and optimized response variables were presented in Table 7. Accordingly, IN of 391.57mg/g and yield of 0.57 were determined at the optimum conditions of independent variables.

Table 6: Predicted optimum points

	Variable	Optimum value
1	Concentration of H_3PO_4	4.37M
2	Impregnation Ratio	2.02 W/W
3	Carbonization Temperature	527.08℃
4	Holding Time	**30.0** min
5	Iodine number Pred. Value	391.57m**g/g**
6	Yield	0.57

To validate the model five confirmation experiments were conducted at optimum point and varying one factor at time as shown in Table 8. The experimental result is fitted against predicted value as presented in the plot below. As shown in plots there is good agreement between the predicted and experimental results IN ($R^2 = 0.93$) and yield ($R^2 = 0.96$). This agreement validated the adequacy of models.

Table 7: Confirmation experimental set up and result

	Factor combination				IN (mg/g)		Yield	
	A	B	C	D	Pred.	Exp.	Pred.	Exp.
1	4	2	538	30	387.3289	363	0.564589	0.54
2	7	2	538	30	456.4539	431	0.564589	0.51
3	4	3	538	30	437.1665	442	0.602402	0.57
4	4	2	700	30	535.6949	513	0.398693	0.43
5	4	2	538	90	473.8393	447	0.369978	0.41

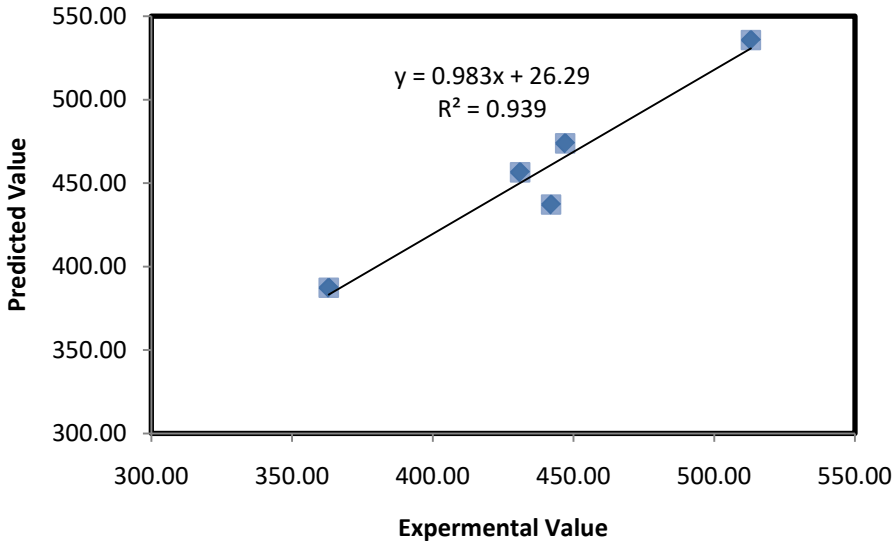


Figure 11: Experimental Vs Predicted Value for coffee husk activated carbon yield confirmation study

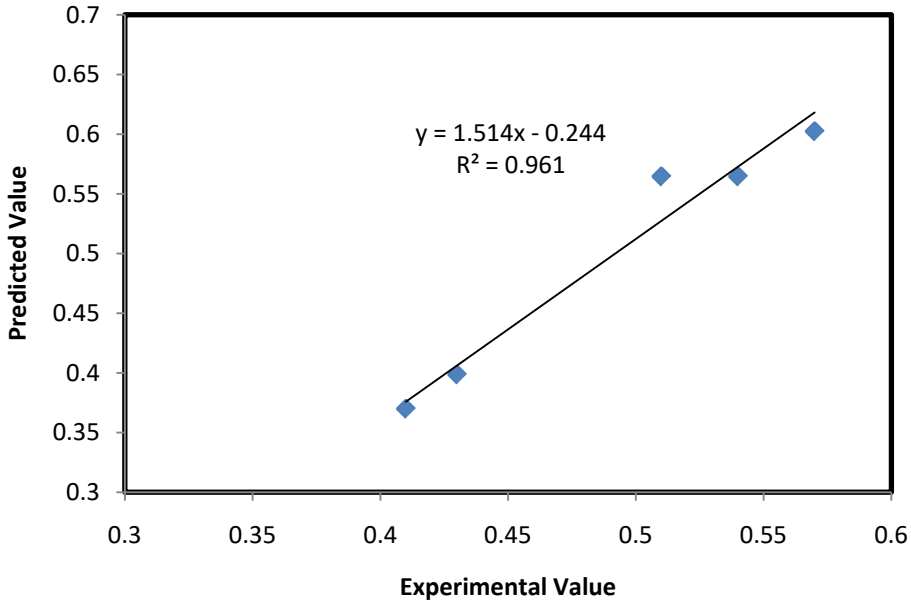


Figure 12: Experimental Vs predicted Value for coffee husk activated carbon yield in confirmation study

4.1.5 Concluding Remark on Modelling and Optimization

To conclude on this section; the section has presented Box-Behnken experimental design for modeling and process optimization, involving a study of a given system by set of variables over specific region of interest by identifying the influence of individual variable. By using this method, four effect variables including concentration of H_3PO_4, impregnation ratio, carbonization temperature and holding time were examined. A second-order polynomial model was developed using multiple linear regression analysis. Statistical test (ANOVA) indicated a good agreement between experimental data and the built model for prediction of IN and yield of coffee husk activated carbon. The optimal operating conditions were determined using numerical optimization techniques by desirability approach. The IN and yield of coffee husk activated carbon were optimized while minimizing consumption of activation agent and minimizing power consumption. Accordingly, H_3PO_4 concentration of 4.37M, impregnation ratio of 2.02, carbonization temperature of 527.08 ^oC and holding time 30 minutes were best conditions for coffee husk activated carbon production which optimize IN and yield of coffee husk activated

carbon. Under these conditions, IN of 391.57mg/g and yield of 0.57 were predicted. Confirmation experiment conducted showed agreement between experimental value and predicted value with R^2 of 0.93 and 0.96 for IN and yield respectively. This study demonstrated that AC with good IN can be prepared from coffee husk at reasonable yield rate and RSM is important tool to model and optimize process parameters in production of coffee husk activated carbon.

4.2 Characteristics of Coffee Husk Activated Carbon

This section of the work is presented to address specific objective two which is intended to describe physico- chemical and surface characteristics of coffee husk activated carbon produced at previously predicted optimum production parameters.

The Physico-chemical parameters of activated carbon obtained from coffee husk were illustrated in Table 9.

Table 8: Physico-chemical property on coffee husk activated carbon

Characteristics	Value at optimum point	Mean (±SD) value
Activated carbon yield	57%	43.79 (0.078)
pH	5.4	5.1 (0.2)
Bulk Density	0.69 g/mL	-
Porosity %	57.3	-
Conductivity	0.48 ms/cm	-
Moisture content	6.3%	-
Ash content	9.4%	-
Volatile matter	13.2%	-
Fixed carbon	71.1%	-
Water soluble matter	0.29%	-
Acid soluble mater	0.93%	-
Zero point charge in pH units	4.2	4.3 (0.05)
Iodine Number	396 mg/g	494.6 (93.30)
Methyl Blue Value	319 mg/g	387.65 (56.4)

4.2.1 Proximate Analysis

Proximate analysis is one of the thermal analysis techniques. These are analytical techniques in which a physical property is measured with a temperature-programmed variation. In this case, the property measured is the weight. Proximate analysis provides an approach to estimate the content of: moisture, volatile matter, fixed carbon, and ash. Moisture measurements refer to the matter volatilized until near 373K, mostly water. Volatile matter is determined by the same procedure but in a temperature range of 373 to 1223K. Fixed carbon is the material burned in air at 1223K in a third step and is made of the more stable organic structures. Lastly, the non-combustible matter is the ash. Generally, the composition of ash, fixed carbon, and volatile matter are given on a dry basis. The representation of weight versus temperature (or time) also gives information about the thermal stability of the activated carbon. The proximate analyses a presented in Table: 10 showed a less amount of moisture, ash and volatile matter, and high value of fixed carbon indicating that high graphitization grade and low amount of functional groups. This in turn shows that the activated carbon can be an excellent raw material for adsorbents to be used in column or fixed-bed reactors. Ash content can also affect activated carbon i.e. it reduces the overall activity of activated carbon. It also reduces the efficiency of reactivation, the lower the ash value therefore the better the activated.

Table 9: Proximate values of comparative low-cost activated carbon

Activated carbon	MC %	VC %	Ash %	FC %	Reference
Coffee husk	6.03	24.62	2.01	67.34	Mohd Azmier Ahmad and Nazira Khabibor Rahman (2011)
durian shell	5.53	69.59	2.52	22.36	Chandra *et al*. (2009)
Fluted steam activation	19.50	40.15	22.38	-	Ekpete O.A. and Horsfall M.JNR (2011)
Fluted seed shell	4.2	-	16	64.0	Verla *et al*. (2012)

Volatile content in AC is mainly due to the presence of non carbonaceous matters. The elimination of non-carbonaceous matters is controlled by activating agent and temperature. The acid attacks non-carbonaceous matters present in the feed and detaches them from their native

sites. The deep penetration of acid detaches more non-carbonaceous matters. The application of temperature aids in moving these matters from the surface during activation.

4.2.2 pH and pH_{pzc} Determinations

pH_{pzc}, is the pH value at the point where net surface charge of the adsorbent is 0. pHpzc values for activated carbon produce at optimized operational parameter is 4.2 while the mean and SD for all samples was 4.3 and 0.05 respectively. The mean and SD of their pH values ranged was 5.1 and 0.2. The pH values of the adsorbents generally fall in the slightly acidic region and values of $pH_{pzc}<7$ show dominancy of acidic groups over basic groups. The presence of acid functional group such as carboxyl, phenolic and others on the surface of carbon may cause the acidic property of activated carbon. Net surface charge of the activated carbon under pHpzc is positive, while it is negative above pHpzc. Therefore, knowledge of this value helps deciding at which pH value one should work during adsorption studies.

4.2.3 Iodine and Methylene Blue Number

Iodine and MB number is a fundamental parameter used to characterise activated carbon performance. MB number and iodine sorption capacity have relationship with the pore structure of adsorbents. Since I_2 is a small molecule with a size of 0.56nm, the iodine sorption capacity is related to the degree of micro and mesopores present in the activated carbon, while MB number indicate the capacity of an adsorbent to adsorb large molecular size species into its macropores. The micropores are responsible for the large surface area of activated carbon particles and are created during the activation process. It is in the micropores that adsorption largely takes place. Increasing surface area and surface active groups cause a rise in iodine and MB adsorption. I_2 and MB numbers are given in Table 10. I_2 number gives information about microporous structure lower than 1nm, rather than about total surface area. It is apparent that increase in iodine and MB adsorption occurs with increasing surface area. Surface functional groups are also effective on iodine and MB adsorption, besides to the surface area.

4.2.4 FTIR

Adsorption capacity of AC is defined not only by its pore structure but also by the chemical nature of its surface. In AC structure, many heteroatoms (oxygen, hydrogen, nitrogen and others)

exist as single atoms and/or in the form of functional groups. Oxygen is the most dominant heteroatom in the carbon matrix. Carbon–oxygen surface compounds are the most important centres having an effect on surface reactions and surface behaviours of activated carbon. Adsorption properties of AC can be controlled by modification of surface groups.

An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material when IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is transmitted. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in qualitative identification of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. The spectra of activated coffee husk were measured at 400-4000cm^{-1}. FTIR test of activated coffee displays a number of absorption peaks as shown in (Table 12). The FTIR spectrum analysis of phosphoric acid treated coffee husk displays a number of functional groups on its surface indicating the complex nature of the adsorbent. The adsorption capacity of activated coffee husk depends upon porosity as well as chemical reactivity of functional groups at the adsorbent surface.

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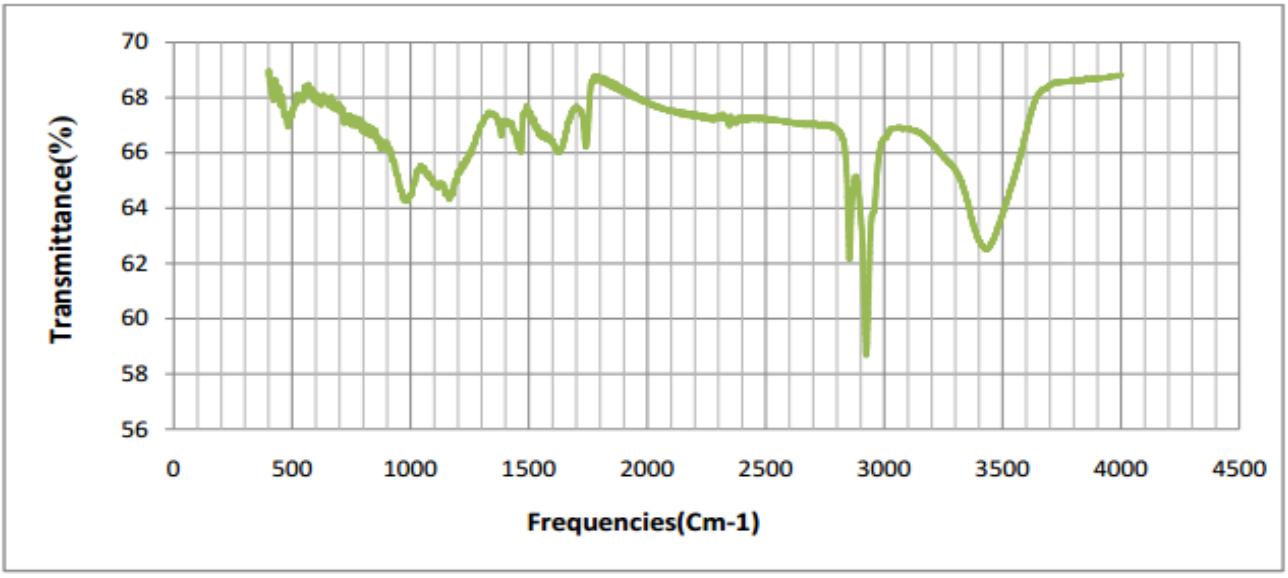

Figure 13: FTIR (Fourier transform infrared spectrophotometer) spectra of activated coffee husk

Table 10: Frequencies and respective functional groups present on the surface of activated coffee husk

Wave number (cm^{-1})	Bond	Functional group
3600-3000	Stretching O-H, N-H	Hydroxyl, carboxylic acid
3000-2800	Stretching C-H	Aliphatic, olefinic, and aromatic hydrocarbons
1770-1650	Stretching C=O	Carbonyl
1700-1600	Stretching C=C	Olefinic structures
1480-1420	Bending C-H	Aliphatic structure
1430-1360	Bending O-H and C-H	Hydroxyl, carboxylic acid, Olefins, methyl
1120-1070	Stretching C-O	Secondary Hydroxyl
1060-1000	Stretching C-O	Primary Hydroxyl

4.3 Batch Adsorption of Cr(VI) Onto Activated Coffee Husk

4.3.1 Effect of pH on Cr(VI)/Coffee Husk Activated Carbon

The result presented in Figure-13 asserted that solution pH is one of the parameters having considerable influence on the adsorption of metal ions. This may be attributed to the surface charge density of the adsorbent and the metallic species which depend on the pH. The behaviour for better adsorption at low pH by activated carbon may be attributed to the large number of H^+ ions present at low pH values which in turn neutralize the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion of chromate ions (Veena Devi *et al*., 2012). From Figure-13, it is evident that at pH 2 the adsorption is maximum. The adsorption increases from 10.8 mg/g (27% removal) to 38.8 mg/g (97% removal) because of the decrease of pH from 8 to 2. This indicates that the Cr(VI) adsorption capacity of the adsorbent is dependent upon pH. Similar observations have also been reported by other investigators (Demiral *et al*., 2008, Anandkumar and Mandal, 2011, Veena Devi *et al*., 2012, Tamirat Dula *et al*., 2014, Julio *et al*., 2008, Zainul Akmar Zakaria *et al*., 2009, Shadreck Mandina *et al*., 2013, Hasan *et al*., 2008).

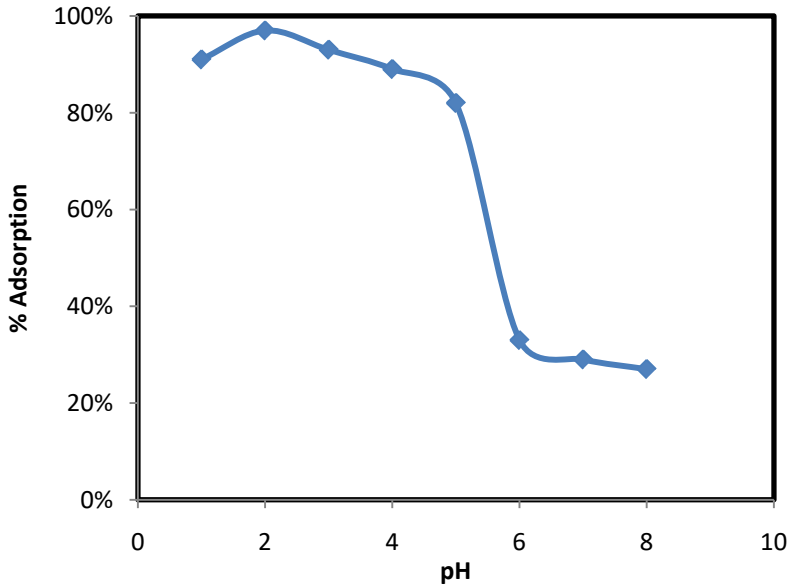

Figure 14: Effect of pH on Cr(VI) adsorption onto coffee husk activated carbon, adsorption condition: Volume of solution 100mL, Cr(CI) concentration 200mg/L, amount of coffee husk activated carbon 0.5g, temperature 30^{o}C, and contact time 6h

4.3.2 Effect of Contact Time and Initial Cr(VI) Concentration

The result were shown in figure the q_e (mg/g) of Cr(VI) was found 39.4, 66 and 78 mg/L for initial Cr(VI) concentration of 100, 200, and 300 mg/L respectively. The extent of adsorption increased rapidly in the initial stages but became slow in the later stages till the attainment of equilibrium. Equilibrium time for the adsorption of Cr(VI) on coffee husk activated carbon at various Cr(VI) concentrations was found to be 8 H, which showed that equilibrium time was independent of initial Cr(VI) concentration. The curves are single smooth and continuous suggesting the formation of monolayer of adsorbate on the surface of the adsorbent.

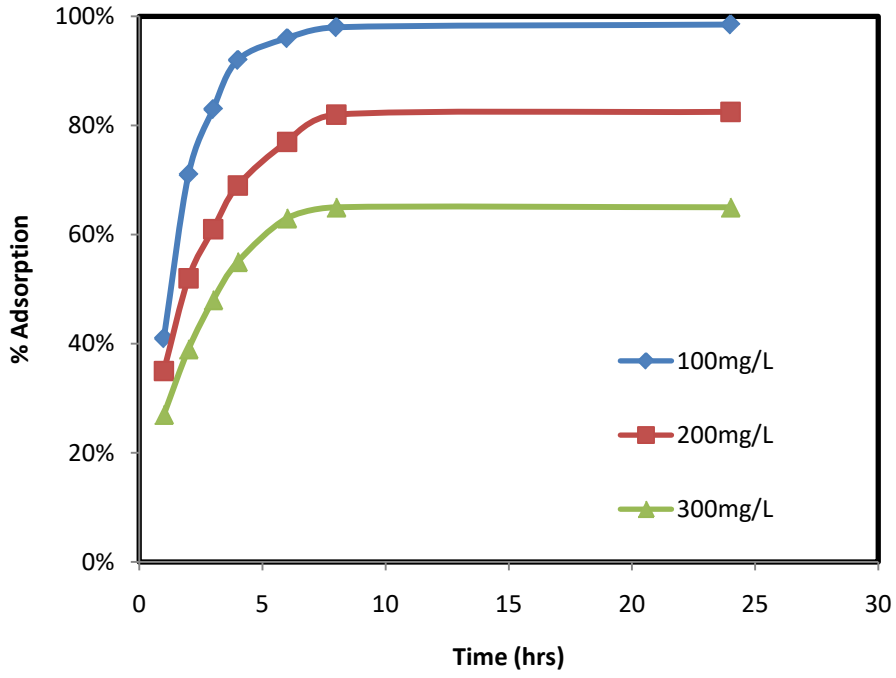

Figure 15: Effect of Cr(VI) concentration and contact time on Cr(VI) adsorption onto coffee husk activated carbon. Adsorption conditions: Volume of solution 200mL, pH 2, amount of coffee husk activated carbon 0.5g temperature 35°C.

4.3.3 Kinetic Study

Adsorption kinetics is expressed as the solute removal rate that controls the residence time of the sorbate in the solid–solution interface (Febrianto *et al*., 2009, Anuradha Jabasingh and Valli Nachiyar, 2010). Adsorption kinetics is of great significance to evaluate the performance of a given adsorbent and gain insight into the underlying mechanisms. From the kinetic analysis, the

solute uptake rate, which determines the residence time required for completion of adsorption reaction, may be established. Also, one can know the scale of an adsorption apparatus based on the kinetic information (Qiu *et al*., 2009, Ho and McKay, 1999). Several mathematical models have been proposed to describe adsorption data, which can generally be classified as adsorption reaction models and adsorption diffusion models. Both models are applied to describe the kinetic process of adsorption; however, they are quite different in nature. Adsorption diffusion models are always constructed on the basis consecutive steps. According to Lazaridis and Asouhidou (2003) these steps are: (1) diffusion across the liquid film surrounding the adsorbent particles, i.e., external diffusion or film diffusion; (2) diffusion in the liquid contained in the pores and/or along the pore walls, which is so-called internal diffusion or intra-particle diffusion; and (3) adsorption and desorption between the adsorbate and active sites, i.e., mass action. However, adsorption reaction models originating from chemical reaction kinetics are based on the whole process of adsorption without considering these steps mentioned above (Qiu *et al*., 2009).

In the present study, kinetic data were analyzed against four kinetic models and the mechanism of the adsorption processes was established. From which three were adsorption reaction models, viz., pseudo first-order (Lagergren, 1898), pseudo second-order (Ho *et al*., 2000), and Elovich (Chien and Clayton, 1980, Sparks, 1986) and one is adsorption diffusion model intraparticle diffusion (Srivastava *et al*., 1989, Weber and Morris, 1963), analyzed to identify rate the limiting step.

4.3.3.1 Pseudo First-Order

The pseudo first-order equation (Lagergren, 1898), is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad \text{Eq. 20}$$

where: q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g), k_1 is the rate constant of pseudo first-order adsorption (l/min). After integration and applying boundary conditions t= 0 to t= t and q_t= 0 to q_t= q_t, the integrated form becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad \text{Eq. 21}$$

The values of $\log(q_e - q_t)$ were linearly correlated with t. The plot of $\log(q_e - q_t)$ vs. t (Figure 15) gives a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

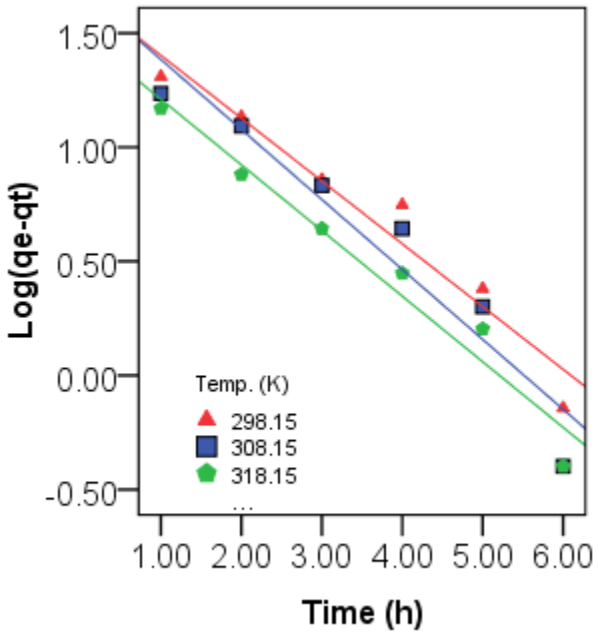

Figure 16: Plot of pseudo-first order kinetic modeling fitting at conditions of: volume of solution = 200mL, initial Cr(VI) concentration= 100mg/L, pH=2, amount of coffee husk activated carbon = 0.5g, contact time =1- 8h at temperature of 25, 35, and 45^{o}C.

4.3.3.2 Pseudo Second-Order

The pseudo second-order adsorption kinetic rate equation(Ho *et al*., 2000) is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad \text{Eq. 22}$$

where: k_2 is the rate constant of pseudo second-order adsorption (g/mg/min). For the boundary conditions t= 0 to t = t and q_t= 0 to q_t= q_t, the integrated form becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \qquad \text{Eq. 23}$$

which is the integrated rate law for a pseudo second-order reaction. This equation can be rearranged to obtain a linear form which is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \quad \text{Eq. 24}$$

if the initial adsorption rate, h (mg/g/min) is given by :

$$h = k_2 q_e^2 \quad \text{Eq. 25}$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}(t) \quad \text{Eq. 26}$$

The plot of (t/qt) and t (Figure 16) of Eq. (7) should give a linear relationship from which qe and k_2 can be determined from the slope and intercept of the plot, respectively.

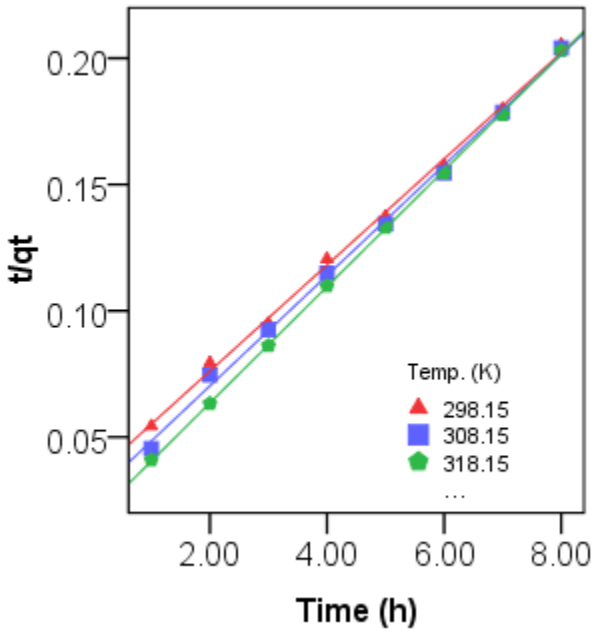

Figure 17: Pseudo second order model fitting Cr(VI) adsorption onto coffee husk activated carbon: at conditions of: volume of solution = 200mL, initial Cr(VI) concentration= 100mg/L, pH=2, amount of coffee husk activated carbon = 0.5g, contact time =1- 8h at temperature of 25, 35, and 45°C.

4.3.3.3 Elovich Model

The Elovich model equation is generally expressed as (Chien and Clayton, 1980, Sparks, 1986):

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad \text{Eq. 27}$$

where: α is the initial adsorption rate (mg/g/min), β is the desorption constant (g/mg) during any one experiment. To simplify the Elovich equation, Chien and Clayton (1980) assumed α βt >> t

and by applying the boundary conditions qt= 0 at t= 0 and q_t= q_t at t = t the above equation becomes:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad \text{Eq. 28}$$

If Cr(VI) adsorption fits the Elovich model, a plot of qt vs. $\ln(t)$ (Figure 17) should yield a linear relationship with a slope of $\frac{1}{\beta}$ and an intercept of $\frac{1}{\beta}\ln(\alpha\beta)$.

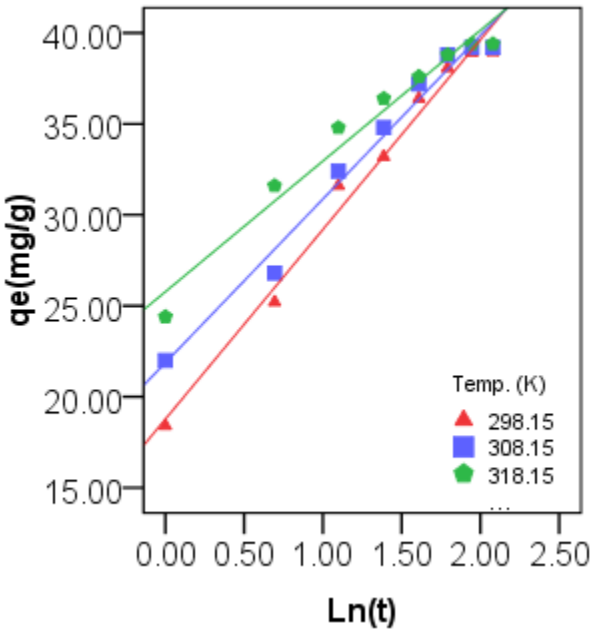

Figure 18: Plot of kinetic data fitting on Elovich model for Cr(VI) adsorption onto coffee husk activated carbon, at conditions of: volume of solution = 200mL, initial Cr(VI) concentration= 100mg/L, pH=2, amount of coffee husk activated carbon = 0.5g, contact time =1- 8h at temperature of 25, 35, and 45^{o}C.

4.3.3.4 Intraparticle Diffusion Model

It is generally known that a typical liquid/solid adsorption involves film diffusion, intraparticle diffusion, and mass action. For physical adsorption, mass action is a very rapid process and can be negligible for kinetic study. Thus, the kinetic process of adsorption is always controlled by liquid film diffusion or intraparticle diffusion, i.e., one of the processes should be the rate limiting step. Therefore, adsorption diffusion models are mainly constructed to describe the process of film diffusion and/or intraparticle diffusion (Qiu *et al*., 2009). Weber and Morris (1963) expressed intraparticle diffusion model as;

$$R = k_{id}(t)^2 \qquad \text{Eq. 29}$$

A linearized form of the equation is followed by

$$\log R = \log k_{id} + a \log(t) \quad \text{Eq. 30}$$

$$q_t = k_{id} t^{0.5} + C \quad \text{Eq. 31}$$

where: R is the per cent Cr(VI) adsorbed, t is the contact time (h), a is the gradient of linear plots k_{id} is the intraparticle diffusion rate constant (1/h), a depicts the adsorption mechanism k_{id} may be taken as a rate factor, i.e., per cent Cr(VI) adsorbed per unit time. The values of k_{id} were calculated from the slope of such plots of q_t Vs. $t^{0.5}$

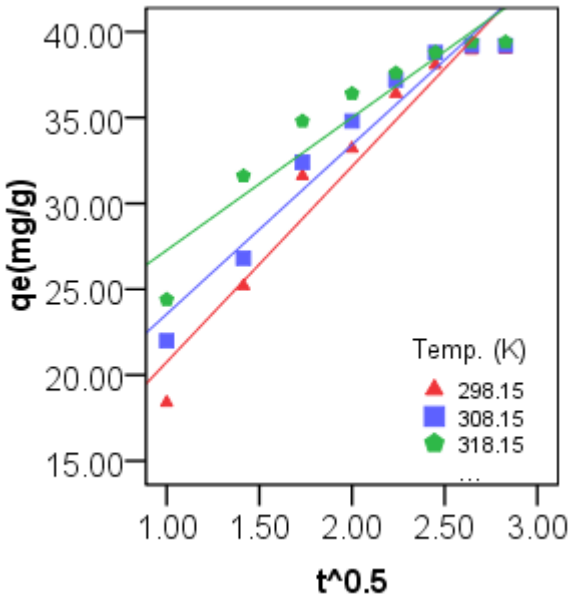

Figure 19: Interaparticle kinetic model fitting Cr(VI) adsorption onto coffee husk activated carbon at conditions of: volume of solution = 200mL, initial Cr(VI) concentration= 100mg/L, pH=2, amount of coffee husk activated carbon = 0.5g, contact time =1- 8h at temperature of 25, 35, and 45^{o}C.

Model constants were presented in Table 12. Based on the result presented, pseudo second-order kinetic model best fit the experimental data with highest r^2 and lowest χ^2 value. Similar finding that assert adequacy of pseudo-second order kinetic model to describe rate of Cr(VI) adsorption on low-cost activated carbon was reported by other numerous authors (Erhan Demirbas *et al*., 2004, Amany El-Sikaily *et al*., 2007, Demiral *et al*., 2008, Hasan *et al*., 2008, Babu and Gupta, 2008, Anandkumar and Mandal, 2011, Xin-jiang Hu *et al*., 2011, Tamirat Dula *et al*., 2014, Ali Kara and Emel Demirbel, 2012)

Table 11: Summary of regression equations, model constants and correlation coefficients calculated for adsorption kinetic at three temperature

Kinetic Constants		**Value**		
		25°C	**35°C**	**45°C**
	qe (exp.) (mg/g)	38.96	39.2	39.4
1	**pseudo first-order**			
	Regression eq. of $\log(q_e - q_t)$ Vs. t	y = -0.2752x + 1.6774	y = -0.3067x + 1.6914	y = -0.2876x + 1.498
	$q_{e,m}$.(mg/g)	46.078	47.51	30.89
	k_1 (min-1)	0.647	0.72	0.67
	r^2	0.9479	0.9212	0.9582
	χ^2	1.09	1.45	2.34
2	**Pseudo-second-order**			
	Regression eq. of $\frac{t}{q_t}$ Vs. t	y = 0.021x + 0.0341	y = 0.0219x + 0.0266	y = 0.023x + 0.0174
	$q_{e,m}$.(mg/g)	47.61	45.66	43.47
	k_2(mg/g/hr)	0.013	0.018	0.03
	r^2	**0.9977**	**0.9976**	**0.9998**
	χ^2	**1.57**	**0.91**	**0.038**
3	**Elovich model**			
	Regression eq. of q_t Vs. $\ln(t)$	y = 10.428x + 18.772	y = 8.9982x + 21.872	y = 7.186x + 25.774
	A (mg/g/hr)	63.113	101.8	257.9
	β (g/mg)	0.096	0.111	0.139
	r^2	0.984	0.981	0.968
	χ^2	78.2	101.17	144.17
4	**Intraparticle diffusion**			
	Regression eq. $\boldsymbol{q_t}$ Vs. $\boldsymbol{t^{0.5}}$	y = 11.401x + 9.3578	y = 9.871x + 13.68	y = 7.7277x + 19.549
	k_d(mg/g/hr)	11.417	9.892	7.749
	C (mg/g),	9.175	13.43	19.3
	r^2	0.939	0.9415	0.8917
	χ^2	96.69	50.57	20.93

4.3.4 Isotherm Study

Equilibrium relationships between the adsorbate concentration in the liquid phase and that on the adsorbent's surface at a given condition, generally known as adsorption isotherms, describe how pollutants interact with the adsorbent materials, and thus are critical for optimization of the adsorption mechanism pathways, expression of the surface properties and capacities of adsorbents, and effective design of the adsorption systems (Demiral *et al*., 2008, Foo and Hameed, 2010). Thus an accurate mathematical description of equilibrium adsorption capacity is indispensable for reliable prediction of adsorption parameters and quantitative comparison of adsorption behaviour for different adsorption system or for varied conditions within any given systems. There are many equations for analyzing experimental adsorption equilibrium data. In this study the experimental data was analyzed against two parameter isotherm equations, namely Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D-R) isotherm equations.

4.3.4.1 Langmuir Isotherm

The Langmuir isotherm model estimates the maximum adsorption capacity produced from complete monolayer coverage on the adsorbent surface. The non-linear equation of Langmuir isotherm model can be expressed in the following non-linear form:

$$\boldsymbol{q_e = \frac{q_m b C_e}{1 + b C_e}} \qquad \textbf{Eq. 32}$$

This can be linerazed in different ways. One of these linear forms is;

$$\boldsymbol{\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{1}{q_m} C_e} \qquad \textbf{Eq. 33}$$

A plot of $\frac{C_e}{q_e}$ Vs. C_e (Figure 19) should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium. The slope and the intercept of this line then give the values of q_m and b.

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L, also known as the separation factor, given by;

$$\boldsymbol{R_L = \frac{1}{1 + b C_o}} \qquad \textbf{Eq. 34}$$

If the average of the R_L values for each of the different initial concentrations used is between 0 and 1, it indicates favourable adsorption.

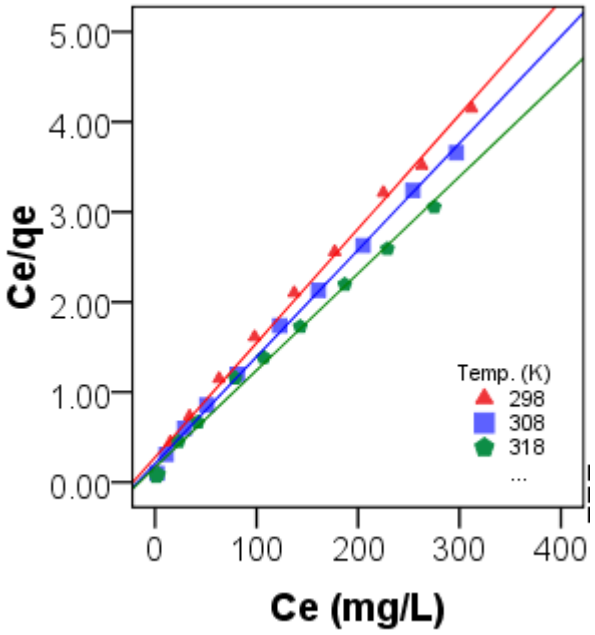

Figure 20: Plot of fitting equilibrium data on Langmuir Isotherm for Cr(VI) adsorption onto coffee husk activated carbon at conditions of: volume of solution = 200mL, Cr(VI) concentration= 50-500mg/L, pH=2, amount of coffee husk activated carbon = 0.5g, contact time = 8h at temperature of 25, 35, and 45^{o}C.

4.3.4.2 Freundlich Isotherm

The Freundlich isotherm is an empirical model that is based on adsorption on heterogonous surface and is given by the following equation:

$$q_e = K_f + C^{1/n} \quad \text{Eq. 35}$$

Which is linearized as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \text{Eq. 36}$$

K_f and n are Freundlich constants, which represent adsorption capacity and adsorption intensity, respectively. The Freundlich constants were determined from the slope and intercept of a plot of $\log q_e$ versus $\log C_e$ (Figure 20).

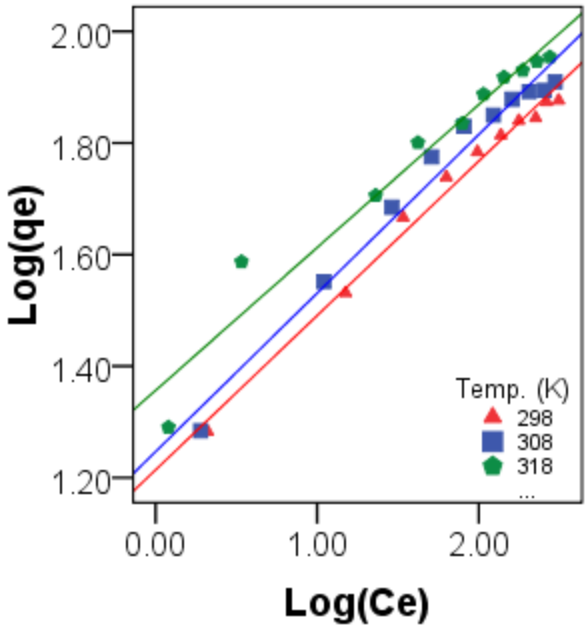

Figure 21: Plot of fitting equilibrium data on Freundlich Isotherm for Cr(VI) adsorption onto coffee husk activated carbon at conditions of: volume of solution = 200mL, Cr(VI) concentration= 50-500mg/L, pH=2, amount of coffee husk activated carbon = 0.5g, contact time = 8h at temperature of 25, 35, and 45°C.

4.3.4.3 Dubinin–Radushkevich (D–R) Isotherm

Another equation used in the analysis of isotherms was proposed by Dubinin–Radushkevich (D–R)

$$q_e = q_m \exp(-B\varepsilon^2) \quad \text{Eq. 37}$$

Where q_s is the D–R constant and ε can be correlated as;

$$\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right] \quad \text{Eq. 38}$$

The isotherm constants of q_e and B are obtained from the intercept and the slope of the plot of $\ln q_e$ versus ε^2, respectively. The constant B gives the mean free energy, E, of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed by using the following relationship.

$$E = \left[\frac{1}{\sqrt{2B}}\right] \quad \text{Eq. 39}$$

The magnitude of E is useful for estimating the type of adsorption process.

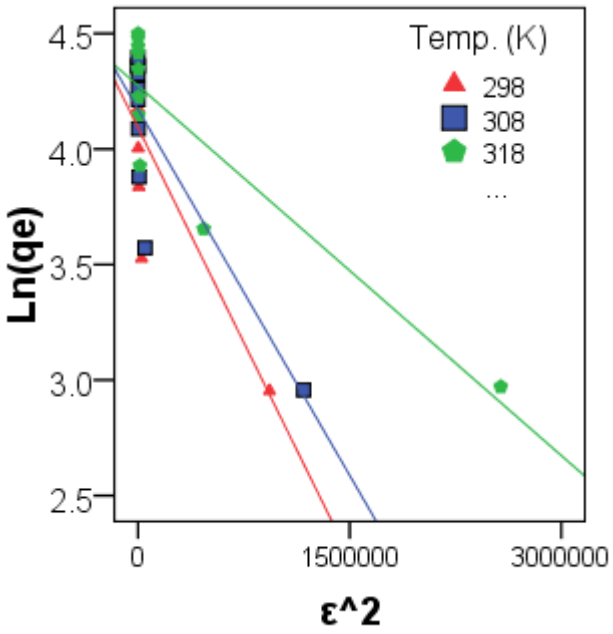

Figure 22: Plot of fitting equilibrium data on Dubinin–Radushkevich (D–R) Isotherm for Cr(VI) adsorption onto coffee husk activated carbon at conditions of: volume of solution = 200mL, Cr(VI) concentration= 50-500mg/L, pH=2, amount of coffee husk activated carbon = 0.5g, contact time = 8h at temperature of 25, 35, and 45^{o}C.

4.3.4.4 Temkin Isotherm

Temkin and Pyzhev considered the effects of indirect adsorbate/adsorbent interactions on adsorption isotherms. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions. The Temkin isotherm has been used in the form as follows;

$$q_e = \frac{RT}{b} \ln AC_e \qquad \text{Eq. 40}$$

Linearized as;

$$q_e = B_1 \ln A + B_1 \ln C_e \qquad \text{Eq. 41}$$

A plot of q_e versus $\ln C_e$ (Figure 22) enables the determination of the isotherm constants of B_1 and A from the slope and the intercept respectively.

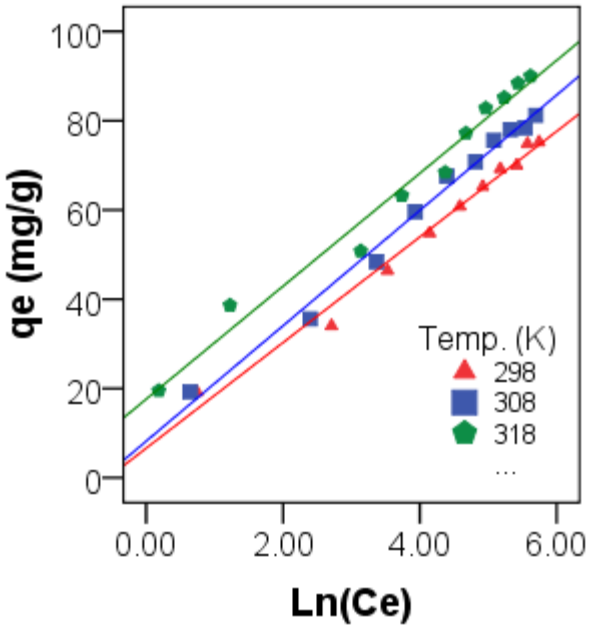

Figure 23: Plot of fitting equilibrium data on Temkin Isotherm for Cr(VI) adsorption onto coffee husk activated carbon at conditions of: volume of solution = 200mL, Cr(VI) concentration= 50-500mg/L, pH=2, amount of coffee husk activated carbon = 0.5g, contact time = 8h at temperature of 25, 35, and 45^{o}C.

The isotherm constants were calculated from the slope and intercept of Figure 19-22 presented in Table 14. As shown in the Table 14 the higher value of r^2 and lowest value of χ^2 was associated with Langmuir isotherm at all the three temperatures. That means Langmuir equation represented the adsorption process very well.

Value of q_m, which is defined as the maximum capacity of sorbent, was calculated from the Langmuir plots. The maximum capacity of coffee husk activated carbon for Cr(VI) was calculated in the range of 78.74–92.59 mg/g at different temperatures that indicated the good adsorbing capacity of the coffee husk activated carbon. The equilibrium parameter R_L is in the range of $0< R_L <1$ which reflects the favorable adsorption process. This indicated to the fact that the sorption process was very favorable and the adsorbent employed exhibited a good potential. Similar results on Cr(VI) adsorption were reported by other researches (Amany El-Sikaily *et al*., 2007, Hasan *et al*., 2008, Demiral *et al*., 2008, Attia *et al*., 2010, Talokar, 2011, Mohannad Qurie *et al*., 2013, Wei Caoa *et al*., 2013, Goswami *et al*., 2014, Wu *et al*., 2014)

Table 12: Two parameter isotherm models, value of respective parameters at different temperature and correlation coefficient

	Isotherm & parameters	Value of parameter at three temperatures		
		25°C	35°C	45°C
1	Langmuir			
	Regression eq. of $\frac{C_e}{q_e}$ Vs. C_e	y = 0.0127x + 0.2771	y = 0.0119x + 0.2058	y = 0.0108x + 0.1655
	q_m(mg/g)	78.74	84.03	92.59
	b(L/mg)	0.045	0.057	0.065
	r^2	0.995	0.997	0.993
	χ^2	99.96	107.12	128.05
2	Freundlich			
	Regression eq. of $\log q_e$ Vs. $\log C_e$	y = 0.2767x + 1.2142	y = 0.2841x + 1.2468	y = 0.2561x + 1.3567
	K_f (mg/g)	16.37	17.65	22.73
	N	3.61	3.52	3.90
	r^2	0.988	0.9751	0.9535
	χ^2	1197.18	1307.62	1059.86
3	Temkin			
	Regression eq. of q_e Vs. $\ln C_e$	y =11.834x + 6.6241	y = 12.926x + 8.215	y = 12.65x + 17.628
	K_T (L/mg)	1.75	1.88	4.02
	B_T	11.834	12.926	12.65
	r^2	0.984	0.988	0.9781
	χ^2	1985.5	2124.3	2680.9
4	Dubinin-Radushkevich			
	Regression eq. $\ln q_e$ Vs. ε^2	y = -1E-06x + 4.0923	y = -1E-06x + 4.1716	y = -5E-07x + 4.2745
	q_m (mg/g)	178.73	179.43	163.77
	ß ($mmol^2/J^2$)	$4x10^{-6}$	$3x10^{-6}$	$5x10^{-7}$
	r^2	0.7007	0.7165	0.7979
	χ^2	847.17	797.56	609.29

4.3.5 Thermodynamic Study

The thermodynamic parameters that help us to understand the nature of the adsorption of Cr(VI) on adsorbents are the standard change in Gibbs free energy (ΔG°), the standard change in entropy

(ΔS°), and the standard change in enthalpy (ΔH°). The relation between ΔG°, ΔH° and ΔS° is as follows: (Oguz, 2005, Romero-Gonzalez *et al*., 2005)

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad \text{Eq. 42}$$

Thermodynamic parameters can be evaluated from the variation of the thermodynamic equilibrium constant K_c at different temperature. It is defined as Eq.(42) for adsorptive reactions (Li *et al*., 2009).

$$K_c = \frac{\alpha_s}{\alpha_e} = \frac{v_s q_e}{v_e C_e} \qquad \text{Eq. 43}$$

Where α_s and, α_e refer to the activity of adsorbed Cr(VI) and the activity of Cr(VI) in solution at equilibrium, v_s and v_e denote the activity coefficient of the adsorbed Cr(VI) and the Cr(VI) in solution, respectively.

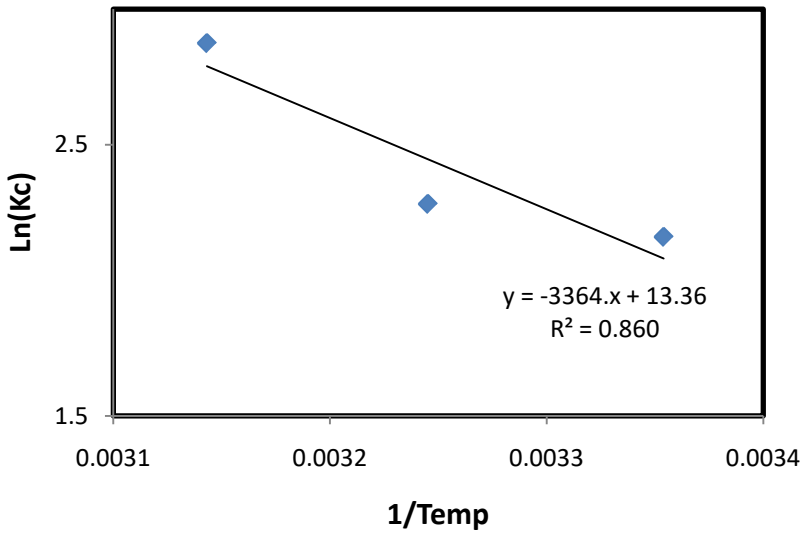

Figure 24: Van't Hoff plot for determination of thermodynamic parameters

As the Cr(VI) concentration in the solution decreases and approaches to zero, K_c can be obtained by plotting $\frac{q_e}{C_e}$ versus q_e and extrapolating q_e to zero (Li *et al*., 2009). Gibbs free energy was calculated by the following equation using K_c:

$$\Delta G^{\circ} = -RT \ln K_c \qquad \text{Eq. 44}$$

Based on the above equations the following van't Hoff equation can be derived:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \text{Eq. 45}$$

ΔH° And ΔS° were obtained from the slope and intercept of the plot of $\ln K_c$ versus 1/T. The van't Hoff plot for the adsorption of Cr (VI) onto activated carbon is shown in Figure 5. The calculated value of ΔH°, ΔS° and ΔG° of for Cr(VI)/coffee husk activated carbon system at different temperature was presented in Table 14.

Table 13: Thermodynamic parameters for Cr(VI)/coffee husk activated carbon adsorption system

Temp. K	K_c	ΔH° KJmol^{-1}	ΔG° KJmol^{-1}	ΔS° Jmol^{-1}K^{-1}
298.15	8.67	27.972	-5.155	111.108
308.15	9.79		-6.266	
318.15	17.72		-7.377	

The negative adsorption standard free energy changes (ΔG°) and positive standard entropy changes (ΔS°) at all temperatures indicated that the adsorption reactions were general spontaneous process. The decrease of ΔG° with increasing temperature indicated a higher adsorption impetus at higher temperature. The positive value of enthalpy indicated that the adsorption was endothermic.

It is well known that, the physical adsorption is generally exothermic reaction. Hence, logical cause of the observation is that the adsorption should include some endothermic chemical reactions, which are supported by increasing adsorptive capacity with rising temperature. The positive value of entropy showed the increased randomness at the solid liquid interface during the adsorption process. This occurs as a result of redistribution of energy between the adsorbate and the adsorbent (Anandkumar and Mandal, 2011). Similar results have been reported for the Cr(VI) adsorption (Demiral *et al*., 2008, Anandkumar and Mandal, 2011, Zainul Akmar Zakaria *et al*., 2009, Hasan *et al*., 2008, Granados-Correa and Jimenez-Becerril, 2009, Goswami *et al*., 2014, Barkat *et al*., 2009, Malkoc and Nuhoglu, 2007, Acharya *et al*., 2009).

4.3.6 Activation Energy

Activation energy is important parameter as it gives clue on the adsorption process. Weak van der Waals forces are responsible in case of physical adsorption and its activation energy is not more than 4.184 kJ/mol. Activation energy greater than this is usually an indication for involvement of chemical adsorption. Activation energy was calculated using Arrhenius equation;

$$\boldsymbol{K_{ad} = k_0 exp\left(-\frac{E_a}{RT}\right)} \quad \textbf{Eq. 46}$$

Linearized as;

$$\boldsymbol{ln\, k_2 = ln\, k_o - \frac{E_a}{RT}} \quad \textbf{Eq. 47}$$

where k_2 is adsorption rate constant, k_o is frequency factor and E_a is activation energy. Pseudo-second-order rate constant was used as adsorption rate constant. Activation energy was calculated from the linear plot of Arrhenius equation $\ln k_2$ Vs $\frac{1}{T}$. From the plot in Figure 25 (R^2 = 0.9788) E_a was determined as 32.884 kJ/mol. The value of E_a being much higher than that of in the weak van der Waals forces confirms involvement of chemical adsorption or reduction reactions.

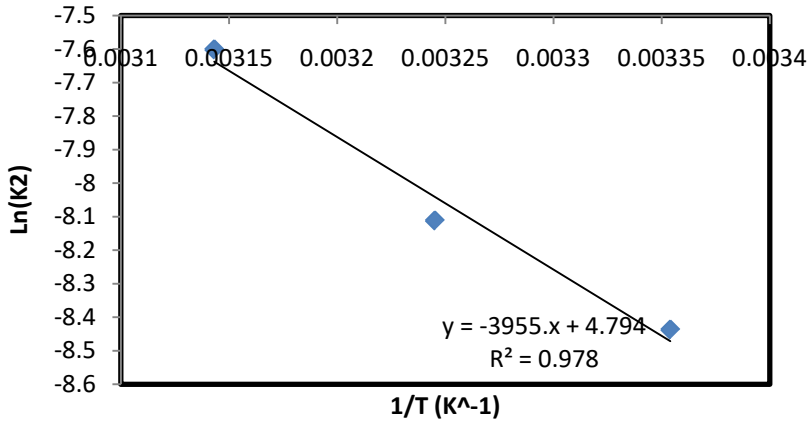

Figure 25: Plots of Arrhenius equation $\boldsymbol{\ln k_2}$ Vs. 1/T for determination of E_a

4.3.7 Comparison of Adsorption Capacity with Other Low- Cost Adsorbents

The adsorption capacity of Cr(VI) onto coffee husk activated carbon was compared with other low-cost adsorbent reported in literature and is shown in Table 15. It can be observed that the

activated carbon produced from coffee husk compares well with the activated carbons from most of the raw materials listed. Tannery waste, maize bran and Brazilian-pine fruit coat are a few raw materials that exhibited very high adsorption capacity; this could be primarily due to the initial carbon content, activation process as well as the pore development due to the basic morphology of the raw material. Hence, coffee husk activated carbon can be considered to be viable adsorbent for the removal of Cr(VI).

Table 14: Cr(VI) adsorption capacity of previously reported low cost activated carbons

Adsorbent	Maximum q_m(mg/g)	Ref.
Wheat bran	0.942	Nameni *et al*. (2008)
Sawdust	2.2899	Hamadi *et al*. (2001)
Coconut tree sawdust	3.46	Selvi *et al*. (2001)
pre-boiled sunflower stem	5.37	Jain *et al*. (2009)
Trapa natans husk	11.83	Liu *et al*. (2010)
Mucor racemosus sorbent	18.8	Anuradha Jabasingh *et al*. (2015)
Olive stones	25.6	Attia *et al*. (2010)
Sugar industrial waste	28.44	Fahim *et al*. (2006)
Matured tea leaves	32.04	Goswami *et al*. (2014)
Eucalyptus bark	45	Sarin and Pant (2006)
Waste tyres	58.4795	Hamadi *et al*. (2001)
Rubber wood sawdust	65.78	Karthikeyan *et al*. (2005)
Tamarind hull-based	81	Verma *et al*. (2006)
Olive bagasse	109.89	Demiral *et al*. (2008)
Acid activated *Ulva lactuca*	112.36	Amany El-Sikaily *et al*. (2007)
Date palm seed	120.48	Ahmed El Nemr *et al*. (2008)
Sugar beet tailing	123	Dong *et al*. (2011)
Steam activated peach stone	143	Duranoğlu *et al*. (2010)
Tannery waste	217.39	Anandkumar and Mandal (2011)
Brazilian-pine fruit coat	240	Vaghetti *et al*. (2008)
Maize bran	312.52	Hasan *et al*. (2008)

4.3.8 Concluding Remark on Cr(VI) Adsorption

The study shows that chemically modified coffee husk, can be used as an adsorbent for removal of Cr(VI) from aqueous solutions. The adsorption characteristics were shown to be influenced by several factors. The adsorption process was highly pH dependent and the optimum pH for maximum adsorption was found to be at pH 2. The isotherms exhibited the Langmuir behaviour at all temperatures, which indicates a monolayer surface binding. The adsorption data showed good agreement with the pseudo-second-order kinetic model for different adsorbent concentration. The rate constant increased with increase in temperature indicating endothermic nature of adsorption. The values thermodynamic parameters of ΔH°, ΔS° and ΔG°, and an activation energy (E_a) were estimated. Based on these values, the adsorption of Cr (VI) onto chemically modified coffee husk was a spontaneous, endothermic process with involvement of some level of chemisorptions.

5. Conclusions and Recommendations

Response Surface Method (RSM) using Box-Behnken design technique was applied to optimize process parameters involved in preparation of activated carbon from coffee husk by chemical activation using H_3PO_4. The effect of concentration of H_3PO_4, impregnation ratio, carbonization temperature and holding time on Iodine number (IN) and yield of coffee husk activated carbon is better described by quadratic polynomial model adequately. Analysis of variance (ANOVA) revealed a good agreement between experimental and predicted value. Confirmation experiment conducted showed agreement between experimental value and predicted value.

The result of the characterization showed that the coffee husk activated carbon has good properties and compared favorably with other reference activated carbons. The surface functional group was investigated by Fourier transformation infrared spectroscopy techniques and pH_{ZPC} indicate the activated carbon has acidic surface functional group.

The parametric effects of pH, initial concentration of Cr(VI), and contact time on Cr(VI)/coffee husk activated carbon system were investigated. The system was found to be pH dependent and maximum adsorption yield was obtained at lower pH. The adsorption kinetics of Pseudo-first order, Pseudo-second order and Elovich kinetic models were examined and showed that pseudo-second order rate expression best fitted for all temperature. Equilibrium isotherms were measured experimentally at all temperature and results were analyzed by the Langmuir, Freundlich, Dubinin-Redushkevich, and Temkin equations using linearized correlation coefficient. Thermodynamic analysis asserted endothermic and spontaneous nature with involvement of chemical adsorption process.

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Annex

Raw data:

pH_{ZPC}

pH of the blank	pH with activated carbon
1	2.8
1.5	3.3
2	3.7
2.5	3.9
3	4
3.5	4.1
4	4.2
4.5	4.2
5	4.3
5.5	4.5
6	4.7
6.5	4.9
7	5.3

Effect of pH on adsorption

Adsorption condition; Volume of solution 200mL, Cr(CI) concentration 100mg/L, amount of coffee husk activated carbon 0.5g, temperature 30^oC, and contact time 6Hrs

pH	Ce (mg/L)
1	9
2	3
3	7
4	11
5	18
6	67
7	71
8	73

Effect of contact time and initial concentration of metal ion

Adsorption conditions; Volume of solution 200mL,initial concentration 100, 200 and 300mg/L pH 2, amount of **coffee husk activated carbon** 0.5g temperature 30^{o}C, contact time 1-24hrs

	Ct at three conc. level		
Time (hr)	Ct(100mg/L)	Ct(200mg/L)	Ct(300mg/L)
1	59.00	130.00	219.00
2	29.00	96.00	183.00
3	17.00	78.00	156.00
4	8.00	62.00	135.00
6	4.00	46.00	111.00
8	2.00	36.00	105.00
24	1.50	35.00	105.00

Data on kinetic study at three temperatures

Adsorption Condition

volume of solution = 200mL, initial Cr(VI) concentration= 100mg/L, pH=2, amount of coffee husk activated carbon = 0.5g, contact time =1- 8hrs at temperature of 25, 35, and 45^0C.

	Concentrations at given time (mg/g)		
Contact time (Hrs)	Ce(25)	Ce (35)	Ce(45)
1	54	45	39
2	37	33	21
3	21	19	13
4	17	13	9
5	9	7	6
6	4.8	3	3
7	2.7	2	1.5
8	2.6	2	1.5

Data on Equilibrium study at three temperatures

Adsorption condition: volume of solution = 200mL, Cr(VI) concentration= 50-500mg/L, pH=2, amount of coffee husk activated carbon = 0.5g, contact time = 8hrs at temperature of 25, 35, and 45^0C.

	Equilibrium concentration (mg/g)		
Co (mg/L)	Ce (25)	Ce (35)	Ce (45)
50	2.1	1.9	1.2
100	15	11	3.4
150	34	29	23
200	63	51	42
250	98	81	79
300	137	123	107
350	177	161	143
400	225	205	187
450	263	254	229
500	312	297	275