ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF GRADUATE STUDIES
SCHOOL OF CHEMICAL AND BIO ENGINEERING DEPARTEMENT
ENVIRONMENTAL ENGINEERING STREAM

REACTIVE AZO DYE REMOVAL FROM AQUEOUS SOLUTION USING ORANGE PEEL AS BIO-ADSORBENT

A thesis submitted to the School of Graduate Studies of Addis Ababa University in partial fulfillment of the Degree of Master of Science in Environmental Engineering

By
Nuriya Jemal

Advisor
Dr.S.Anuradha Jabasingh (Assoc. Professor)

July, 2015
Addis Ababa

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DECLARATION

I, the undersigned, declare that this thesis entitled “Reactive Azo dye removal from aqueous solution using orange peel as bio-adsorbent” is my original work, and it has notbeen presented in this and any other person for an award of degree in this or other University, allsources of materials used in this thesis work have been duly acknowledged.

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Lists of Abbreviations

AAiT	Addis Ababa University Institute of Technology
Abs.	Absorbance
AC	Activated Carbon
ASTM	American society for testing and materials
COD	Chemical Oxygen Demand
C.I	Color Index
EU	European Union
FTIR	Fourier Transform Infrared
IUPAC	International Union of Pure and Applied Chemistry
OP	Orange Peel
POP	Powdered Orange Peel
POPA	Powdered Orange Peel Adsorbent
RR-DEXF	Reactive Red DEXF dye
SEM	Scanning Electron Microscopy
UV	Ultraviolet
zpc	Zero Point of Charge

Abstract

Presence of dyes in the aquatic systems has become a serious environmental problem. Concerning the environmental awareness and the economical point of view, the use of low-cost and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing textile dyes from wastewater. This study explores the feasibility of using orange peel, an agricultural waste, for removal of synthetic dye from aqueous solution. The adsorption characteristics of RR- DEXF dye onto powdered orange peel (POP) as a bio adsorbent that has been previously physically treated was investigated. Batch adsorption experiments were carried out for the adsorption of the dye molecule from aqueous solution onto the POPA at constant room temperature 27^{o}C and agitation speed 200rpm. Variation effect of different parameters like solution pH, adsorbent dose, contact time and the initial concentration of the dye were studied. U V. spectrophotometer technique was used for the measurement of concentration of dye before and after adsorption.

Experimental results revealed that optimal adsorption took place at an acidic solution pH. The effective solution pH, adsorbent dose and contact time on the dye removal efficiency of the adsorbent were found to be 3, 0.2g/100mL and 80min, respectively for the adsorption studies. At these experimental conditions the dye removal efficiency of 90% was achieved. The experimental results have been fitted well by the Langmuir isotherm model with the higher correlation coefficients of $R^2 = 0.995$. Thus, indicating to the applicability of monolayer coverage of the dye on the surface of the adsorbent and it was found to be 3.03 mg/g. Adsorption kinetics was determined using pseudo first order and pseudo second order models and it was found that the adsorption process follows pseudo second order model. Generally the results indicate that POP may be used as a low cost adsorbent, alternative for treatment of effluents containing reactive red dye in water.

Keywords: RR-DEXF dye; Powdered orange peel adsorbent (POPA); UV. Spectrophotometer; Adsorption isotherm; Kinetics models; effluents.

1. Introduction

Water is vital to almost all life forms in existence and it is believed that, even, the first life started in water. Although more than 70% of earth surface is covered with water, majority of it is not suitable to sustain human life and only limited potable water resources are available. The extensive use of chemicals for various purposes in day-to-day life and the growing industrialization led to unwanted contamination of our existing natural resources by the release of diverse organic and inorganic pollutants into water system (Ramakrishna, 2013).

Of various pollutants contained in industrial wastewaters, dye is considered to be very important from the aesthetic point of view and is stated as visible pollutant. Dyes usually have a synthetic origin and complex aromatic molecular structures, which make them more stable and more difficult to biodegrade and are widely used in textiles, paper, plastic, leather, cosmetics and food industries to color their products. The extensive use of dyes often caused pollution problems in the form of colored wastewater discharged in to environmental water bodies (Aseel M. and Kadim Aljebori, 2010).

Today there are more than 100,000 commercially available dyes exist with over 7×10^5 metric tons of dyestuff produced annually. Among the chemical classes of dyes, azo dyes are more versatile and account to more than half of the annual dye production. It is estimated that 2 % of dyes produced annually are discharged in effluent from different manufacturing operations. While in the textile industry, it is estimated that 10% to15% of the dye used during the manufacturing of textile products is released into the environment worldwide annually (Tan J. R., 2010).

Reactive azo dyes extensively used in textile dying process in Ethiopia, they have good water solubility and easily hydrolyzed into insoluble forms. Textile dyes wastewater, in particular characterized by intense color, high level of chemical oxygen demand (COD), dissolved solids highly fluctuating pH (Meroufel & Zenasn, 2013). Among all these color is the first wastewater contaminant to be recognized, since a very small amount of dye concentration in water even (<1ppm) are highly visible that affects aesthetic merit, transparency and water-gas solubility (Adamu, 2008). Therefore, it is desirable to remove dyes from colored effluents for safe discharge in receiving water bodies to keep the environment sustainable.

Several treatment methods have been adopted to remove dyes from textile wastewater, which can be divided into physical, chemical, and biological methods. Among physicochemical methods mainly adsorption process is one of the most effective and economically feasible methods for dye removal from textile wastewater. A variety of natural adsorbents for dye removal have been reported in the literature (Beyene, 2014). Orange, as a kind of biological resources is available in large quantities in many parts of the world. Orange peel principally consists of cellulose, hemicelluloses chlorophyll pigment lignin and other low molecular weight hydrocarbon. These components contain various functional groups, such as carboxyl and hydroxyl groups which make orange peel to be a potential adsorbent material for removing different ionic compounds from aqueous solution (Said & Mansour, 2012).

The present study was intended to remove Reactive Red DEXF dye from aqueous solutions using orange peel as a low cost bio adsorbent. The effect of operating parameters like, initial pH, contact time, adsorbent dose and initial dye concentration studies were investigated in batch adsorption techniques and the equilibrium effective conditions for these parameters were evaluated. Study of adsorption isotherms and kinetics were carried out and best fitting models for the dye adsorption process were suggested. These fundamental data will be useful for further applications in the treatment of practical waste or process effluents (Tan J. R., 2010)

1.2 Statement of the problem

Environmental pollution is an inevitable consequence of economic development and people’s desire to improve their quality of life. With the increasing demand of textile industries in Ethiopia discharge colored effluents is also increased. Ayka Addis textile manufacturing industry is one of the largest economic sectors in Ethiopia, which discharge 1,800m^3/day of dyes colored wastewater into the nearby water bodies. These colored effluents give undesirable perspective to the water streams where as some dyes and their metabolites pose toxic, carcinogenic and mutagenic effects (Adamu, 2008).

Dyes also prevent light penetration and reduce photosynthetic activities of water streams and disturb aquatic equilibrium. Moreover wastewater containing dyes is difficult to treat, since dyes are recalcitrant organic molecules, resistant to biological degradation and are stable to light or any exposure due to their complex aromatic molecular structures. As a result, removal of dyes from wastewater has a considerable attention over the past decades to decrease their impact on the environment (Seeds & Sepehr, 2011).

Several physical, chemical and biological methods have been developed for the removal of synthetic dyes from wastewater. So far treatment of textile wastewaters in Ethiopia has been based mainly on aerobic biological processes followed by chemical coagulation. Although chemical and biological methods are effective for removing dyes, they require specialized equipment and are usually quite energy intensive; in addition, large amounts of byproducts are often generated that creates a secondary disposal problem which requires safe disposal (Adamu, 2008).

Due to the high cost and disposal problems involved in the above said methods, further investigation of new techniques have been come up. Physical methods, mainly adsorption on various supports were recognized to be a promising and effective process to remove dyes from textile wastewaters. Exploration of good low cost and non-conventional adsorbents may contribute to the sustainability of the environment and offer promising benefits for the commercial purpose in future (Durairaj & Shankar, 2012).

The successful dye removal using low cost adsorbents has been carried out by several researchers. (Saeedeh Hashemian, 2013) studied removal of reactive azo dyes (violet B and violet 5R) from aqueous solutions using bio peels. Besides that, natural materials such as rice husks, several bio-sorbent peels and wheat straw also occupy a position in the production of inexpensive adsorbents to remove non-biodegradable organic compounds like synthetic dyes from wastewater (Eng-Cheong Khoo, 2011). This has led to an increased interest in the subject of adsorption of dye molecules from textile wastewaters. Thus, investigating the suitability of orange peel as low cost alternative and effective adsorbent to remove textile dye from aqueous solution is found to be necessary.

1.3 Objective of the study

1.3.1 General objective

The main objective of this study is to investigate dye removal efficiency of orange peel from aqueous solution.

1.3.2 Specific objectives

- Preparation of powdered orange peel adsorbent (POPA), and characterize by proximate analysis
- Investigate the effect of variation parameters for initial solution pH, POPA dose, contact time and initial RR-DEXF dye concentration in order to determine effective condition for adsorption of the dye by the adsorbent
- Determine dye removal efficiency of the adsorbent
- Study the equilibrium adsorption isotherm and kinetics of dye adsorption by the adsorbent

1.4 Significance of the study

This study should be significant in the sense that:

- Add to the knowledge of dye adsorption process by orange peel adsorbent.
- Its application in textile wastewater treatment method can be a choice, to reduce the impact of dyes colored wastewater on the environment.
- Improve the value such a material are important for the economy of the countries where this species grows abundantly by reducing cost of solid waste management.

2. Literature Review

2.1 Treatment of wastewater containing dyes

In this chapter, literature surveys on synthetic dyes and wastewater treatment methods are described. The classification methods of dyes are introduced according to the chemical structure and application or usage methods. The most common methods for wastewater treatment are described and special attention has been given to adsorption processes for the treatment of wastewater containing dye. Finally factors affecting dye adsorption process and general back ground about adsorption isotherm and kinetic is described.

2.2 Synthetic dyes

Over 700,000 tones dye stuff are produced annually estimated to consist of more than100,000 commercially available dyes. Mauveine was the first modern synthetic organic dye discovered by chance by William Henry Perkin in London in 1856. Actually, this dye was neither the first synthetic dye to be produced in the laboratory nor even the first to be manufactured. The first synthetic organic dye was picric acid, which had been manufactured in 1845 by nitrating phenol (Kassa, 2007).

In 1875, the dye chemist Otto N. Witt proposed a color theory and constituted that a compound is colored due to the presence of certain arrangements of atoms or groups, called chromophores. And the other groups called auxochromes enable the dye to bond to fibres and modify the color. Dyes are colored compound used to impart its color to a substrate material of which it becomes an integral part by one of the various processes dyeing, printing, and surface coating. Generally, the substrate includes textile fibres, polymers, foodstuffs, oils, leather, and many other similar materials (Malinauskiene, 2012).

The major components of dye molecules are chromophores and auxochromes. A chemical structure which is colored is normally accomplished in the synthesis of dyes using a chromogen -chromophore with an auxochrome. The chromophore group is a ‘color giver’ which forms a basis for the chemical classification of dyes when coupled with the chromogen. The most important chromophores are azo (–N=N-), carbonyl (-C=O), and nitro ($-NO_2$) groups. The chromogen, which is the aromatic structure normally containing benzene, naphthalene or anthracene rings, is part of a chromogen-chromophore structure along with an auxochrome. The presence of ionizing groups known as auxochromes results in a much stronger alteration of the maximum absorption of the compound and provides a bonding affinity (Velmurugan & Dhinakaran, 2011).

2.2.1 Classification of dyes

There are two methods used to classify dyes, either according to their chemical structure (particularly considering the chromophoric structure present in the dye molecule) or according to how it is applied to the substrate. The first method is adopted by practicing dye chemists and includes azo, anthraquinone, etc. dyes. The latter method is adopted by the colour index (Malinauskiene, 2012).

I Chemical structure method

The most appropriate way to classify dyes is by chemical structure which has many advantages as follows (Muhi Mohammed, 2011):

- It easily indentifies dyes as relating to a group which has characteristic properties, for example azo dyes (strong, low cost) and anthraquinone dyes (weak, expensive).
- There are a manageable number of chemical groups

In this method of classification, dye molecules are grouped to shared structural groups. For example, the azo dyes are the most important class and contain at least one azo group (-N=N-) which is attached to two radicals of which at least one but perhaps both are aromatic. The next most important dye class contains carbonyl functions (-C=O).

Synthetic dyes have many structural varieties, such as, acidic, basic, disperse, azo, diazo, anthroquinone based and metal complex dyes, that fall into either the cationic, nonionic or anionic type. Anionic dyes include the direct, and the most problematic water-soluble acid and reactive dyes. Nonionic dyes refer to disperse dyes that do not ionize in aqueous medium and some of them have the ability of bioaccumulation. Whereas anthroquinone based dyes are the most resistant to degradation due to their fused aromatic ring structure (Koyuncu, 2009).

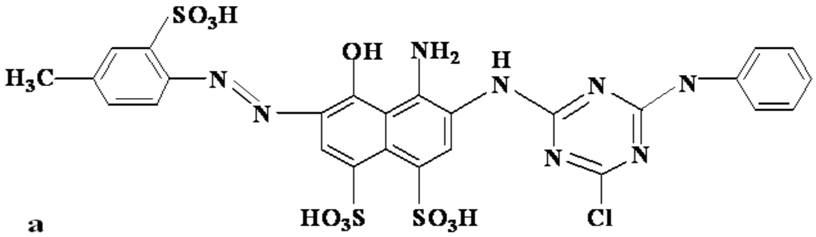

Figure 1: Chemical structure of azo dye (Reactive red 45)

Table 1: Classification of dyes based on applications methods

Dye Class	**Main application**	**General description**	**Chemical type**
Reactive	Used for all cellulosic goods (knitted fabric), wool, silk, and nylon	Easy application; moderate price, good fastness, anionic compounds, and highly water soluble	azo,anthraquinone, phthalocyanine, formazan, oxazine, and basic
Direct	Cellulosic fibers, rayon, silk, and wool	Simple application, cheap, moderate colour fastness, anionic compounds, and highly water soluble	azo, phthalocyanine, stilbene, nitro, and benzodifuranone
Disperse	Polyester, acetate, nylon, and acrylic	Require skill in application (by carrier or high temperature), good fastness, and limited solubility in water	azo, anthraquinone, nitro, and benzodifuranone
Acid	Wool, silk, paper ink, nylon, and leather	Easy application, poor fastness, anionic compounds, and highly water soluble	Azo(including premetallized),anthraquinone, azine, triphenylmethane, xanthene, nitro and nitroso
Basic	Acrylic, polyester, wool, and leather	careful application required to prevent unlevel dyeing and adverse effect in hand feel, cationic, and highly water soluble	cyanine, azo, azine, hemicyanine, diazahemicyanine, triarylmethane, xanthen, acridine, oxazine, and anthraquinone
Vat	Cotton, wool, and rayon	Difficult to apply, expensive, good fastness except indigo and sulphurised vat species, and insoluble in water	anthraquinone (including polycyclic quinones) and indigoids
Sulphur	Used for heavy cellulose goods in dark shades, and rayon	Difficult to apply, cheap, poor fastness, and insoluble in water	indeterminate structures

II. Usage or application methods

The classification of dyes by usage or application method is the principal approach adopted by the color index due to the fact that most textile fibers are polyester and cotton. This classification is listed in Table 1, which is organized according to color index application, shows the principal substrates, the methods of application, and the chemical types of each class of dye (Muhi Mohammed, 2011).

The type of dyestuff used is determined by the specific substrate being dyed and by the fastness properties desired. Reactive dyes are extensively used for textile dyeing because of their wide variety of color shades, high wet fastness profiles, simplicity of application, brilliant colors, and minimal energy consumption (Alenka ojstrsek & Fakin, 2008).

Eighty to ninety- five percent of all reactive dyes are based on the azo chromogen. There are a number of different classes of azo dyes (Table 1), but this study will focus only on fiber-reactive azo dyes. Since reactive azo dyes is the most common dye applied for cellulosic substrate (for example cotton) which is nearly about 90 % of Ethiopia textile manufacturing products. Therefore, it can be expected that, reactive azo dyes constitute the vast majority of the dyes wastewater discharged from textile-processing industries (Kassa, 2007).

2.3. Impact on the environment

Any industrial activities causes pollution in one form or the other so is the textile industry. Wastewater is the most environmentally damaging, and the wastewater from textile plants is classified as the most polluting of all the industrial sectors, considering the volume generated as well as its composition. The dyestuff lost through the processes of the textile poses a major problem for wastewater treatment (Malinauskiene, 2012).

Through the dyeing process, depending on the class of the dye, its loss in wastewaters could vary from 2% for basic dyes to as high as 50% for reactive dyes, leading to severe contamination of surface and ground waters. Color is the first wastewater contaminant to be recognized, since a very small amount of dye concentration in water (<1ppm) are highly visible that affects aesthetic merit, transparency and water-gas solubility. Moreover reducing light penetration through water decreases photosynthetic activity, generating oxygen deficiency and de-regulating the biological cycles of aquatic biota (Mohammadine El Haddad, 2013).

Many dyes are also highly toxic to the ecosystem and mutagens, meaning they can have acute to chronic effects upon organisms, depending on exposure time and dye concentration. For example, dye effluent has been connected to growth reduction, metabolic stress and death in fish, and growth and productivity in plants. Contamination therefore limits downstream human water use such as recreation, drinking, fishing and irrigation (Chequer, 2013). Therefore, wastewater containing residual dyes need to be treated before discharging to the receiving environment to keep the environment eco-friendly and sustainable.

2.4 Environmental Legislation

With respect to legislation, there is as yet no international consensus concerning discharging textile effluent, including dyes, and there is no official document listing the different effluent limit values applied in different countries. Many developed countries, such as the United States of America, Canada, Australia and the nations of the EU enforce environmental legislation, which establishes limits. Countries, such as Thailand, have copied the US system, whereas others, such as Turkey and Morocco, have copied the EU model. In other nations, including India, Pakistan and Malaysia, the effluent contamination limits are recommended, but not mandatory. In the majority of developing countries like Ethiopia, dye limitations are not specified as separate from that of groupings such as ‘total dissolved solid’ concentration (Chequer, 2013).

2.5 Wastewater treatment methods

Pollution by organic chemicals including that by dyes is one of the most serious environmental problems facing life on earth. There are several sources of water pollution by dyes and pigments, such as leather tanning, paper, rubber, food technology and the textile industry. These dyes have a variety of complex organic compounds and toxic substances with unknown environmental behaviour such as aromatic amines (C_6H_5-NH_2), which are suspected to have carcinogenic effect, phenyl (C_6H_5-CH_2) and naphthyl (NO_2-OH). The resistance of these organic compounds to decomposition due to the complex chemical structure of synthetic pigments in dyes results in a difficult to treat wastewater which is also resistant to degradation by biological methods (Velmurugan & Dhinakaran, 2011)

Many researchers have studied different methods to remove dyes from wastewater including chemical, physicochemical and biological processes such as, adsorption, chemical precipitation, electrochemical oxidation, chemical oxidation, and aerobic and anaerobic biological processes (Maria, 2014). Several reported methods for removal of dye pollutants from wastewater are summarized in Table 2.

2.5.1 Biological Method

Biological treatment is relatively economical methods compared to other physical and chemical processes. Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial wastewater because many microorganisms such as bacteria, yeasts, algaes and fungi are able to accumulate and degrade different pollutants (Hasan, 2008).

However, their application is often restricted because of technical constraint. According to (Wallace, 2001), biological treatment requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation. Further, biological treatment is incapable of obtaining satisfactory dye removal with current conventional biodegradation processes. Moreover, although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin.

2.5.2 Chemical Methods

Chemical methods include coagulation or flocculation combined with flotation and filtration, precipitation–flocculation with Fe(II)/$Ca(OH)_2$, electroflotation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. These chemical methods are often expensive, and although dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use (Maria, 2014).

Table 2: Principal existing and emerging processes for dyes removal (Hasan, 2008)

Dye removal method		**Advantages**	**Disadvantages**
Conventional treatment process	Coagulant Flocculant	Simple, economically feasible	High sludge production, handling and disposal problems
	Biodegradation	Economically attractive, publicly acceptable treatment	Slow process, necessary to create an optimal favorable environment, maintenance and nutrition requirement
	Adsorption on activated carbon	The most effective adsorbent, great, capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dye, the regeneration is expensive and result in loss of the adsorbent, non-destructive process
Establish recovery process	Membrane separation	Remove all dye types, produce a high-quality treated effluent	High pressure, expensive, incapable of treating large volumes
	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dye
	Oxidation	Rapid and efficient process	High energy cost, chemical required
Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
	Selective Bio adsorbents	Economically attractive, Regeneration is not necessary, high selectivity	Requires chemical modification, nondestructive process
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on microorganis	Slow process, performance depends on some external factors (pH, salts)

Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for pollutant degradation. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems (Beyene, 2014).

2.5.3 Physical methods

Different phsical methods are also widely used, such as membrane – filtration processes (nano filtration, reverse osmosis) and adsorption techniques. The major disadvantages of the membrane processes are: (i) a limited lifetime before membrane fouling occurs and (ii) cost of periodic replacement which need to be included in any analysis of their economic viability (Durairaj & Shankar, 2012).

In accordance with the very abundant literature data, liquid-phase adsorption is one of the most popular methods for the removal of pollutants from wastewater since proper design of the adsorption process will produce a high-quality treated effluent. This process provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pretreatment step before its application (Beyene, 2014).

Generally, all the dye removal methods have their own advantages and disadvantages as reviewed in Table 2. There is no obvious stand out method; all have both advantages and disadvantages. This work examines the potential for the adsorption process to overcome some, if not all of the problems with adsorption by using powdered orange peel (POP) as bio-adsorbent and thereby to make it the treatment method of choice for textile dye removal from wastewater.

2.6 Adsorption

Adsorption is the process in which different molecules, ions and atoms of a liquid or gas get attached to the surface. Adsorbate is attached in the form of a film on the surface of the adsorbent. This process is different from absorption since in absorption, the substrate which is usually in the form of fluid percolates into the absorbent (Ramakrishna, 2013). Thus absorption includes the whole matter whereas adsorption is only effective on surfaces. But both the terms are included in a single term called “sorption”, and the reverse of “sorption” is called “desorption”. Adsorption is proving to be a better and more efficient method of waste water treatment in recent years. It is the process of formation of a layer of solid or gas on the substrate. Thus in the process of adsorption, the substance gets separated from fluid phase and gets accumulated on the solid phase substrate (Abbas F. S., 2013).

And it is a well known equilibrium separation process and an effective method for water de-contamination application. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances. The process is influenced by many physicochemical factors such as dye/sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time (Ramakrishna, 2013) as (described in section 2.4.1).

Most of the solid adsorbents of great industrial applications possess a complex porous structure that consists of pores of different sizes and shapes. In terms of the adsorption science, total porosity is usually classified into three groups. According to international union of pure and applied chemistry (IUPAC) recommendation, the micro-pores are defined as pores of a width (<2nm), mesopores are pores of a width (2-50nm), but macro-pores represent pores of a width (>50nm) (Hasan, 2008).

However, the importance of porous structure on adsorption of many contaminants in aqueous solution is not well understood. As to physisorption on porous materials, it’s generally accepted that adsorption mechanism and process may be significantly different as a consequence of porous structure. Further, a powder is easily recognized as a mass of small dry particles, but the precise definition is inevitably somewhat arbitrary. The term fine powder is also used in an imprecise manner, but it seems reasonable to apply it to a material consisting of particles less than about 1μm. The unit mass of a fine powder contains a large number of small particles and exhibits an appreciable surface area (Serin & Selen, 2012)

In addition to the performance, a number of other factors greatly influence the choice and viability of waste materials as adsorbents, for example the cost of processing materials, wastewater selectivity and regeneration of materials. Cost is a very important factor when considering materials for use as adsorbents. It is generally recognized that a material can be deemed low-cost if it requires little processing, is abundant in nature, or is a byproduct or waste material from another industry (Eng-Cheong Khoo, 2011).

2.6.1. Adsorbent for dye removal

Virtually every solid surface has the capacity to adsorb sorbate but the effectiveness of these solids in the wastewater treatment process is a function of its structure, degree of polarity, porosity and specific area. The adsorbate may be an organic compound with undesirable properties such as color, odour, etc. The principal types of adsorbents include activated carbon, organic polymers and silica-based compounds (Muhi Mohammed, 2011)**.**

A. Commercial activated carbons

Adsorption techniques employing solid sorbents are widely used to remove certain classes of chemical pollutants from waters, especially those that are practically unaffected by conventional biological wastewater treatments. However, amongst all the adsorbent materials proposed, activated carbon is the most popular for the removal of pollutants from wastewater. In particular, the effectiveness of adsorption on commercial activated carbons for removal of a wide variety of dyes from wastewaters has made it an ideal alternative to other expensive treatment methods. This is mainly due to their structural characteristics and their porous texture which gives them a large surface area, and their chemical nature which can be easily modified by chemical treatment in order to increase their properties (Singh & M.K., 2000).

However, activated carbon presents several disadvantages. It is quite expensive, the higher the quality, the greater the cost, nonselective and ineffective against disperse and vat dyes. The regeneration of saturated carbon is also expensive and results in loss of the adsorbent. In contrast, the utilization of alternative low-cost materials with high adsorption capacity to solve environmental problems has received considerable attention over the recent years (Eng-Cheong Khoo, 2011).

B. Non-conventional low-cost adsorbents

Due to the problems mentioned above, research interest into the production of alternative sorbents to replace the costly activated carbon has intensified in recent years. Attention has focused on various natural solid supports, which are able to remove pollutants from contaminated water at low cost. Cost is actually an important parameter for comparing the adsorbent materials. Researchers are always in a hunt for developing more suitable, efficient and cheap and easily available types of adsorbents, particularly from the waste materials (Ramesh, 2013).

C. Raw agricultural solid waste

Raw agricultural solid wastes and waste materials from forest industries such as sawdust and bark have been used as adsorbents. These materials are available in large quantities and may have potential as sorbents due to their physico-chemical characteristics and low-cost. Agricultural waste materials have little or no economic value and often pose a disposal problem, so utilization of the material is of great significance (Eng-Cheong Khoo, 2011).

A number of agricultural waste materials are being studied for the removal of different dyes from aqueous solutions at different operating conditions. These include mangrove bark (Tan J. R., 2010), wheat straw (Nader Yousefi A. F., 2011) and orange peel and rice husk (Y.C.Wong and K.N. Ranjini, 2014). Many researchers have been investigating the suitability of many of agricultural by products as bio-adsorbent to remove organic pollutants including different groups of synthetic dye which is the focus of this study that is to explore the feasibility of powdered orange peel (POP) as bio-adsorbent to remove azo dye (Reactive red DEXF) from aqueous solution.

Orange peel was investigated by (Benaissa, 2005) for the removal of four type acid dyes namely (Nylosane Blue, Erionyl Yellow,Nylomine Red and Erionyl Red) from aqueous solution. Equilibrium isotherms were determined and analyzed using the Langmuir and Freundlich isotherms. The kinetic data were analyzed using pseudo-first-order and pseudo second- order models. The pseudo second-order reaction rate model adequately described the kinetics of dyes sorption with high correlation coefficients.

The chemical nature of biological materials is complex and a variety of mechanisms may be operative simultaneously under the given conditions. The variety of structural components present in bio-peels means that different functional groups are able to interact with pollutants. For example carboxyl, phosphate, hydroxyl, are common functional groups present in varying degrees and are affected by physicochemical factors. The diversity of chemical structure encountered in organic pollutants (molecular size, charge, solubility, hydrophobicity, and reactivity), the type of bio-adsorbent and wastewater composition affect bio sorption as well (Ramakrishna, 2013).

D. Orange peel and its characteristics

Orange, as a kind of biological resources is available in large quantities in many parts of the world. Orange peel principally consists of cellulose, hemicelluloses chlorophyll pigment lignin and other low molecular weight hydrocarbon. These components contain various functional groups, such as carboxyl and hydroxyl groups which make orange peel to be a potential adsorbent material for removing different ionic compounds from aqueous solution (Said & Mansour, 2012).

Since the orange peel is available free of cost from orange processing industries, only the characterization of it is involved for the waste for wastewater treatment would not only be economical but also will help to solve solid waste disposal problems. (Saeedeh Hashemian, 2013) studied the removal of azo dye from aqueous solutions by using different bio peels. In this work, FTIR spectrum of the orange peel evidenced the presence of carboxyl and hydroxyl groups, which are important functional groups for dye removal by biological materials (Singh & M.K., 2000). Besides that this component is widely used to be manufactured as an adsorbent to adsorb (CO_2) gas (Mahdi, 2014) and Ni(II) ions from aqueous solution (Serin & Selen, 2012). Orange peel contain potassium oxide (K_2O) with 1.72%, calcium oxide (CaO) with 1.31% and others components in the minority. Therefore, with the great amount of carbon component, carbon produced from orange peel and also orange peel itself is one of the potential adsorbent to adsorb anionic dyes and different pollutants from aqueous solution (Mahdi, 2014).

2.6.2 Factor affecting dye adsorption

Many physicochemical factors influence the amount of adsorption of a adsorbate (dye) onto an adsorbent and these include: surface area of adsorbent, initial dye concentration, temperature, pH and contact time between adsorbate and adsorbent etc.

A. Initial dye concentration

The initial dye concentration is important in adsorption, since a given mass of sorbent material can only adsorb a fixed amount of dye. Normally, the dye removal will decrease with increase in initial dye concentration. This is because for a given mass of adsorbent material; the amount of dye that can be adsorbed is fixed. The higher the concentration of the dye, the smaller the volume it can remove. At a low concentration, there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of the dye molecules will be lacking. But the actual amount of dye adsorbed per unit mass of adsorbent increased with increase in dye concentration. This may be due to the high driving force for mass transfer at a high initial dye concentration (Ramesh, 2013).

According to the studied report by (Saeedeh Hashemian, 2013), the effect of various initial dye concentration of azo dye(Violet B and Violet 5R) on different bio peel was investigated. And the study showed that percentage of dye adsorption efficiency decreased with increasing of initial dye concentration in the solution. However, the percentage removal of dye is greater at lower initial concentrations and smaller at higher initial concentrations. Thus the adsorption process is highly dependent on the initial concentration of the pollutant.

The capacity of the adsorbent material gets exhausted sharply with increase in initial dye concentration. This may be probably as a result of the fact that for a fixed adsorbent dose, the total available adsorption sites remain invariable for all the concentrations checked. With increasing concentration the available adsorption sites become fewer and hence the percent removal of dye is dependent upon the initial concentration (Aseel M. and Kadim Aljebori, 2010).

B. Effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption process can be carried out by preparing adsorbent–adsorbate solution with different amount of adsorbents added to fixed initial dye concentration and shaken together until equilibrium is attained. The percentage of dye removal increases with increasing adsorbent dosage. Initially the rate of increase in the percent dye removal has been found to be rapid which slowed down as the dose increased. This phenomenon can be explained, based on the fact that at lower adsorbent dose the adsorbate (dye) is more easily accessible and because of this, removal per unit weight of adsorbent is higher (Singh & M.K., 2000).

However with rise in adsorbent dose, there is less commensurate increase in adsorption, resulting from many sites remaining unsaturated during the adsorption. But after a certain dosage the increase in removal efficiency is insignificant with respect to increase in dose. This is due to the fact that, at higher adsorbent amount there is a very fast superficial adsorption onto the adsorbent surface that produces a lower solute concentration in the solution than when adsorbent dose is lower. Thus, with increasing adsorbent dose, the amount of dye adsorbed per unit mass of adsorbent is reduced (Saeedeh Hashemian, 2013).

C. Effect of initial pH

The pH factor is very important in the adsorption process especially for dye adsorption. pH of a medium will control the magnitude of electrostatic charges which are imparted by the ionized dye molecules. As a result, the rate of adsorption will vary with the pH of an aqueous solution. At low pH solution, the percentage of dye removal will decrease for cationic dye adsorption, while for anionic dyes the percentage of dye removal will increase. In contrast, at a high solution pH, the percentage of dye removal will increase for cationic dye adsorption and decrease for anionic dye adsorption (Ramesh, 2013). For cationic dyes, lower adsorption at acidic pH was due to the presence of excess H^+ ions competing with the pollutant cations for adsorption sites. At higher pH, the acidic functional groups on the surface of the adsorbent may get ionised, which enhances the adsorption of positively charged cations through electrostatic attraction. In the case of anionic dyes, the lower pH resulted in higher adsorption as the positively charged surface of the adsorbent could adsorb negatively charged anionic dyes (Ramakrishna, 2013).

As per (Nader Yousefi A. F., 2011), study the dye adsorption by modified wheat straw was affected by initial pH changes in the range of 1 to 7. The study showed that as the pH solution increases from 1 to 7 dye removal efficiency with modified wheat straw increases from 61.54 to 83.15%. But as pH increases to greater than 7, the dye removal efficiency quickly drops. At high pH, low adsorption capacity is due to competition between hydroxyl ions and negative charge of dye ions on adsorption sites (Nader Yousefi A. F., 2011).

According to (Saeedeh Hashemian, 2013), the effect of pH on adsorption of azo dye, Violet B and Violet 5R onto orange peel was carried out at room temperature (25 ± 2ºC), at an agitation speed of 150 rpm for the minimum contact time required to reach the equilibrium (60 min). The study showed that with increasing the pH of dye solution from 1 to 7, the percent of dye removal increased from 69 to 90% and 65 to 86% for V5R and VB, respectively.

Several researchers studied the point of zero charge (pH_{pzc}) of adsorbents that are prepared from agricultural solid wastes in order to better understand the adsorption mechanism. Cationic dye adsorption is favored at pH>pHpzc, due to the presence of functional groups such as OH^-, COO^-groups. Anionic dye adsorption is favored at pH<pHpzc where the surface of adsorbent becomes positively charged that acquire adsorption of negatively charged anionic dye (Ramesh, 2013).

D. Effect of temperature

Normally, increasing the temperature leads to a decrease in adsorption due to the adsorbed molecules having greater energies and therefore becoming more likely to release from the surface of the adsorbent. According to (Mafra & Ferreira, 2013), the reason for the fall in the adsorption capacity at elevated temperatures may be that at higher temperatures a part of the dye leaves the solid phase and re-enters the liquid phase.

E. Contact time

The effect of contact time on adsorption of dye can be carried out by preparing adsorbent - adsorbate solution with fixed adsorbent dose and initial dye concentration for different time intervals and shaken until equilibrium. Generally, the rate of removal of dye increases with an increase in contact time to a certain extent. Further increase in contact time does not increase the uptake due to deposition of dyes on the available adsorption site on adsorbent material. At this point, the amount of the dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the dye being adsorbed onto the adsorbent. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions (Adamu, 2008).

2.7. Mechanism of Adsorption

Among the unit operations in waste water treatment, adsorption occupies an important position since it is an efficient and economically feasible process for treatment of wastewater containing dissolved organic pollutants (Aseel M. and Kadim Aljebori, 2010). In the adsorption process, molecules are extracted from one phase (liquid phase, dye solution) and concentrated at the surface of a second phase (solid phase, adsorbent) which occurs due to an attractive force existing between the adsorbent surface and the adsorbate molecules. Therefore, it is a removal process where certain molecules are bound to an adsorbent particle surface by either chemical or physical attraction. The adsorption process consists of three consecutive steps (Muhi Mohammed, 2011):

- Substances adsorb to the exterior of the adsorbent
- Substances move into the adsorbent pores
- Substances adsorb to the interior walls of the adsorbent

While adsorption is the phenomenon of accumulation of a large number of molecular species at the surface of solid or liquid phase in comparison to the bulk. These phenomena can be classified into two types depending on the nature of the bonding between the molecules of the adsorbate and the surface of adsorbent, namely chemisorption and physisorption. Both types take place when the molecules in the liquid phase (sorbate) become attached to the surface of the solid phase (adsorbent) as a result of the attractive forces at the adsorbent surface overcoming the kinetic energy of the adsorbate molecules (Beyene, 2014).

- **Physisorption**

Physisorption or physical adsorption occurs when, as a result of energy difference and / or electrical attractive forces (weak Van der Waals forces), adsorbate molecules become physically fastened to the adsorbent surface. Physisorption takes place with the formation of single or multiple layers of adsorbate on the adsorbent surface and is characterized by a low activation energy (enthalpy) of adsorption.

- **Chemisorption**

Chemisorption or chemical adsorption occurs when a chemical reaction occurs between the adsorbed molecules and the adsorbent. Chemisorption takes place with the formation of a single layer of adsorbate attached to the adsorbent surface by chemical bonds. This type of interaction is strong with a covalent bond between adsorbate and the surface of the adsorbent is characterized by a high enthalpy of adsorption (Beyene, 2014).

2.8 Adsorption isotherm

Adsorption is typically represented through isotherms, that is, the quantity of adsorbate on the adsorbent as a function of its pressure (in case of gas) or concentration (in case of liquid) at a constant temperature. Amount of adsorbate adsorbed is almost continuously normalized by the mass of the adsorbent to permit comparison of various materials. Equilibrium studies on adsorption process provide data on the capacity of the adsorbent (Serin & Selen, 2012).

The equilibrium state is characterized by a concentration (loading) of adsorbate in the solid phase (q_e mg/g) which is in dynamic equilibrium with a solute concentration in the liquid phase (C_e mg/L). A wide range values of q_e versus C_e values may be obtained by varying the amount of adsorbent (m, g), the initial concentration of solute (C_o, mg/L), and the volume of liquid (Asgher, 2011). The relationship between these q_e and C_e can normally be fitted to one or more equilibrium isotherm models. There are many models to describe the equilibrium behaviour for adsorption of contaminants from water (Nader Yousefi A. F., 2011).

1. Langmuir model

The Langmuir model Equation (1) was originally developed to describe and quantify sorption on a set of distinct localized adsorption sites, and has been used to describe both physical and chemical adsorption. This model is based upon the following main assumptions (langmuir, 1916).

- Each active site interacts with only one adsorbate molecule.
- Adsorbate molecules are adsorbed on well defined localized sites and the saturation coverage corresponds to complete occupancy of these sites.
- The adsorption sites are all energetically equivalent (homogeneous), and there is no interaction between adjacent adsorbed molecules.

Based on these assumptions, the Langmuir relationship between *qe* and *Ce* is given by:

$$q_e = \frac{q_m \ k_L C_e}{1+k_L \ C_e} \qquad (1)$$

Where, q_m (mg g^{-1}) and k_L (L mg^{-1}) are the Langmuir constants related to the capacity of adsorbent and energy of adsorption respectively. This model is the most widely applied adsorption isotherm and has produced good agreement with a variety of experimental data (Abbas & Kadim, 2010).

2. Freundlich model

The Freundlich equation is an empirical relationship which describes the adsorption of the solutes from a liquid to solid surface. The Freundlich model (Equation (2)) describes adsorption in terms of adsorbate concentration (Meena Soni and Ashok Sharma, 2012).

Linearized form of the Freundlich equation is as follows:

$$\mathrm{Log}\mathbf{q_e} = \log \mathbf{k_f} + \frac{\mathbf{1}}{\mathbf{n}} \log \mathbf{C_e} \qquad (2)$$

Where, k_f and 1/n are freundlich isotherm constants related to adsorption capacity and adsorption intensity respectively.

2.9 Adsorption kinetics

Adsorption processes are characterized by their kinetic and equilibrium behaviour. The transport of the adsorbate at the solid-solution interface (adsorbent) and the attachment of the adsorbate onto the adsorbent surface (i.e. the rate of the physiochemical interaction at the surface) determine the uptake rate of the adsorbate and thus the kinetics of the process (Husein, 2012).

The degree of purification that may be achieved, the approximate amount of adsorbent required to reach that degree of purification and the sensitivity of the process to the concentration of the solute are predicted by the isotherms. Many mathematical models have been studied in order to describe the kinetics of adsorption processes. The pseudo first-order equation and pseudo second order equation are the widely used models for the adsorption kinetics of organic compounds (Beyene, 2014).

A study of the kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for the efficiency of the process. In addition, the design of an adsorption system for water treatment may be influenced or even controlled by the adsorption kinetics (Muhi Mohammed, 2011). The rate of adsorption may be controlled by mass transfer, intra-particle diffusion, or surface chemical kinetics. Several kinetic models for the liquid phase have been widely used to describe experimental data. These include pseudo first order, pseudo second order, and mass transfer/intra-particle diffusion models (Koyuncu, 2009).

The pseudo first-order model is expressed as follows:

$$\frac{\mathbf{dq_t}}{\mathbf{d_t}} = \mathbf{k_1}(\mathbf{q_e} - \mathbf{q_t}) \tag{3}$$

The pseudo second-order model is expressed as:

$$\frac{\mathbf{dq_t}}{\mathbf{d_t}} = \mathbf{k_2}(\mathbf{q_e} - \mathbf{q_t})^2$$

(4)

Where, q_e and q_t are the amounts of adsorbate adsorbed (mgg^{-1}) at equilibrium and at any time t and k_1 (min^{-1}), k_2 (min^{-1}) are the pseudo first and second-order rate constants respectively.

3. Material and Methods

3.1 Preparation of adsorbent

Oranges are found in Ethiopia. Their peels can easily be obtained from any juice shop or fruit stall. Since peel does not have any significant use, they are treated as waste materials. The orange peels were thoroughly washed with distilled water to remove dirt and unwanted particles adhered to it. After washing, the peels were cut into small pieces for making it easier to grind them. The peels were then kept in hot air oven at 70°C for 24h to dry. After drying, the materials were crushed in a mixer grinder until they became fine powder. Powdered orange peel of (500g) sample was washed with distilled water, by shaking till the wash water was completely decolorized, since the pigment present in POP could interfere with the spectrum of the dye. After washing, the sample is vacuum-filtered using filter paper and dried in hot air oven at 70°C for 24h.

The dried powdered orange peel (POP) was sieved at average geometrical mean size of 150μm so that all the size of the powdered adsorbent to be used is of similar size and named as powdered orange peel adsorbent (POPA). It was stored in an air tight container for the adsorption studies without any further treatment. The sequence of preparation of POPA is schematically represented by Fig. 3.

Figure 2: Powdered orange peel sample used for dye adsorption

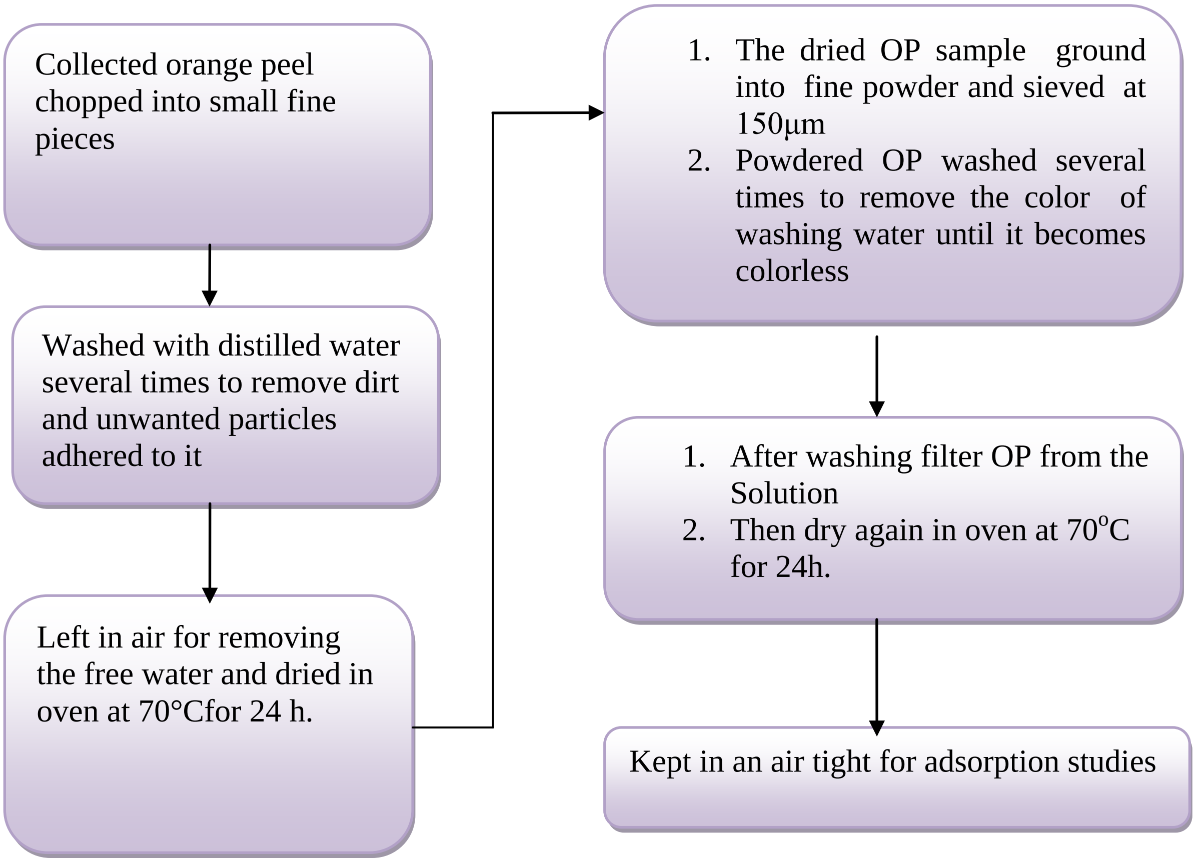

Figure 3: Schematic diagram indicate the sequence of preparation of the orange peel

3.2 Characterization of orange peel

1 Proximate analysis

i. Moisture content

A crucible was taken and weighed. 2g of sample (POPA) was added in the crucible and weighed. It was kept in hot air oven at 105°C for 24h. It was taken out and kept in the desiccators. Then the weight was measured and the moisture content is calculated as:

$$M=100\text{x}\frac{(\mathbf{B}-\mathbf{F})}{(\mathbf{B}-\mathbf{G})} \qquad (5)$$

Where, M = moisture content (%), B= mass of crucible plus sample (39.40g), F = mass of crucible plus dried sample (39.34g), G = mass of empty crucible (37.40g). Accordingly, moisture content is calculated to be 3%.

ii. Ash content

2 g of sample was taken in crucible and weighed. The sample was kept in a muffle furnace for 2h at a temperature of 550°C. Then, it was taken out and kept in desiccators for half an hour to cool down. Then, again the weight was measured and ash content is calculated as:

$$A=100 \text{ x } \frac{F-G}{B-G} \tag{6}$$

Where, A = Ash content, B= Mass of crucible plus sample (38.80g), F= mass of crucible plus ash sample (after heating) 36.89g, G = mass of empty crucible (36.80g). So, ash content is calculated to be 4.5%.

iii. Volatile Matter

A crucible was taken and weighed. 2g of sample was added in the crucible and weighed. It was kept in the muffle furnace at a temperature of 650°C for 10 minutes. Then it was taken out and kept in the desiccators for half an hour to cool down. The weight of the sample in crucible was measured again. Percent volatile matter was then calculated as,

$$V = 100 \times \frac{100(B-F)-M*(B-G)}{(B-G)*(100-M)} \tag{7}$$

Where, V= volatile matter (%), B= mass of crucible plus sample (38.87), F=mass of crucible plus ash sample (37.49g), G = mass of empty crucible (36.87), M=3%. So as Eq. (7), percent volatile matter was found to be 36%.

iv. Carbon Content

Carbon content is calculated as following:

%Carbon =100 – (% moisture content + %volatile content + % ash content) (8)

% Carbon = 100 - 43.5 = 56.5%

v. Point of zero charge

Point of zero charge of the orange peel sorbents was measured by the batch equilibrium technique in 0.01 M NaCl. Ten series of test solutions 100mL were prepared in conical flask by varying initial pH of the test solution from pH 3 to 12. 2g of the adsorbent was added to each test solutions. And the solutions were shaken for 24h at 150rpm in room temperature 27°C. The point of zero charge was then determined from a plateau in the pH $_{\text{final}}$ versus pH $_{\text{initial}}$ plot.

3.3 Adsorbate preparation

For this study Reactive Red DEXF dye (RR-DEXF) powder was taken from Ayka Addis textile industry and it was used as adsorbate molecule in adsorption experiments. Since Reactive red DEXF dye is one of the most common dyes that have been used for cotton textile dyeing in this industry. It is a diazo compound; in aquatic solutions this dyes carry a net negative charge due to the presence of sulphonate groups. Due to their strong interaction with many surfaces of synthetic and natural fabrics, reactive azo dyes are used for dyeing wool, cotton, nylon and silk (Veeramalini & Amarnath, 2012). The main characteristic of the dye is given in Table 3.

A stock solution of the dye, 500 mg/L was prepared by mixing 0.5 g of the dye powder in 1000 mL distilled water. The aqueous solutions of varied concentrations of RR-DEXF dye was prepared by dilution from its stock solution and the study were done by varying different parameters.

Table 3: Main characteristics of Reactive Red DEXF (RR-DEXF) dye

Dye type	Class	C.I name	Molecular weight (g/mol)	Max. wavelength absorbanceλ_{max}(nm)
Azo	Anionic	Reactive Red DEXF (RR-DEXF)	795.96	540

3.4 Analytical methods

In order to know the maximum wave length absorbency of RR-DEXF dye, 20mg/L of the dye solution was taken and scanned using UV-vis spectrophotometer (Jenway 6300 England) and it was found that maximum absorbency (λ_{max}) of the dye is 540nm. To calculate the dye concentration from each batch adsorption experiment, a calibration curve was first prepared by using the standard RR-DEXF dye solution with known concentrations. Different concentrations were prepared and absorbance values were recorded at λ_{max} of the dye using UV-visible spectrophotometer.

Absorbance versus concentration of the standard dye solution was recorded as presented in Table 4 to obtain absorbance-concentration profile. Linear calibration curve of this data was served as the basis for determining the dye concentration variation as a result of the dye adsorption process during the experimental work.

Table 4: Absorbance value of RR-DEXF dye concentration at 540nm

Conc. of the dye Co (mg/L)	Max. wave length absorbance of the dye	Abs. value
4	540	0.096
8	≫	0.147
12	≫	0.288
16	≫	0.292
20	≫	0.347

3.5 Bach adsorption experimental procedure

Batch experiments were conducted in a series of conical flask of 250 mL capacity. In all the experiments, solution volume was 100 mL and the mixture of solution and the adsorbent was agitated by using rotary incubator shaker at 200 rpm (Excella E-24 Model as in Fig.4) for desired time at (27°C) temperature. Initial pH of the solution was measured using an electronic pH/conductivity meter (Jenway 430 Model) by adding 0.1M HCl or 0.1M NaOH before adding the adsorbent.

At the end of each adsorption experiment, small amount of the test solutions were withdrawn at predetermined time and centrifuged at 2000 rpm for 15 min and concentration of the residual dye was measured using UV-visible spectrophotometer (Jenway 6300 Engand) at a λ_{max} corresponding to the maximum adsorption for the dye solution (λ_{max} = 540nm). All experiments were performed in duplicate and the mean value was presented. The adsorption experimental data were annexed.

Textile dye effluents have variety of chemical composition and their binding interactions with adsorbent depend on the chemical structure of a particular dye, the specific chemistry and morphology of the bio-sorbent surface and properties of the dye solution or wastewater (Asgher, 2011). Therefore, the effect of different experimental parameters upon adsorption efficiency of POPA was studied as follows.

The effect of pH on percentage removal of RR-DEXF dye by the adsorbent was studied at initial concentration of the dye 12mg/L for pH values at 3,5,7,9 and 11 using 0.2 g of POPA in 100mL of the solution at 27°C. The test solutions were shaken at agitation speed 200 rpm for 60 min in order to determine the effective pH for the dye removal.

The effect of adsorbent dose was studied by adding different amount (0.05, 0.1, 0.2, 0.3 and 0.4) g of the adsorbent at 12mg/L in 100 mL of the dye solutions at constant pH for 60 min contact time. To determine the adsorbent dose at which maximum dye removal efficiency achieved.

The effect of initial dye concentrations was carried out by shaking 100 mL the dye solutions of desired concentrations (4, 8, 12, 16 and 20 mg/L) with constant amount 0.2 g of the adsorbent. All the samples were adjusted to constant pH 3.0 prior to adding the adsorbent. The test solution samples were then, withdrawn from the shaker at pre-determined time intervals of (20, 40, 60, 80 and 100 min).

The amount of RR-DEXF dye adsorbed onto the unit weight of POPA at equilibrium and at any time t were calculated based on mass balance equations given by the following equations, respectively (Meroufel & Zenasni, 2013).

$$\mathbf{q_e = \frac{V(C_o - C_e)}{m}}$$

$$\mathbf{q_t = \frac{V(C_o - C_t)}{m}}$$

Where, q_e and q_t are the amounts adsorbed (mg/g) at the equilibrium and at any time t, respectively. C_o, C_e and C_t are the concentration of the dye in the solution (mg/L) at the initial, equilibrium and at time t, respectively; V is the volume of the solution (L); and m is the dry weight of POPA (g).

The removal efficiency (E) of the adsorbent can be calculated as (Seeds & Sepehr, 2011):

$$\text{Removal E (\%)} = \frac{(C_o - C_t)}{C_o} \times 100 \qquad (9)$$

Where, C_o and C_t (mg/L) are the initial and concentration at time t of the dye in the solution, respectively; V is the solution volume and m is the mass of the adsorbent (g).

Figure 4: Incubator shaker used for experimental setup

3.5.1 Adsorption isotherm study

Various linear and nonlinear adsorption isotherms were used to characterize adsorption process for evaluating the adsorption capacity of the adsorbent. An isotherm describes the relationship between the amount of dye adsorbed and the dye concentration remaining in solution (Subasri & Mani, 2015). Langmuir and Freundlich isotherms are the most widely used two parameter linear isotherms. Regression methods are generally used to determine the coefficients of the isotherm equations. The Langmuir isotherm assumes that all binding sites have equal affinity resulting in the formation of monolayer of adsorbed molecules (langmuir, 1916).

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{1}{q_m} C_e \quad (10)$$

Where, q_m (mg/g) is the amount of dye adsorbed per unit mass of the adsorbent equivalent to formation of a complete monolayer, k_L (L/mg) is the Langmuir constant related to the equilibrium constant of the adsorption process. C_e (mg/L) and q_e (mg/g) are the equilibrium liquid phase concentrations and amount of solute adsorbed at equilibrium, respectively. The Freundlich isotherm defines adsorption to heterogeneous surfaces having adsorption sites of varying affinities (Freundlich, 1906). The Freundlich isotherm equation is given as:

$$\text{Log } q_e = \log K_f + \frac{1}{n} \log C_e \quad (11)$$

Where, K_f (mg/g) and n (mg/L) are Freundlich coefficients.

3.5.2 Kinetic study

Kinetic models are used to investigate the controlling mechanism of sorption process such as chemical reaction, diffusion control and mass transfer (Meena Soni and Ashok Sharma, 2012). The kinetics of RR-DEXF dye adsorption onto OPA was analyzed using pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order equation is generally expressed as follows:

$$\text{Log } (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (12)$$

Where, q_e and q_t are the amounts adsorbed (mg/g) at equilibrium and at any time t, k_1 (min^{-1}) is the adsorption rate constant. If the rate of adsorption is a second order mechanism, the pseudo-second-order kinetic rate equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (13)$$

Where, k_2 (g/mg.min) is the equilibrium rate constant of pseudo second order adsorption.

4. Result and Discussion

The following chapter provides result of laboratory analysis made for powdered orange peel preparation and study on some factors affecting dye adsorption such as initial solution pH, adsorbent dose, initial dye concentration and contact time by powdered orange peel adsorbent from aqueous solution and findings of other scientific data generated from this study.

4.1 Characterization of POPA

Proximate analysis was performed for the prepared orange peel to analyze its different physical characteristics such as moisture content, ash content and volatile matter. Table 4 summarized some of the characteristics of POPA. It was revealed that the carbon content is reasonably good enough to make orange peel as a good low-cost adsorbent.

The moisture content of the POPA was found to be 3% which is slightly lower than the value reported elsewhere by (Benaissa, 2005), (3.8%).

The ash content is a reflection of the amount of inorganic substituent present and was obtained as 4.5 %. The ash content of most AC from agricultural products is within 0.2 to 13.4 % (Nasiru Abdus-Salam P. a., 2014).

Volatile matter is due to the residual organic compounds in the prepared OP adsorbent. The volatile matter obtained was 36 %, which is lower than the value reported in the literature, (43.7 %) (Velmurugan & Dhinakaran, 2011).

Carbon content was calculated using Eq. (8) and it was found to be

%Carbon =100 – (% moisture content+%volatile content+% ash content)

$$\%\text{Carbon} = 100 - 43.5 = 56.5\%$$

As reported in the literature, orange peel principally consists of cellulose, hemicelluloses chlorophyll pigment lignin and other low molecular weight hydrocarbon. These components contain various functional groups, such as carboxyl and hydroxyl groups which make orange peel to be a potential adsorbent material for removing different ionic compounds from aqueous solution (Said & Mansour, 2012).

Figure 5: Proximity analysis results of POPA

Contents	**Value (%)**
Moisture content	3
Ash content	4.5
Volatile	36
Carbon matter	56.5

iii. Point of zero charge of the adsorbent

The value of pH affected a net zero charge on a solid in the absence of specific bio sorption is called the pHzpc. The pHzpc was found to be 4.50 for the physically treated POPA as represented in Fig.5. This is a convenient index of a surface when the latter becomes either positively charged or negatively charged ion as a function of pH. When the pH of the aqueous solution is below the pHzpc, the surface of the adsorbent will become positively charged. Meanwhile, the surface of the adsorbent will become negatively charged when the solution pH is greater than zero point of charge. Similar works was reported in the literature to determine point of zero charge of mangrove bark sorbent, an agricultural waste (Tan & Rozaini, 2010).

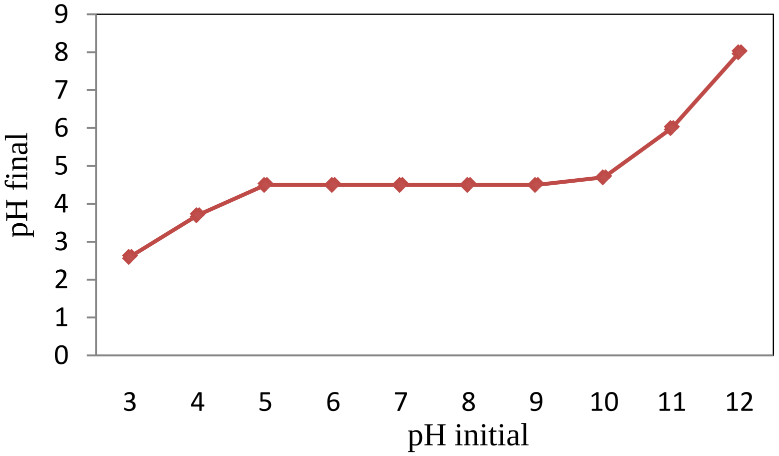

Figure 5: Determination of point of zero charge of POPA

4.2 Adsorption studies result and discussion

4.2.1 Effect of solution initial pH

The pH of the system exerts profound influence on the adsorptive uptake of adsorbate molecules most probably due to its influence on the surface properties of the adsorbent and ionization or dissociation of the adsorbate molecule (Santhi & Smitha, 2010). Figure 6, shows the variations in the percentage removal of the RR-DEXF dye from aqueous solution at different initial solution pH by POPA. From the Figure, it is evident that, percentage removal of the dye significantly decreased from 85 % to 28 % as the solution initial pH increases from 3.0 to 11. This indicates that acidic pH is favourable for the dye adsorption by the adsorbent.

This is due to the fact that low pH value leads to an increase in H^+ ion concentration in the system and the surface of POPA may acquires positive charge by absorbing H^+ ions. As the POPA is positively charged at low pH value, a strong electrostatic attraction appears between the negatively charged anionic dye and the POPA leads to maximum adsorption of the dye. On the other hand, increase in pH value led to increase in the number of negatively charged sites on the adsorbent (Santhi & Smitha, 2010). The negatively charged surface on POPA doesn't favour the sorption of anionic dyes due to electrostatic repulsion appears between the negatively charged anionic dye molecules and the adsorbent surface leads to minimum adsorption of the dye. Based on the result high dye removal efficiency of 85% was achieved at pH 3.0.

The other possible reason is that the point of zero charge of any adsorbent is a very important characteristic that determines the pH at which the surface has net electrical neutrality. It is well-known that for anionic dye adsorption, positively charged groups on the adsorbent are necessary, as discussed elsewhere (Meena Soni & Yadav, 2012).

From the Figure, it is evident that the maximum removal of RR-DEXF dye is observed at pH 3 and quickly decreased with increasing pH from 3 to 11. It was evident that as discussed in the previous section the pHzpc of POPA was found at 4.5. The percentage removal of the dye decreased with increasing pH values (pH > pHzpc), is possibly because the surface of POPA acquire negative charge as the solution pH increased, thus result in the electrostatic repulsions with the dye anions.

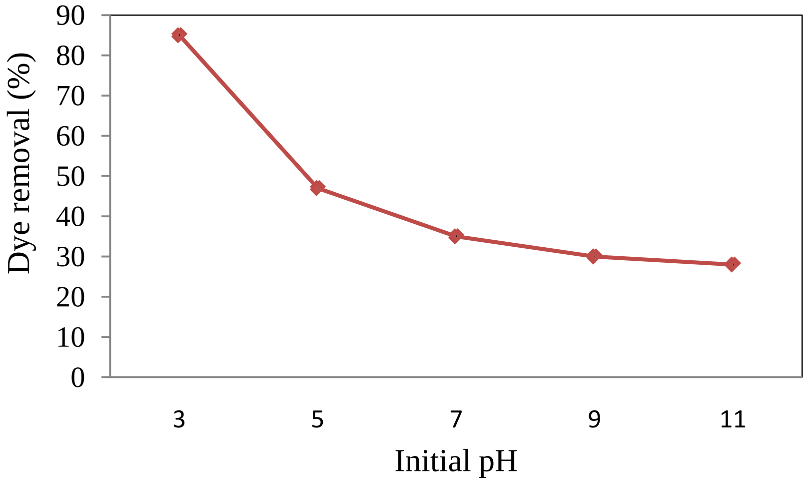

Figure 6: Effects of initial pH on dye adsorption onto POPA (At 12mg/L, dose 0.2g/100mL and contact time 60 min)

In contrast, at lower pH value (pH < pHzpc) the surface charge of the adsorbent may get positively charged as a result of being surrounded by H^+ ions in solution which enhance the negatively charged RR-DEXF dye anion adsorption through electrostatic forces of attraction. A similar trend was also observed for the adsorption of C.I. Direct Red 79 and C.I. Direct Yellow 27 onto orange peel waste as adsorbent and demonstrated the high dye removal at pH 3.0 (Said & Mansour, 2012).

4.2.2. Effect of POPA dosage

Adsorbent dose is representing of important parameter due to its strong effect on the capacity of an adsorbent at given initial concentration of adsorbate (Meena Soni & Yadav, 2012). The effect of adsorbent dose on the removal percentage of the dye was conducted over a range of POPA doses of 0.05 to 0.4 g /100 mL at initial concentration of the dye (4, 8, 12, 16 and 20 mg/L) for minimum contact time 60 min at constant pH 3.0 and the results are presented in Fig.7. From the Figure, it is clearly observed that with increasing the adsorbent dose from 0.05 to 0.4g, dye removal efficiency was increased from 62 to 85% at 4mg/L of the dye concentration. This phenomenon was observed at the dye concentrations studied. The increase in percentage removal with the adsorbent dose can be attributed to the increase of the available sorption surface and availability of more adsorption sites. (Hossam Altaher, 2011), explained the increase in the removal of methylene blue dye with the adsorbent dose and related this to the increase of surface area and the sorption sites. As per (Seeds Reza, 2011) noted the increase in dye removal efficiency of *Moringa oleifera* from 59.5 to 83% for an increase in adsorbent dose from 0.05 to 1g for orange 7 dyes.

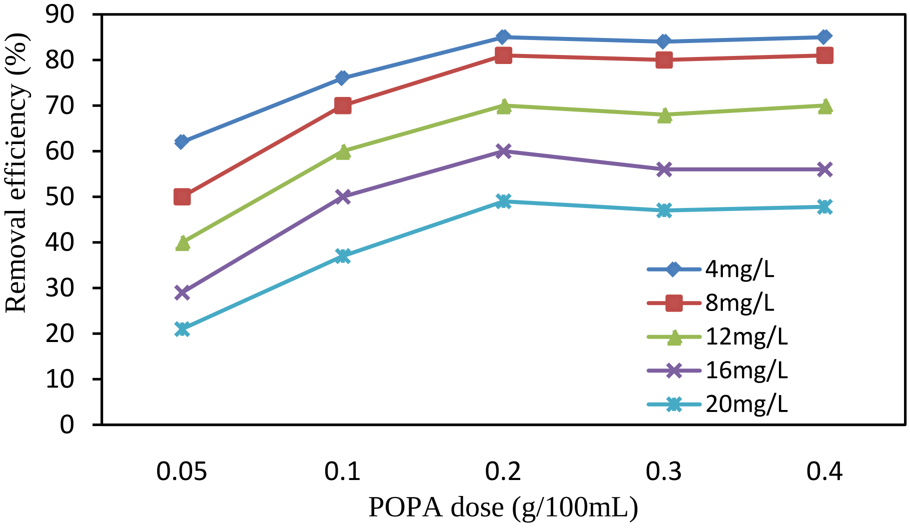

Figure 7: Effects of adsorbent dose on dye removal efficiency onto POPA (At contact time: 80 min and solution pH 3.0.)

It is obvious from the figure that increasing the adsorbent dosage above 0.2 g had very slight influence on the percentage removal of the dye. Hence, further addition of POPA above 0.2 g in 100 mL of the dye solution was considered to be reasonably inappropriate for the dye concentrations studied, and it is be considered the best dosage of adsorbent. When too much adsorbent was added into the dye solution, the transportation of dye ions to the active adsorption sites will be limited as well, hence reduced the adsorption efficiency. This is basically due to sites remaining unsaturated during the adsorption process (Tan & Rozaini, 2010).

4.2.3. Effect of contact time and initial dye concentration

The relation between removal of the RR-DEXF dye and reaction time were studied to see the rate of dye removal by POPA. The effects of contact time on the removal of the dye by using fixed amount of 0.2g/100mL of POPA at different initial concentration are presented in Fig. 8. The results indicate that the rate of dye removal increased depending on the contact time. For the first 40 minutes, the percentage removal of the dye by the adsorbent is rapid and thereafter it proceeds at a slower rate and finally attains saturation at different contact time for different initial concentration. The higher concentration solution of dyes employed, the longer equilibrium time was needed. The rate of removal of the dye is higher in the beginning due to the large surface area of the adsorbent available for the adsorption of dye ions. After a certain period, only a very low increase in the dye uptake was observed because there are few active sites on the surface of the adsorbent (Meena Soni & Yadav, 2012).

From the contact time studied, it was revealed that 80 min of agitation time is sufficient to reach equilibrium when 20 mg/L of dyes concentration was employed. Therefore, equilibrium time of 80 min was selected for the adsorption of RR-DEXF dye for further studies. From the figure, it is obvious that the time profiles of the dye adsorption were single, smooth and continuous curves leading to saturation, suggesting the possible monolayer coverage of dyes on the surface of the adsorbent.

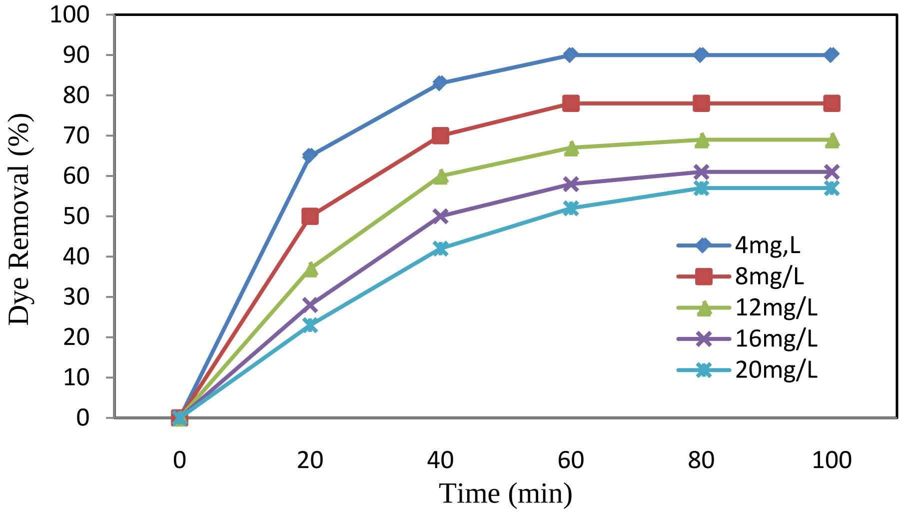

Figure 8: Effect of contact time at different dye initial concentration on percentage removal of the dye onto POPA (At dose: 0.2g/100ml and solution pH 3.0)

The initial dye concentration is another important variable that can affect the adsorption process. From the figure, it is also evident that using fixed amount of 0.2g of the adsorbent, the percent removal of the dye was decreased from 90% to 57% when the initial concentration of the dye increased from 4 to 20 mg/L at equilibrium contact time 80 min.

This can be explained by the fact that the initial concentration of dye had a restricted effect on dye removal capacity; simultaneously the adsorbent media had a limited number of active sites, which would have become saturated at a certain concentration. This was lead to the increase in the number of dye molecules competing for the available functions groups on the surface of adsorbent material (Abbas F. S., 2013). Since the solution of lower concentration has a small amount of the dye molecules than the solution of higher concentration of it, so the percent removal was decreased with increasing initial concentration of the dye.

In addition, it was found that the adsorption capacity of the adsorbent increased from 1.8 to 5.718 mg/g as the dye concentration increased from 4 to 20 mg/L. This effect might be attributed to an increase in the driving force of the ionic gradient with the increase in the initial dye concentration (Meena Soni & Yadav, 2012), justified the increase in sorption capacity due to increase in the amount of interactions between dye anions and the adsorbent. A similar phenomenon was observed on removal of methly red azo dye from aqueous solution by using agricultural waste (*Annona squmosa seed*) as adsorbent (Santhi & Smitha, 2010). As per (Seeds Reza, 2011), study investigated the uptake of Orange 7 dyes by *Moringa oleifera* and reported the increase in adsorption capacity with increasing the dye concentrations.

4.3. Adsorption isotherm

The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. Adsorption isotherm is important from both a theoretical and a practical point of view. In order to optimize the design of an adsorption system to remove the dye, it is important to establish the most appropriate correlations of the equilibrium data of each system (Asgher, 2011). Equilibrium isotherm equations are used to describe the experimental adsorption data. These data provide information about the capacity of the adsorbent or the amount required for removing a unit mass of pollutant under the system concentrations (Said & Mansour, 2012).

The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich isotherm (Seeds & Sepehr, 2011). These two most common isotherm equations have been tested in the present study to analyze equilibrium data of solute between adsorbent and solution. The parameters obtained from these different models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficients.

4.3.1 Langmuir isotherm model

The Langmuir isotherm is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface (langmuir, 1916). Therefore, the Langmuir isotherm model was chosen for estimation of the maximum adsorption capacity corresponding to complete mono-layer coverage on POPA surface. The experimental data are analyzed according to the linear form of the Langmuir isotherm equation. The linear Langmuir isotherm equation is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{1}{q_m} C_e \qquad (14)$$

Where, C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg/g). q_m and k_L are Langmuir constants related to the adsorption efficiency and energy of adsorption, respectively (Patil, 2014). The linear plots of C_e/q_e versus C_e suggest the applicability of the Langmuir isotherms for the removal of RR-DEXF dye onto POPA. The values of q_m and k_L of linear expression of Langmuir adsorption isotherm was calculated from the slopes and intercept of the linear plot of C_e/q_e versus C_e and are shown in Fig.9. The results of correlation coefficients predicted from this model for the removal of RR-DEXF dye by POPA are represented in Table 5. The correlation coefficients reported in the table showed strong positive evidence on the adsorption of the dye onto the adsorbent follows the Langmuir isotherm represents the best fit of experimental data than the Fruendlich isotherm equation.

The applicability of the linear form of Langmuir isotherm model to POPA was proved by the high correlation coefficients $R^2 > 0.99$. This suggests that the Langmuir isotherm provides a good model of the dye adsorption system. The fact that Langmuir isotherm fits the experimental data very well confirms the monolayer coverage of dye onto POPA ($q_m =$

3.03mg/g) and also the homogeneous distribution of active sites on the adsorbent, since the langmuir equation assumes that the surface is homogeneous (Dakhil Nassir Taha, 2013).

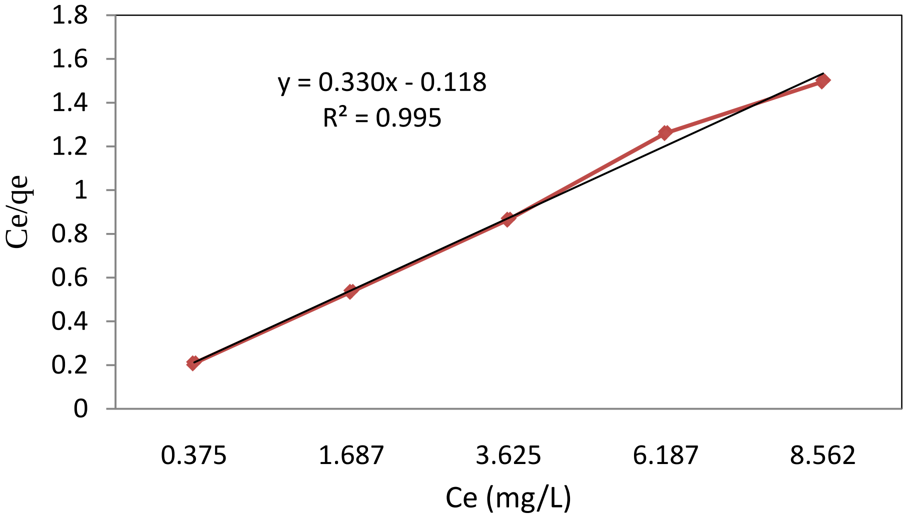

Figure 9: Langmuir adsorption isotherm for the dye onto POPA

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor R_{L}, also called equilibrium parameter which is defined by equation (15). The value of R_L indicates the shape of the isotherms to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Seeds Reza, 2011)

$$\mathbf{R_L} = \frac{\mathbf{1}}{(\mathbf{1+k_LC_o})} \qquad (15)$$

Where, C_o(mg/L) is the initial dye concentration and k_L(L/mg) is the Langmuir constant related to the energy of adsorption (Seeds Reza, 2011). The influence of isotherm shape on whether adsorption is favourable or unfavourable has been considered. For a Langmuir type adsorption process, the isotherm shape can be classified by a dimension less constant separation factor R_L, given by equation (15). The calculated R_L values at different initial RR-DEXF dye concentrations are represented in Fig. 10. It was found to be between 0 and 1 for POPA suggesting the isotherm to be favourable at the concentrations studied. Also lower R_L values at higher initial RR dye concentrations showed that adsorption was more favourable at higher concentration. The degree of favourability is generally related to the irreversibility of the system, giving a qualitative assessment of the POPA-Reactive Red dye interactions. The degrees tended toward zero (the completely ideal irreversible case) rather than unity (which represents a completely reversible case).

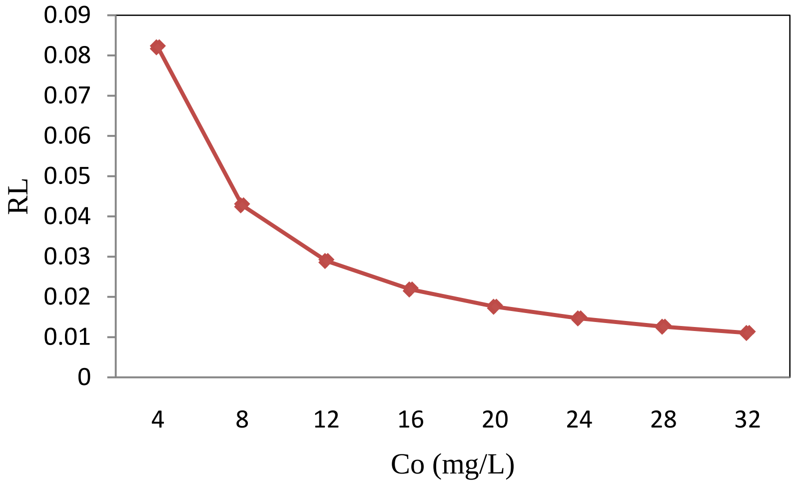

Figure 10: Plot of separation factor versus initial concentration of the dye

4.3.2 Freundlich isotherm model

While Langmuir isotherm assumes that enthalpy of adsorption is independent of the amount adsorbed, the empirical Freundlich equation, based on adsorption on heterogeneous surface, can be derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites (Freundlich, 1906). The Freundlich equation is purely empirical based on adsorption on heterogeneous surface and is commonly given by the following non-linear equation:

$$\mathbf{q_e = K_f C_e^{1/n}} \qquad (16)$$

The linear form of Freundlich isotherm equation is represented by:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (17)$$

Where, q_e is the amount of the dye adsorbed (mg/g), C_e is the equilibrium concentration of the dye in the solution (mg/L) and K_f and n are Freundlich isotherm constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. K_f and 1/n can be obtained from the intercept and slope of the linear plot of log q_e versus log C_e (Patil, 2014).

The applicability of the Freundlich adsorption isotherm was also analyzed, using the same set of experimental data. The Freundlich plots between log q_e versus log C_e for the adsorption of RR-DEXF were drawn in Fig.11 and Table 5. It was found that the correlation coefficient values were less than 0.99 at the dye concentrations studied indicating that Freundlich model was not applicable to the present study.

The favourable adsorption of this model can be characterized; the magnitude of the exponent n gives an indication on the favourability of adsorption. It is generally stated that values of sorption intensity, n in the range 2 to 10 represent good, 1 to 2 moderately difficult, and less than 1 poor adsorption characteristics (S. Anuradha Jabasingh, 2015). In the present study the value of n (n= 8.4) is greater than 1, indicating that the adsorption process is favourable. However, the values of correlation coefficients are lower than that of the Langmuir isotherm value.

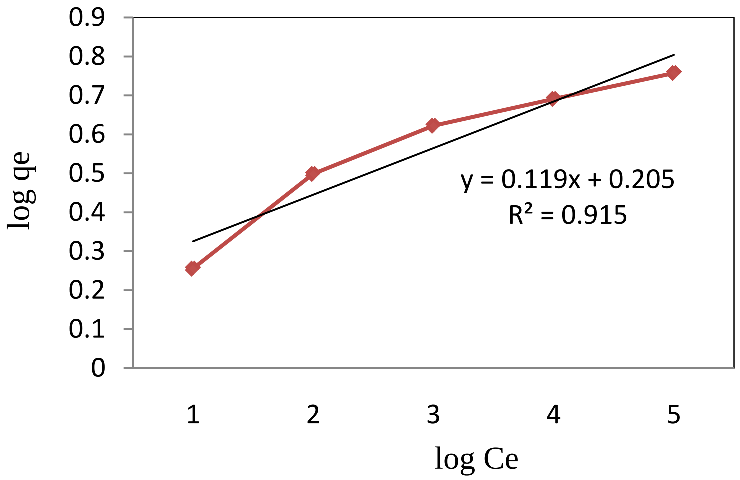

Figure 11: Freundlich adsorption isotherm for the dye onto POPA

Table 5: Langmuir and Freundlich isotherm model constants and correlation coefficients for adsorption of RR-DEXF dye onto POPA

Langmiur			**Freudlich**		
q_m (mg/g)	K_L(L/mg)	R^2	K_f	1/n	R^2
3.03	2.797	0.995	1.603	0.119	0.915

As indicated in Table 5, the coefficients of determination (R^2) of the Langmuir model are greater than 0.99 and close to one, which indicates that the Langmuir model adequately describes the experimental data of RR-DEXF dye adsorption experiment. These facts suggest that the dye is adsorbed in the form of monolayer coverage on the surface of the prepared adsorbent. Similar works were observed by (Asgher, 2011), that the adsorption of four reactive dyes; (Reactive red 45, Reactive blue 19, Reactive blue 49 and Reactive yellow 42) from aqueous solution by *citrus* waste followed the Langmiur isotherm model.

4.4. Adsorption kinetics

Kinetic models have been used to investigate the mechanism of sorption and potential rate controlling steps, which is helpful for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes (Santhi & Smitha, 2010). Thus, the kinetics of RR-DEXF dye adsorption onto POPA was analyzed using pseudo-first-order and pseudo-second-order kinetic models. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients. The relatively higher value is the more applicable model to the kinetic of the dye adsorption onto the adsorbent. The pseudo-first-order rate expression based on solid capacity is generally expressed as follows (Meroufel & Zenasn, 2013)**:**

$$\frac{dq_t}{d_t} = k_1(q_e - q_t) \tag{18}$$

After integration and applying boundary conditions, $t = 0$ to t and $qt = 0$ to q_e; the integrated form of equation (18) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{19}$$

Where, q_e (mg/g) is the amount of dye adsorbed at equilibrium, q_t (mg/g) is the amount of dye adsorbed at time t and k_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption. In order to obtain the rate constants, the values of log $(q_e - q_t)$ were linearly correlated with t from which k_1 and predicted q_e can be calculated from the slope and intercept of the plot, respectively and the results are presented as in Fig. 12. The variation in rate should be proportional to the first power of concentration for strict surface adsorption (Santhi & Smitha, 2010).

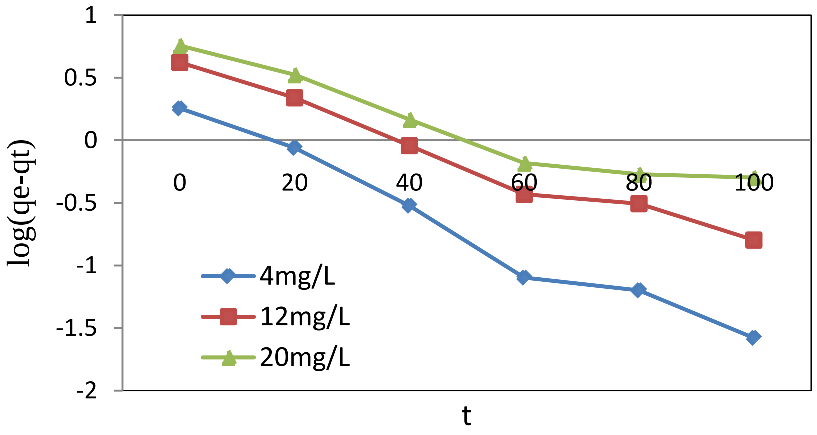

Figure 12: Pseudo-first-order kinetic for adsorption of the dye onto POPA

From the figure, it is evident that the pseudo-first-order equation fits only for the first 60 min and thereafter the experimental data deviate from kinetic theory. Thus, the model represents the initial stages where rapid adsorption occurs well but cannot be applied for the entire adsorption process. Although the correlation coefficients for the model were reasonably high in some cases, however, all the intercepts of the straight line plots did not yield predicted q_e values equal or reasonably close to the experimental q_e values (Table 6). This similar kind of trend was observed by (Patil, 2014) for the removal of Sudan Red G dye from aqueous solution by activated carbon prepared from *mosambi* and *cotton* an agricultural waste. Hence, the use of pseudo first order kinetic model for RR-DEXF adsorption onto POPA for the entire adsorption period was found to be inappropriate; and the reaction mechanism is not a first-order reaction. Consequently, kinetic data was treated with pseudo second order model.

The adsorption kinetic may be described by the pseudo-second order model (Meroufel & Zenasni, 2013). The pseudo-second-order equation based on adsorption equilibrium capacity may be expressed in the form:

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \qquad (20)$$

Where, k_2 (g mg^{-1}.min^{-1}) is the rate constant of pseudo-second-order adsorption and q_e is the equilibrium adsorption capacity (mg/g). For the same boundary conditions the integrated form of equation (20) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 qe^2} + \frac{t}{q_e} \qquad (21)$$

To understand the applicability of the models linear plots of t/qt versus t at different RR-DEXF dye concentrations (4, 12 and 20 mg/L) for adsorption onto POPA have been plotted, and the results are presented in Fig. 13.

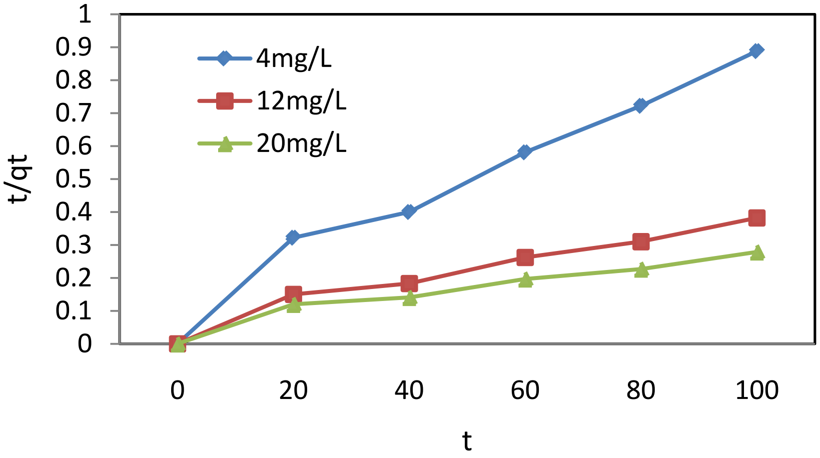

Figure 13: Pseudo-second-order kinetic for adsorption of the dye onto POPA

It was mentioned that the curve fitting plot of log $(q_e - q_t)$ versus t does not show good results for the entire adsorption period (Fig.12), while the plot of t/q_t versus t gives relatively a straight line as showed in Fig. 13, confirming the applicability of the pseudo-second-order equation. Values of k_2 and equilibrium adsorption capacity q_e were calculated from the intercept and slope of the plots of t/q_t versus t, respectively.

The values of correlation coefficients R^2, for the pseudo-second-order kinetic model were found to be between (0.974 and 0.942) as presented in Table 6. This indicates that the adsorption system of POPA obeys the pseudo-second-order kinetic model for the entire adsorption period, based on the assumption that the rate-limiting step may be chemisorptions involving valency forces through sharing or exchange of electrons between the adsorbent and adsorbate molecules (Mafra & Ferreira, 2013).

Table 6: Pseudo first order and pseudo second order constants and correlation coefficients for adsorption of RR-DEXF dye onto POPA.

Dye Concentration (mg/L)	**q_e**.exp. (mg/g)	Pseudo-first-order Kinetics			Pseudo-second-order Kinetics		
		q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2	R^2
4	1.8	4.121	0.8636	0.977	2.01	0.287	0.974
12	4.187	7.345	0.6587	0.975	4.76	0.156	0.961
20	5.718	8.26	0.725	0.925	6.17	0.153	942

Where q_e.exp. is the experimental value of equilibrium adsorption capacity q_e(mg/g)

It is evident from Tables 6, that the experimental data can be explained by the pseudo second order kinetics model, also qe, calculated values are approximately equal to qe, experimental values. The rate constant for pseudo second order kinetics decreases with increase in adsorbate concentration. This similar trend was reported by (Meroufel & Zenasni, 2013), who evaluated the adsorption potential of *algerian kaolin* for the removal of toxic anionic dye namely congo red from aqueous solutions. The experimental data fitted sound by the second-order kinetic model that proved the chemical sorption to be the rate limiting step.

5. Conclusion and Recommendation

5.1. Conclusion

The results presented in the paper clearly suggest the efficiency powdered orange peel adsorbent for the removal of RR-DEX dye from aqueous solution. Effects of different operational parameters namely the solution pH, adsorbent dosage, initial dye concentration, and contact time govern the overall process of the dye adsorption by OP adsorbent. It was found that maximum adsorption of the dye took place at an acidic solution pH. The effective solution pH, OP adsorbent dose and contact time were found to be 3, 0.2g/100mL and 80 min, respectively for the dye adsorption studies at constant room temperature of 27^oC. At these experimental conditions, the dye removal efficiency of 90% was achieved. Equilibrium and kinetic studies were conducted for the adsorption of the dye from aqueous solution onto orange peel adsorbent. The equilibrium data have been analyzed using Langmuir and Freundlich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The Langmuir isotherm was demonstrated to provide the best correlation for the adsorption of the dye. This indicates the adsorption capacity to the applicability of monolayer coverage of the dye on to the surface of the adsorbent. Adsorption kinetics was determined using pseudo first order and pseudo second order models and it was found that the adsorption follows pseudo second order model. Thus, it may be concluded that POPA could be used as a low-cost, effective and alternative for the removal of textile reactive dyes from aqueous solution.

5.2 Recommendation

- It is recommended that powdered orange peel can be used, as a low cost adsorbent for the removal of textile dyes and it may be an alternative to more costlier materials.
- For orange peel to be used as adsorbent for the dye molecules, the treatment method is expected to be economical and environmental friendly.
- During the preliminary adsorption study by orange peel, an yellowish colored leachate was observed and could be improved by further washing with distilled water.
- Based on the results presented, and powdered orange peel adsorbent is suggested as a significant potential adsorbent, that could be an ideal alternative treatment for reactive red dye removal from aqueous solution; however, much work is necessary in the area of predicting the performance of adsorption process for the dye removal from real textile effluents under the range of operating conditions.
- Further, there is scope for more study and research which can enhance the percentage removal of reactive red dye and also, the economical feasibility of orange peels for removal of the dye.

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Annexes

Lists of adsorption experimental data used to determine effect of initial solution pH, POPA dosage, initial RR-DEXF dye concentration and contact time on the dye adsorption capacity of the adsorbent.

1. **Effect of initial pH on the dye removal efficiency, At condition (conc. 12mg/L, Time: 60 min, POPA dosage: 0.2g/100mL)**

Initial pH	Abs. values		Co-Ct		Removal Efficiency (%)		Average
	1st Run	2nd Run	1st	2nd	1st	2nd	
3	0.067	0.068	10.25	10.18	85.42	84.8	85.01
5	0.14	0.141	5.68	5.625	47.33	46.82	47
7	0.164	0.163	4.25	4.25	34.89	35.42	35
9	0.173	0.1732	3.62	3.612	30.21	30.10	30.15
11	0.177	0.176	3.37	3.437	28.08	28.04	28.06

2. **Effect of POPA dosage ,At(initial pH:3.0, dye conc. 4mg/L, contact time 80 min)**

POPA dose g/100mL	Abs. values		Co-Ct		Removal Efficiency (%)		Average
	1st Run	2nd Run	1st	2nd	1st	2nd	
0.05	0.063	0.0631	2.5	2.494	62	62.34	62.17
0.1	0.054	0.0541	3.06	3.056	76.56	76.04	76.3
0.2	0.048	0.049	3.41	3.375	85.94	84.37	85.15
0.3	0.049	0.0492	3.375	3.362	84.37	84.06	84.13
0.4	0.048	0.0492	3.375	3.362	84.37	84.06	84.13

3. Effect of contact time and initial dye concentration at (POPA: 0.2g/100mL, initial solution pH 3.0)

Time(min)	Conc. (mg/L)	Abs. values	Ct (mg/L)	Removal Efficiency (%)	Amount adsorbed qt(mg/g)
20	4	0.061	1.375	65	1.31
40	4	0.049	0.625	83	1.68
60	4	0.045	0.375	90	1.8
80	4	0.045	0.375	90	1.8
100	4	0.045	0.375	90	1.8
20	8	0.103	4	50	2
40	8	0.077	2.375	70	2.81
60	8	0.066	1.168	78	3.15
80	8	0.066	1.168	78	3.15
100	8	0.066	1.168	78	3.15
20	12	0.160	7.562	37	2.218
40	12	0.115	4.75	60	3.625
60	12	0.102	3.937	67	4.031
80	12	0.097	3.625	69	4.187
100	12	0.097	3.625	69	4.187
20	16	0.222	11.437	28	2.281
40	16	0.166	7.937	50	4.131
60	16	0.146	6.687	58	4.656
80	16	0.138	6.187	61	4.906
100	16	0.138	6.187	61	4.906
20	20	0.283	15.25	23	2.375
40	20	0.223	11.5	42	4.25
60	20	0.192	9.562	52	5.218
80	20	0.176	8.562	57	5.718
100	20	0.176	8.562	57	5.718