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THESIS ON:

ADSORPTIVE REMOVAL OF DYES FROM WASTE WATER USING ACTIVATED BIOCHAR DERIVED FROM SOLID FOOD WASTE

BY: GEMECHU BUKURU

MAY, 2023

JIMMA, ETHIOPIA

ADSORPTIVE REMOVAL OF DYES FROM WASTE WATER USING ACTIVATED BIOCHAR DERIVED FROM SOLID FOOD WASTE

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DECLARATION

I, hereby declare that this thesis entitled **“Adsorptive Removal of Dyes from Waste Water Using Activated Biochar Derived from Solid Food Waste”,** has been carried out by me under the guidance, and supervision of Dr. Abera Gure and Mr. Feyisa Wodajo.

The thesis is my original work and has not been presented for the award of any degree or other in any institution or university.

Declared by	**Signature**	**Date**
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As thesis research advisors, we here certify that we have read and evaluated this thesis prepared under our guidance by Gemechu Bukuru entitled "**Adsorptive Removal of Dyes from Waste Water Using Activated Biochar Derived from Solid Food Waste".** We recommend that this thesis can be submitted as it fulfills the requirement for Master of Science in Chemistry.

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Abbreviations and Acronyms

COD	Chemical Oxygen Demand
EDCs	Endocrine Disrupting Compounds
MB	Methylene Blue
PAHs	Polycyclic Aromatic Hydrocarbons
RO	Reverse Osmosis
TCS	Triclosan
VOCS	Volatile Organic Compounds
WRRF	Water Resource Recovery Facility

Abstract

Dyes are extensively used to color various products in many industries. These can be lost as effluent to the aquatic environment. The waste water Loaded with toxic dyes is not acceptable to environmental regulations and exhibit to humans, aquatic organisms, and the environment in general. Based on this idea, focusing environmental issue and economic point of view, the use of low cost and eco-friendly food wastes were investigated for the removal of MB dye from waste water. In this study, the usage of food wastes like Injera, peels of potatoes, onions, and garlic adsorbents (acid activated biochar) for the removal of MB dye from the aqueous solution were investigated. Some physicochemical properties of the adsorbents such as porous characteristics, surface area, surface functional group and point of zero charge were determined. The batch adsorption studies of methylene blue were carried out by Injera, peels of onion, garlic, and potatoes wastes independently. The optimum removing efficiencies of potato, garlic and onion peels activated biochars were known to be 99.213% at optimum (initial concentration of 10 mg/L, temperature of 313 K, pH of 10 of mass of 0.5 g and time of 180 minutes), 99.833% at optimum (initial concentration of 10 mg/L, temperature of 313 K, pH of 7 of mass of 0.1 g and time of 30 minutes), and 99.994% at optimum (initial concentration of 10 mg/L, temperature of 343 K, pH of 4 of mass of 0.4 g and time of 20 minutes) respectively. The modeling studies revealed that the studied process obeys the pseudo-second-order model and Langmuir isotherm model. Finally, the determination of thermodynamic parameters indicated the exothermic and spontaneous type of the removal process of MB onto all activated biochars prepared.

Key words: *Activated biochar, MB, Adsorption Kinetic, Adsorption isotherm*

1. Introduction

1.1. Background of the study

Dyes are widely used to color various products in many industries and have significantly affect water quality. The discharge of dyes into water is attributed to industries such as textile, leather, paper, plastics, etc. Dyes as wastewater pollutants represent a big concern for the environment, because these dyes exhibit toxicity to humans, aquatic organisms, and the environment in a general.

Different studies have been conducted to solve the problem of water pollution, such as photo catalysis and adsorption. Adsorption is one of the most used techniques for wastewater purification, applied to remove organic molecules at industrial scale due to its low cost and its ease of operation. Among the different adsorbents used for wastewater treatment, activated carbons show the most suitable characteristics, such as high porosity, well developed internal surface area and high adsorption capacity [1].

However, the production costs lead to a serious drawback for the use of activated carbons as industrial adsorbents. To overcome this drawback, recent years have seen an increasing interest in the production of activated biochar from biomass, being a renewable and low cost adsorbent material. Biochar is the solid residue of biomass pyrolysis and it is characterized by high porosity and high amount of carbon in aromatic form. When properly activated, this material presents sorption capacity and surface area similar to that of activated carbon [2].

The activation of biochar is required to improve the biochar characteristics needed in the adsorption process. Different methods are available for the activation of biochar. Physical activation consisting in a high temperature treatment in a continuous flow of gas such as CO_2 or H_2O enhances the surface area and porous structure, and thus the sorption capacity for water contaminants. Furthermore, heavily condensed polycyclic aromatic and π-electron rich sites are formed during physical activation providing hydrophobic properties to biochar which leads to enhanced properties to adsorb hydrophobic organic compounds [3].

Chemical activation consisting in the reaction of biochar with a chemical agent such as an acid or a base leads to the formation of micro pores by subsequent dehydration and/or oxidation. Although chemical activation presents some difficulties due to corrosion of the apparatus by chemicals and complicated recovery of chemicals, and it is much higher efficiency in the activation of biochar with respect to the physical treatment makes its application very interesting. In the literature many studies on the adsorption of dyes by means of chemically activated biochar are available. The chemical activation is usually performed on the biochar and then the activated material is subjected to an additional thermal treatment [4,5].

In this study the adsorption capacity of biochar derived from solid food wastes were tested on the removal of MB. The adsorbents were produced by chemical activation of the biomass followed by thermal treatment due to high removal efficiency of chemical activated biochar. In this method, lower temperature is used for pyrolysis to minimize energy consumption during the production of the adsorbent [6-9]. The adsorption capacities of activated Biochar were compared with that of biochar produced without activation.

1.2. Statement of the problem

Color removal from effluents on a continuous industrial scale has been given much attention in the last few years, not only because of its potential toxicity but also mainly due to its visibility problem. The industries required to treat effluent containing dyes before they are discharged to water bodies. Thus, scientific community takes on the responsibility of contributing to waste treatment through the development of an effective dye removal technique [10].

That is why this study was interested to remove dye from waste water by using biochar derived from solid food wastes. There are several promising methods for removal of dyes from waste water such as: physical, chemical and biological methods which were widely used to treat waste water containing dyes [11].

Physicochemical and electrochemical treatment methods such as photochemical, sono-chemical, electrochemical, coagulation and flocculation, bio-degradation, membrane separation, photo-fenton processes, oxidation or ozonation have been reported [12]. Amongst these technologies, the adsorptive removal process is revolutionary, a cost effective and easy to use alternative with reliable performance [13].

In general, the selection of an adsorbent mainly included: the adsorption capacity, inexpensive, availability, production technology etc. When using solid food wastes adsorbents are prepared and screened, it was expected to remove MB from wastewater effectively.

This study responds to the following questions:

- Does activated biochar have higher efficiency in removing dyes from waste water than non-activated biochar?
- What was the efficiency of activated biochar prepared from potato, onion and garlic peels to remove dyes from waste water?
- Which adsorption isotherm, kinetics and thermodynamics fits more for adsorptive removal dyes from waste water onto activated biochar derived from food wastes?

1.3. Objectives of the study

1.3.1 General objectives

- The general objective of this study was to prepare activated biochar and determine adsorptive capacities of adsorbent prepared from solid food wastes like onion, garlic, potato peels and Injera leftover due to its inexpensive, availability and low cost.

1.3.2. Specific objectives

- To optimize batch adsorption parameters for enhanced MB removal from waste water.
- To determine kinetics of MB dye removal by activated biochar from waste water.
- To determine thermodynamics of MB dye removal by activated biochar from waste water.
- To evaluate adsorption capacity of activated biochar prepared adsorbent in removal of MB
- To characterize the surface functional group of biochar and activated biochar
- To screen out adsorbents for removal of MB dye from aqueous solution by adsorbent prepared from food wastes that is activated and un activated biochar.

1.4. Significance of the study

This study confirmed us food wastes which are widely available in higher learning institutions can be used as low-cost, and eco friendly alternative for removal of environmental pollutants like MB. The findings can also be used as background information for other researchers who want to perform similar studies.

2. Review of Related Literatures

2.1. Dyes

Dyes are colorful substances that have been utilized by humans since 3500 BC in various applications using natural extracts of flowers, fruits, certain insects, etc [14]. These natural dyes constitute a very limited range of colors and are produced in low quantities. However, after the discovery of synthetic colors by Perkins in 1856, a wide range of dyes are used in various fields to color their product such as paper, leather, rubber, textile and plastics.

Synthetic dyes are developed and have replaced natural dyes gradually in different industries because their molecules are stable and can resist degradation upon contact with water, detergents, or any other washing agent [14].They are widely used in textiles, printing, rubber, cosmetics, plastics and leather industries to color their products leads to the production of a large quantity of colored sewage. They constitute a significant group of pollutants as several industries discharge a huge amount of waste water containing various dyes into natural water bodies (nearby rivers) [15].

Dyes are chemical compounds that have a complex aromatic molecular structure that attach to fabrics or surface shells to create color. These structures are present in stable dyes, difficult to treat, and have low biodegradability. The depolarization of waste water from the textile and manufacturing industries is a major challenge for environmental managers because dyes are soluble in water and produce very bright colors in water with acidic properties. The discharge of synthetic dye effluents into the environment affects its ecological status, causing several undesirable changes. Highly colored effluents can be very harmful to receive water bodies as the dyes have high water solubility even at low concentrations [16]. MB is a very commonly used synthetic dye and as a result, is often found in industrial waste water [17].

2.2. Classification of dyes

Generally , the dyes used in the textile industry are : basic dyes ,acidic dyes, reactive dyes , direct dyes, azo dyes, mordant dyes and sulfur dyes, whereas azo derivatives are the major class of dyes that are used in the industry today[18]. There are several ways for classification of commercial dyes. It can be classified based on their chemical structure into azo, anthraquinone, indigoid, nitriso, nitro, and triarylmethane dyes. Sometimes they are classified by their application or by their solubility in water [19]. However, the classification based on application is advantageous before considering chemical structure in detail because of the complexities of dye nomenclature from this type of system [20]. Dyes are also usually classified based on their particle charge upon dissolution in aqueous solution medium; such as cationic (all basic dyes), anionic (direct, acid, and reactive dyes), and non-ionic (dispersed dyes) [21].

2.2.1. Cationic dyes

They are also called basic dyes due to the presence of positive ions in the molecule's structure. Basic dyes are soluble and they are highly visible in water even at very low concentration [22]. Basic dyes consists of monoazoic, diazoic, and azine compounds [23].They are used to color wool, silk, nylon, mod-acrylic and polyester materials [24].Cationic functionality is found in various types of dyes such as cationic azo dyes, methane dyes, anthraquinone, di-& tri-arylcarbenium phthalocyanine dyes, polycarbocyclic and solvent dyes [25].

2.2.2. Anionic dyes

Anionic dyes are dyes that have negative ions due to the presence of excess OH^-ion in aqueous solutions. Anionic dyes are water soluble and they include acid dyes, azo dyes, direct dyes, and reactive dyes [27]. Reactive dyes attach to their substrate by a chemical reaction (hydrolysis of the reactive groups in the water) that forms a covalent bond between the molecule of the dye and that of the fiber. Their removal is the most challenging task as they produce very bright colors in water and show acidic properties [28].

2.2.3. Reactive dyes

Reactive dyes are dyes that contain reactive groups such as vinyl sulphone, chlorotriazine, trichloropyrimidine and difluorochloropyridine that covalently bonded with the fiber during the dyeing process [29].

2.2.4. Azo dyes

Azo dyes have a largest variety of dyes and under anaerobic conditions, the dyes linkage can be reduced to form aromatic amines which are colorless but can be toxic and carcinogenic. It was estimated that 130-3200 azo dyes in use can form carcinogenic aromatic amine during degradation process [30]. Moreover azo dyes represent the largest class of reactive dyes used in the textile industry followed by anthraquinone and phthalocyanine classes [31].

2.3 Methylene blue

MB dye is a cationic dye with heterocyclic aromatic compound, consisting of dark green crystals, which has a molecular weight of 319.85g/mol, with the molecular formula of$C_{16}H_{18}N_3SCl$.MB has a net positive charge and its the structure is shown in Figure 1, which is commonly used for dyeing of cotton, nylon, and silk. About 40% of the synthetic dyes like MB are toxic, mutagenic and carcinogenic compounds that remained in industrial effluent and can cause severe public and environmental health problems [32-33]. The accidental contact of MB with eyes can cause serious problem, being potentially responsible of permanent injury to humans and animals. In addition, its inhalation may cause breathing difficulties and its ingestion produces burning sensation and nausea. Due to this researcher give the attention to the removal MB from waste water using activated carbon and biochar. Hence the treatment of polluted streams containing this dye is mandatory task to significantly limit these negative effects or impacts [34].

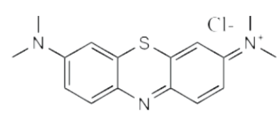

Figure1: Structure of MB.

2.4 .The potential of biochar for the removal of dyes from wastewater

Several advanced tertiary treatment techniques have previously been investigated. For the removal of micro pollutants in water resource recovery facility (WRRF).Treatment processes such as membrane filtration, reverse osmosis (RO), ultra violet treatment, and advanced oxidation methods have proven to be effective techniques for the removal of organic micro pollutants, but are often associated with high infrastructure and operational costs [35-37].

Carbon based adsorbents such as activated carbon is commonly used in water treatment applications, and previous research has demonstrated the ability of a variety of carbonaceous sorbent materials for dye removal from aqueous solutions [38-39]. Activated carbon is commonly produced from bituminous coal or coconut shells, and commercially available activated carbon can cost up to $1,500/ton [40]. Replacing traditional adsorbents such as activated carbon with biochar could greatly reduce treatment costs (e.g. $246/ton non-activated biochar) [41-42].

Biochar is a porous, carbon rich product that is produced via pyrolysis (thermochemical decomposition in the absence of oxygen) or the incomplete combustion of biomass, and has a high surface area to volume ratio [43]. Biochar has been growing in popularity in the last few decades as a potential soil amendment for agricultural gains and carbon sequestration, but also has demonstrated great potential as an adsorbent to remove pollutants from aqueous solutions [44]. Biochar can be produced from a variety of materials, including agricultural residue, animal litters, wood biomass, and sewage sludge or biomass [45-46].

Biochar production from sewage sludge biomass could provide a sustainable reduction in wastes produced from wastewater treatment processes such as activated sludge and also serve as an adsorbent to remove contaminants from water [47-48]. Recent research has demonstrated that thermochemical processes such as pyrolysis can potentially provide a biosolids handling process that offers simultaneous energy recovery and production of useful products such as biomass-derived Biochar [49,50].

Pyrolysis of carbonaceous materials such as biosolids produces a solid phase charcoal-like product known as biochar, a liquid phase called py-oil, and a gas phase known as py-gas[51-52]. All three pyrolysis products are useful products, and could potentially help reduce biosolids disposal costs at WRRF [53]. Additionally, the pyrolysis process itself removes micro pollutants from biosolids [54-55]. Therefore, biochar that is used as an adsorbent for micro pollutants could theoretically be re-pyrolyzed to remove the micro pollutants from the biochar product.

2.5. Biochar as an adsorbent for Removal of dyes

Biochar has recently emerged as a potential replacement to activated carbon due to its low cost, relative abundance, and comparative sorptive abilities [57-58]. Chemical modification or activation of biochar using acids, bases, and polymers can be beneficial for altering the surface chemistry and creating high-affinity sorption sites on the biochar surface for sorbing organic contaminants [59].

Biochar from various feedstock including wood debris, manure, and other agricultural wastes have demonstrated the ability to absorb pollutants including VOCs, PAHs, EDCs, and pesticides[60-61].For example, loblolly pine biochar adsorbents have successfully been used to remove pharmaceutical compounds from aqueous solutions including diclofenac, sulfamethoxazole, ibuprofen, and carbamazepine [62]. Similar to biochar from other feed stocks, biosolids-derived biochar has successfully been used to remove organic pollutants from wastewater and other aqueous solutions [63]. Recent research has demonstrated the ability of biosolids-derived biochar for TCS adsorption in batch equilibrium experiments, with observed adsorption capacities up to 872 µg/g[64].

A similar study conducted with biosolids-derived biochar reported adsorption capacities up to 19.8 mg/g for fluoroquinolone antibiotics such as Gatifloxacin in batch-scale experiments [65]. The Investigated efficiency of various biosolids-derived sorbents for the removal of COD and chromaticity color from wastewater streams through batch-scale adsorption tests and rapid small-scale column experiments. The results of the study demonstrated COD adsorption capacities up to 47.8 mg/g, and overall COD and chromaticity color removal rates of 79.1 and 87.5%, respectively [66].

Sorption of organic contaminants to biosolids-derived biochar has been attributed to various factors including its relatively high surface area, hydrophobicity, and interactions with oxygen-containing functional groups such as hydroxyl and carboxyl groups on the biochar surface [67]. Other studies have suggested that adsorption of organic compounds such as 4-chlorophenol to biosolids-derived biochar sorbents was influenced by dispersive interactions between the π-electrons of the solute aromatic ring and the adsorbent surface [68]. Hydrogen bonding, hydrophobic interactions, and π-stacking may also contribute to the Sorption of organic Micropollutants such as triclosan from aqueous solutions [69].

Generally, recent research has established biosolids-derived biochar as a potential sorbent capable of the removal of organic pollutants from wastewater streams and aqueous solutions.

However, beyond batch sorption testing, there is limited information regarding the application of biosolids-derived biochar in adsorption/filtration systems for removing organic contaminants from drinking, potable reuse, or municipal waste waters. Additionally, previous studies have reported that Freundlich parameters based on column tests were different from those based on isotherm tests conducted via batch-scale experiments, and that adsorption parameters obtained from column tests could provide more realistic information for real world applications [70].

The use of biosolids-derived biochar as a micro pollutant sorbent advances sustainability initiatives by both encouraging biosolids reuse and enhancing micro pollutants removal through wastewater treatment. Additional research in this area is necessary in order to gain a better understanding of the impact of various water qualities on the pollutant removal performance of biosolids-derived biochar [71].

2.6. Factors affecting adsorption

Many factors affecting the adsorption process are: contact time, pH of solution, initial concentration, nature of adsorbate, shaking speed and temperature.

2.6.1. Contact time

Independent of the other parameters, contact time plays a vital role in the adsorption process. The adsorption of adsorbate increases with increasing contact time until equilibrium is reached. Only very slight improvement occurs after equilibrium is reached. This occurs because the active site of the adsorbent are vacant during the initial stage and adsorption can take place rapidly, but the number of remaining active sites of the adsorbent are decreased after equilibrium and these site are occupied with difficulty due to the repulsive forces between the solute molecules on the solid and bulk phase [72].

2.6.2. pH of the solution

pH is the measure of acidity or basicity of an aqueous solution. pH of the solution influences adsorption process by affecting both aqueous chemistry and surface binding site of the adsorbent. At low pH values, surface of the adsorbent becomes positively charged because of protonation of the functional groups on the adsorbent surface [73]. So adsorption of cationic adsorbate decreases because of electrostatic repulsion between adsorbate and protonated adsorbent. As the pH of the dye in the solution increases, deprotonation of positively charged groups on the adsorbent occur. Electrostatic attraction between negatively charged sites on the adsorbent and adsorbate cat ions cause in adsorption. As a result, the cationic species adsorption increases and anionic species show a decrease [74].

2.6.3. Initial concentration

A given mass of sorbent material can only adsorb a fixed amount of dye; hence the initial dye concentration of an effluent is one of the important factors to be studied. The effect of dye initial concentration can be conducted by shaken adsorbent-adsorbate solution until equilibrium, using fixed adsorbent dosage with different initial dye concentration for different intervals. The effect of an increment in dye initial concentration will increase the adsorbent loading capacity [75].

2.6.4. Nature of adsorbate

The important factors affecting adsorption process is nature of adsorbate, which affects their physical properties, as adsorption increases by increasing molecular weight of the adsorbate material. They are also affected by chemical properties in the existence of active groups in the composition of the adsorbate material, and the capacity of adsorption increases by increasing concentration of adsorbate material [76].

2.6.5. Temperature

The effect of temperature varies according to the type of adsorption and the nature of the adsorbent and adsorbate. The adsorption of heat is increased by the exothermal process; in the endothermal process the contrary is achieved. The adsorption increases with higher temperatures, where the kinetic energy of the adsorbed molecules increases and thus increases its ability to enter the solid phase pores and their rapid spread and this may be within a specific range of temperatures.

3. Methods and Materials

3.1. Chemicals

Powder of MB (Nice, India), HCl (37%, Riedel-deHaen, Germany), NaOH (90%, BDH, England), NaCl (Fine Chemical Limited) and distilled water were used for different purposes during laboratory work. Working standard solutions of lower concentration were prepared by dilution method from 1000mg/L standard solution.

3.2. Apparatus and Instruments

A double beam Uv-Vis spectrophotometer (SPECORD 200/plus analytikjena, Germany) pH meter (Bante instrument, pH 202p, USA), Thermostat water bath (model grant GLS400, England), Digital balance, Oven (model GEN LAB WLD NES, England) and Muffle furnace were used during experimental work.

3.3. Collections of adsorbents

For this study, solid food wastes like onion, potato, garlic peels and Injera leftover were collected from Jimma University, main campus, student's meal hall (cafeteria) during the month of October to January 2023 and were used as sample for preparation of activated biochar.

3.4. Preparation of different adsorbents for screening

Before the selection of the utilized adsorbents, a number of locally available food wastes namely, about 500 g of onion, garlic, potato peels and injera leftover were separately collected from Jimma University main campus undergraduate students 'Cafeteria (Café)'. Then each sample was washed with tap water followed by distilled water, and then, dried at room temperature. The dried samples were crushed with pestle and mortar, sieved with 11.81 inch mesh size and stored in dry container for further study.

3.5. Adsorbent preparation

To use as adsorbent, each powdered food waste samples was washed several times with distilled water and then dried at room temperature to remove moisture. The dried samples were taken into thermostat materials and subjected to pyrolysis using muffle furnace following the conditions described in literature [77] to obtain the biochar.

3.6. Chemical Activation of carbonized sample

The obtained adsorbents (biochars prepared from food wastes) were further treated with KOH and HCl to replace the metal ions contained in the part of porous biochar to yield a powdered activated biochar. The modified adsorbents were then separated from the chemical solution through filtration and washed with distilled water until the washout water pH became neutral. The activated biochar was dried and grounded to required size. The powders were sieved to obtain required particle size and stored separately in plastic bottles for further use as an adsorbent. A geometric mean particle size of 0.125 mm and lower were taken for experiments.

During the activation process, 10 g of biochars were taken and added to 50 mL of distilled water contained in a beaker. Then, after adding 10 mL of concentrated HCl, the content was stirred using a magnetic stirrer at 353 K, 700 rpm for 1h. The activation was accompanied by washing with 50 mL of 0.1M NaOH followed by washing with distilled water. The obtained homogeneous mixture filtered out and put in an oven to dry at 373K. After drying, the samples were stored in an air tight plastic bag. Finally, the activated biochar powders were weighed on an analytical balance to obtain different amounts of each adsorbent to carry out adsorption study using batch techniques [77].

3.7. Preparation of MB solution

A stock solution of 1000 mg/L was prepared in distilled water. The working solution was prepared by diluting stock solution of MB with distilled water to the desired concentration of working condition. The pH value of each solution was adjusted to 7 using 0.1M HCl and 0.1M NaOH.

3.8. Preliminary study

3.8.1. Identification potential solid food waste as adsorbent

Batch adsorption of the MB was conducted using the activated biochar of food waste to screen the potential adsorbents. The experiment was carried out for fixed mass of the adsorbent, i.e., 100 mg of each adsorbent (biochar) prepared from potato peel, onion peel, garlic peel and Injera leftover was added to a 40 mL of 5 mg/L MB solution. All experiments were performed at similar condition and kept on the shaker for 24 h to reach equilibrium at 298±1K and the concentrations of MB were analyzed by a double beam UV-Vis spectrophotometer.

3.9. Batch Adsorption equilibrium studies

The batch adsorption equilibrium studies were performed in a set of vials (50 mL), where 40 mL of adsorbate solution was put in contact with the adsorbents (0.5g) in an orbital shaker at a constant temperature of 298±1 K. The aqueous solutions were prepared with MB with different concentrations in distilled water ranging between 10 and 50 mg/L.

Equilibrium studies were performed to investigate the sorption capacities of the adsorbents and to carry out the isothermal adsorption curves. After 24 h equilibration time, the suspensions were filtered and the concentrations of the dye were measured using double beam UV-visible spectrophotometer with a quartz cuvette. The concentration of MB dye in the aqueous solutions was measured at λ_{max} = 665nm. The sorption capacity at the equilibrium, qe (mg/g), was calculated using Equation 1:

$$qe = \frac{(Co-Ce)}{W} V \qquad (1)$$

Where C_o and C_e (mg/l) are the initial and equilibrium concentration of the dye in the solution, respectively, V (L) is the volume of the solution and W (g) is the dry mass of the adsorbent.

Batch kinetic experiments were conducted in the same set-up used for the equilibrium tests; the adsorption capacity as a function of time, qt (mg/g) was calculated using Equation 2:

$$qt = \frac{(Co - Ct)}{W} V \qquad (2)$$

Where, C_t (mg/l) is the dye concentration at time (t).

3.9.1. Study of effect of adsorbent dose

To study the effect of adsorbent dose, each food waste (onion, garlic and potato) biochar was separately studied. Accordingly, the effect of adsorbent dose was studied by adding 0.1 - 0.5 g, 40 mL of 10 mg/L MB solution. The content was shaken for 24 h at 298±1 K. Then, the content was centrifuged for 3 min at 3000 rpm to precipitate small chalked and dispersed solids during long time shaking. The obtained solution was filtered before determination the concentration of MB using double beam UV-Vis spectrophotometer.

3.9.2. Study of effect of pH of adsorbate

The pH of the solution is a crucial factor, which can influence the adsorption process. The effect of pH was studied from 4 -10, by adjusting with 0.1 M NaOH or 0.1M HCl using optimum adsorbent dose: 0.1 , 0.4 and 0.5 g for garlic peel, onion peel and potato, respectively. After 24 h shaking, 15 mL of each sample was withdrawn into centrifuge tube and centrifuged at 3000 rpm for 3 min then supernatant solution was prepared for double beam UV-Vis spectrophotometer analysis after filtration.

3.9.3. Effect of contact time

The effect of contact time is used to determine equilibrium time for the study of adsorption kinetics. Solution containing 40 mL of 10 mg/L MB was withdrawn into 50 mL vial containing the optimum adsorbent dose. Samples solutions were withdrawn at predetermined time intervals (i.e., 10,20,30,60,180, and 300 min) for color removal analysis. 15 mL of each sample was withdrawn into centrifuge tube and centrifuged at 3000 rpm for 3 min and then, the supernatant solution was filtered for the subsequent analysis.

3.9.4 Studies on point zero charge (pHpzc)

The pH at which the surface charge is electrically neutral is known as the point of zero charge (pHpzc). For pHpzc determination, 0.01 M NaCl solutions were prepared in different containers and their pH were adjusted to different values from 4-10 by adding 0.1M NaOH or 0.1M HCl. Then, the optimum dose of each adsorbent was added to all containers. The containers were shaken for 24 h and final pH of the solutions measured using pH meter. Graph was then plotted for absorbents prepared each as ΔpH versus initial pH .

3.9.5. Effect of temperature of shaker

The effect of temperature is used to determine equilibrium temperature for the study of thermodynamics. 40 mL of 10 mg/L MB solution, adjusted as optimum pH was withdrawn into four 50 mL vial containing the optimum adsorbent dose. Each vial was shaken at temperature of 313K, 323K, 333K and 343K for 24 h. Then, 15 mL of each sample was withdrawn separately to centrifuge tube and centrifuged at 3000 rpm for 3 min. afterwards; the supernatant was filtered and analyzed for its MB content.

3.9.6. Effect of initial concentration of adsorbate

Different concentrations of MB (10 - 50mg/L) were used to study the effect of initial concentration on the removal efficiency and adsorption capacity of the adsorbent at constant adsorbent dose, pH, time and temperature.

3.10. Isotherm adsorption and kinetic models

Adsorption isotherm are fundamental to understand the adsorption mechanism and thus, to design the adsorption system. In this study two adsorption isotherm models were taken into consideration, Langmuir (Equation 3) and Freundlich (Equation 4)

$$qe = \frac{QmKLCe}{1 + KLCe} \qquad (3)$$

$$\text{Log } qe = \text{Log}Kf + 1/n \text{ Log } Ce \qquad (4)$$

Where Q_m (mg/g) is the maximum adsorption capacity, KL (L/mg) the Langmuir constant ,Kf and n (L/mg) the Freundlich constants.

Kinetic models are essential to determine the rate of adsorption process and to give important information on the reaction mechanism. Two kinetic models, the pseudo-first order (Equation 5) and the pseudo-second order (Equation 6) were applied to the experimental data.

$$\text{Ln}(qe-qt) = \ln qe - k_1 t \qquad (5)$$

$$\frac{t}{qt} = \frac{t}{k_2 qe_2} + \frac{t}{qe} \qquad (6)$$

Where k_1 (1/min) and k_2 (g/mg.min) are the rate constant of pseudo-first and pseudo-second order adsorption kinetic model respectively.

4. Results and Discussion

4.1 Adsorbent selection

To select appropriate adsorbent from different food wastes: potato peel, garlic peel, onion peel and Injera leftover, for removal of MB dye from water, 100 mg base activated, acid activated and un activated of each food waste candidate were investigated for removal of 5 mg/L MB (initial concentration) at pH 7 and temperature of 298±1 K. Removal efficiency of each adsorbent was calculated using the equation:

$$R\% = \frac{(C_o - C_{eq})\ x\ 100}{C_o}$$

Where R% removal efficiency, C_o is initial concentration of MB, C_{eq} is equilibrium concentration of MB. Table 1 shows adsorption efficiency of base activated, un activated and acid activated. All measurements are the average of triplicate measurements.

Table 1. Un activated, base (KOH) and acid (HCl) activated biochars.

	Adsorbent	**Co mg/L**	**C_{eq} of MB, mg/L**	**%R**
Un activated	Onion peel	5	0.96	80.85
	Garlic peel	5	1.22	75.85
	Potato peel	5	2.70	46.07
	Injera	5	2.86	42.82
Base (KOH) activated	Onion peel	5	0.25	95.03
	Garlic peel	5	0.29	94.23
	Potato peel	5	0.23	94.20
	Injera	5	0.86	82.89
Acid (HCl) activated	Onion peel	5	0.17	96.52
	Garlic peel	5	0.20	95.93
	Potato peel	5	0.50	90.01
	Injera	5	2.34	53.14

Co: initial concentration; C_{eq}: Equilibrium concentration of MB; %R: Removal efficiency

The findings demonstrated that both base and acid activated biochar of onion, garlic and potato peels have shown promising or high removal efficiencies, or above 90% removal efficiencies. However, biochar prepared from Injera leftover showed the lowest removal efficiency and thus, it was not further studied. From the un activated biochars, onion and garlic peels biochars showed good removal efficiency (> 75%), whereas, injera and potato peels biochars exhibited low removal efficiency, i.e., 50%. Removal efficiency of base activated Injera is 82% which is higher when compared to acid activated and un activated one.

4.2. Effect of adsorbent dosage

The removal of MB dye was studied by using different masses of each acid activated biochar (0.1 g, 0.2 g, 0.3 g, 0.4 g and 0.5 g) and optimum adsorbents dosages were determined. Each experiment was conducted in 50 mL vials containing 40 mL of 10 mg/L initial dye concentration of solution, room temperature, pH=7, 200 rpm speed of shaker and kept for 24 h. After 24 h solutions of each adsorbent was centrifuged for 6 minutes at 7000 rpm. The result of this finding showed Optimum dosages of onion, garlic and potato were determined to be 0.4 g (99.534%), 0.1 g (96.588%) and 0.5 g (97.072%), respectively as shown in the Figure 2.

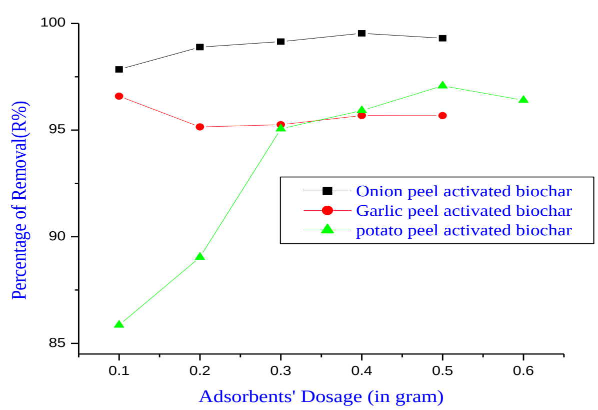

Figure2: Effect of adsorbents dosages on the removal of MB.

4.3. Effect of pH on adsorption of MB by different adsorbents

The pH of the solution influences adsorption process by affecting both aqueous chemistry and surface binding site of the adsorbent. At low pH values, surface of the adsorbent becomes positively charged because of protonation of the functional groups on the adsorbent surface [78].

In this study, effect of initial pH of solution was investigated at various pH values which are 4,7 and 10 keeping other parameters constant. The result of this finding indicated that optimum pH values potato; garlic and onion peels activated biochars were determined to be 10, 7 and 4 respectively as shown Figure 3. This difference in pH may be due to different functional groups present in the biomass.

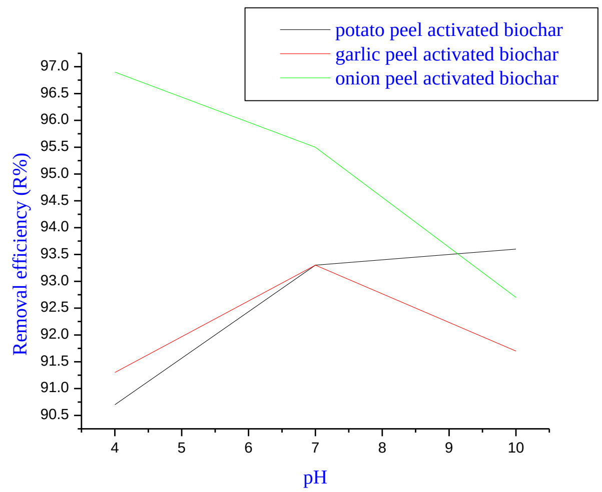

Figure3: Effect of pH on adsorption of MB by different adsorbents.

4.4. pH Point of Zero Charges

The pH at which the surface charge is electrically neutral is known as the point of zero charge (pHpzc). The pHpzc, the surface charge of the biochar is positively charged, which would only promote adsorption of cationic dyes while inhibit the uptake of anionic ones; whereas at

pH above pHpzc, the surface becomes negatively charged and promotes adsorption of anionic dye[79]. The pHpzc is the point where the curve pH final verses pH initial intersects the straight line corresponding to: pH initial=ΔpH. The results indicated the point of zero charge values corresponding to potato peel garlic peel and onion peel activated biochar were determined to be 8.6, 7.4 and 8.6 respectively as shown in the Figure 4.

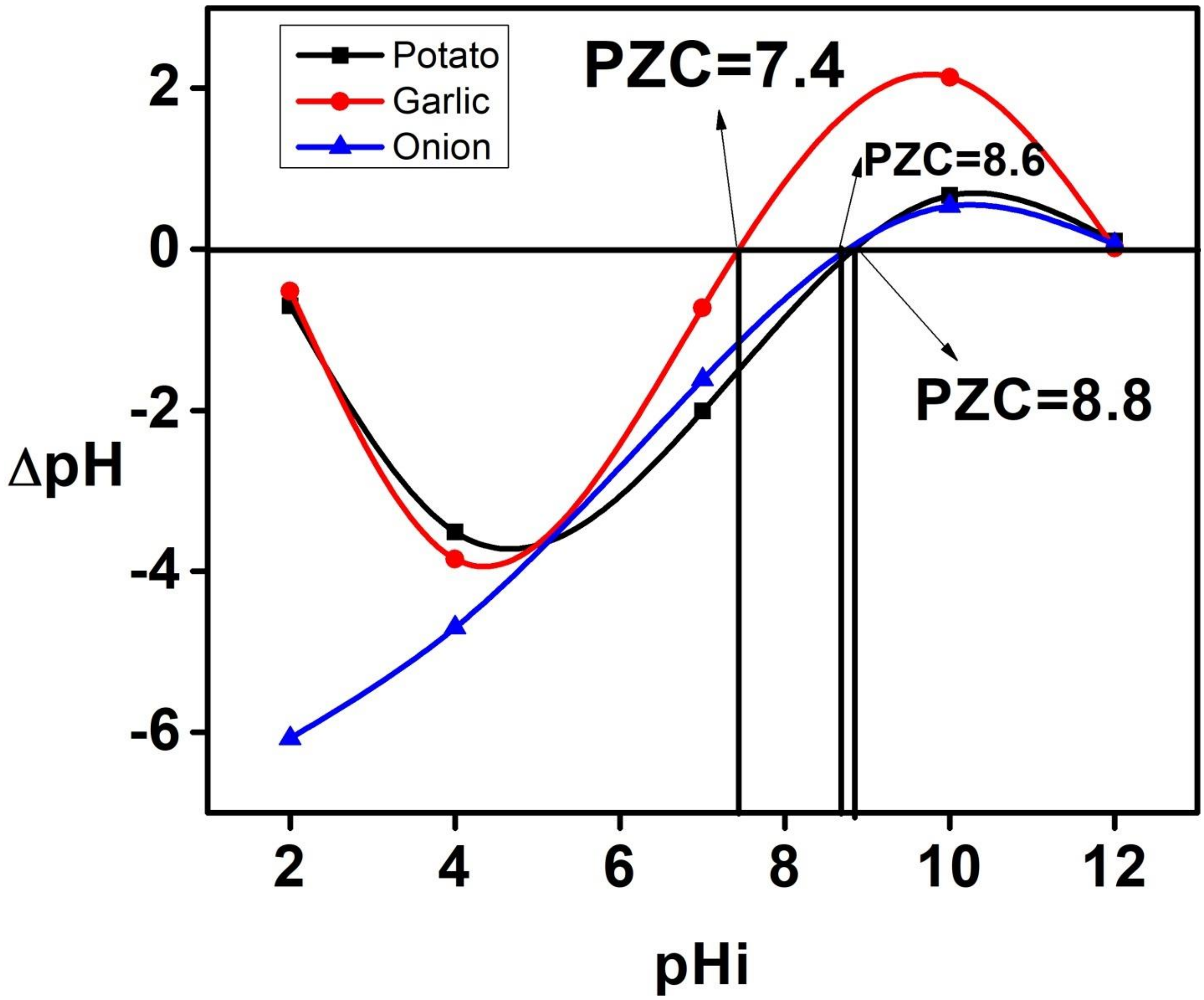

Figure 4: Point of zero charges for onion, potato and garlic peels activated biochars

4.5. Effect of temperature on adsorption of MB by adsorbents

The effect of temperature varies according to the type of adsorption and the nature of the adsorbent and adsorbate. The adsorption of heat is increased by the exothermal process; in the endothermal process the contrary is achieved [80].

The effects of temperature on MB adsorption efficiency by potato, garlic and onion peels were studied. Four different temperatures of 313, 323, 333 and 343 K were considered. From the result of experiment, the obtained removal efficiency of MB by potato peel activated decreases from 99.213% to 97.772%, when the temperature changes from 313 K to 343 K and that of garlic peel activated biochar decreases from 99.333% to 87.351%. These results indicated that the dye adsorption process may be exothermic and can be described out by the fact that the rise in temperature may not be in favor of any agglomeration of MB on the solid surface.

Removal efficiency of onion peel activated biochar increases from 99.301% to 99.994% . This result indicated that the dye adsorption process may be endothermic and can be described out by the fact that the rise in temperature may be in favor of any agglomeration of MB on the solid surface [81].

4.6. Effect of initial concentration of MB on adsorption capacity of adsorbents

The effect of initial MB dye concentrations on the adsorption performances adopted by potato, garlic and onion peels activated biochar under optimum experimental conditions (0.5 g, 0.1 g and 0.4 g and other optimum conditions respectively). The studies were carried out at several initial concentrations ranging from 10 to 50 mg/L. It can be seen that the adsorption amount of MB by potato peel activated biochar increases with the increase of initial MB concentration from 0.7815 to 3.9523 mg/g, for garlic from 3.9949 to14.7599 mg/g and for onion from 0.9768 to 4.8441 mg/g as shown in Figure 7. This significant increase of the adsorption efficiency values were expected because high initial MB concentrations correlate with a higher driving force of concentration gradient and a higher probability of collisions between MB cationic molecules and superficial functional groups of negatively charged of the adsorbent[82].

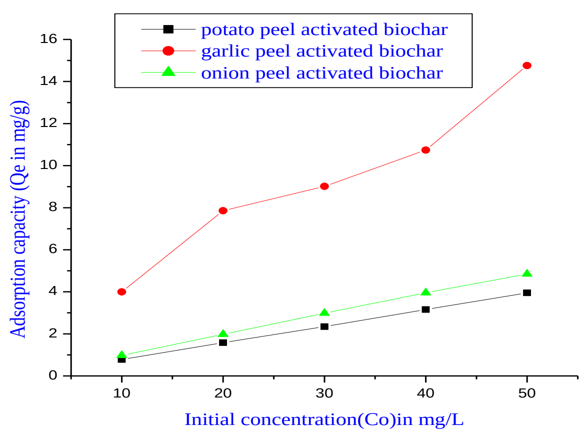

Figure7: Effect of initial concentrations of MB on adsorption of potato, garlic and onion peels activated biochar.

4.7. Effect of Contact Time

Contact time plays a vital role in the adsorption process.

The adsorption of adsorbate increases with increasing contact time until equilibrium is reached. Only very slight improvement occurs after equilibrium is reached. This occurs because the active site of the adsorbent are vacant during the initial stage and adsorption can take place rapidly, but the number of remaining active sites of the adsorbent are decreased after equilibrium and these site are occupied with difficulty due to the repulsive forces between the solute molecules on the solid and bulk phase [83].

The influence of contact time on MB adsorption by potato peel, garlic peel, and onion peel activated biochars were studied at optimum temperature , optimum adsorbent mass , optimum pH of solution and initial MB concentration of 10 mg/L, is illustrated in the Figure8. The experimental data indicated that the adsorption efficiency of the studied dye onto adsorbents increases with the increase of contact time (ranging from 0.2 h to 5 h), and reaches the maximum values for potato peel activated biochar 97.766% after 3 h, for garlic peel activated biochar,99.833% after 0.5 h and for onion peel activated 99.931% after 0.3 h as shown in Figure 8 below.

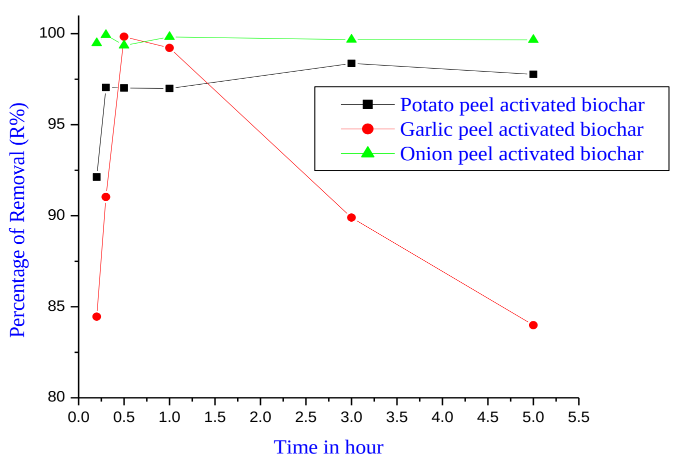

Figure8: Effect of contact time of MB on adsorption of different adsorbents.

4.8. Adsorption Isotherm

The isotherms models are applied for analyzing adsorption equilibrium results through experiments and studying the surface properties of the adsorbent and its affinity for an adsorbate. Figure 9 (a – c) and Figure 10 (a – c) show the Langmuir and Freundlich adsorption isotherm model, respectively. The values of the correlation coefficients indicate the favorable nature of adsorption of MB dye on all adsorbents.

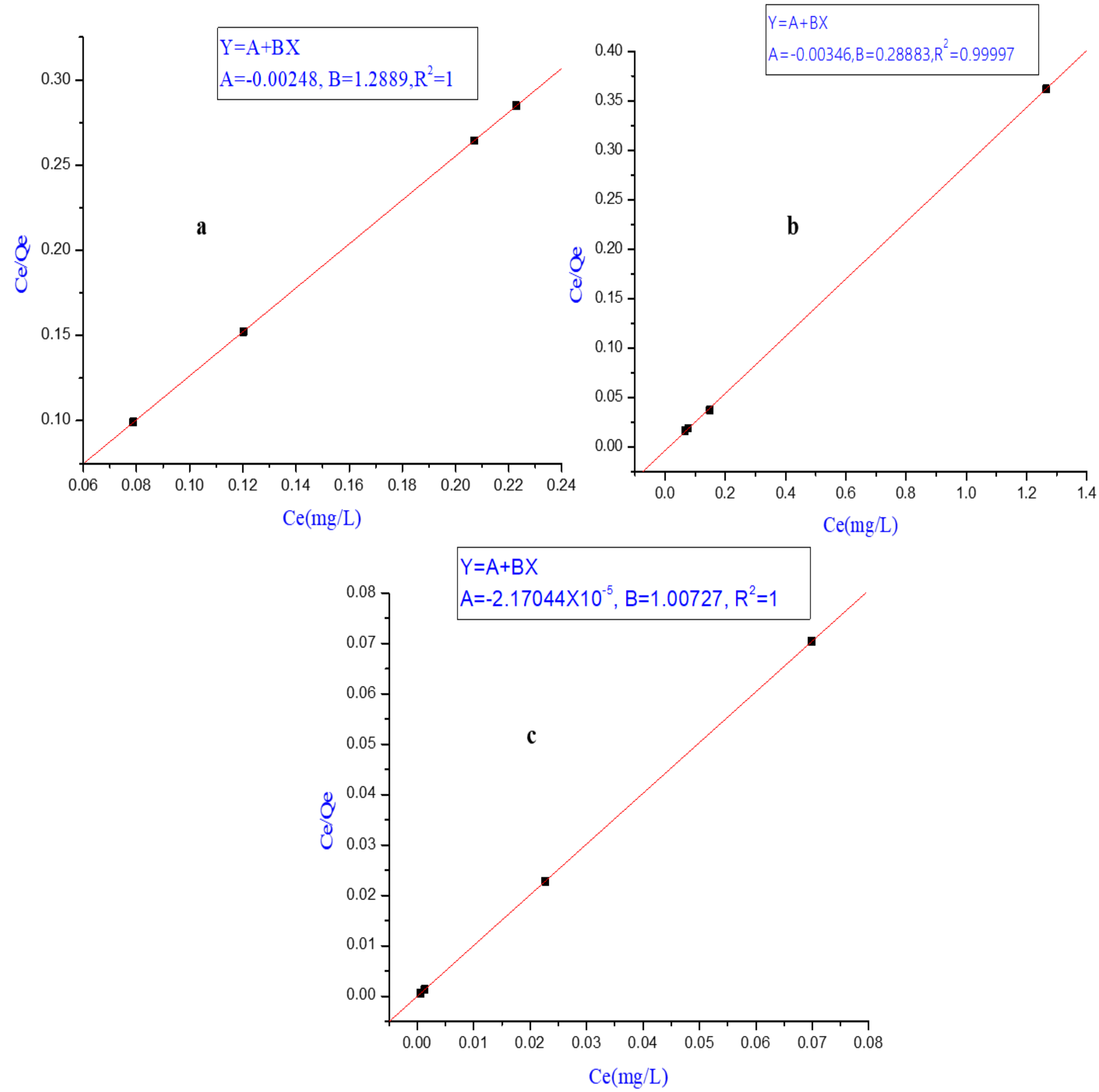

Figure 9: Langmuir adsorption isotherm of a) *Solanum tuberosum* (Potato), b) *Sativum* (garlic) and c) onto *Allium cepa* (onion) peels activated biochars.

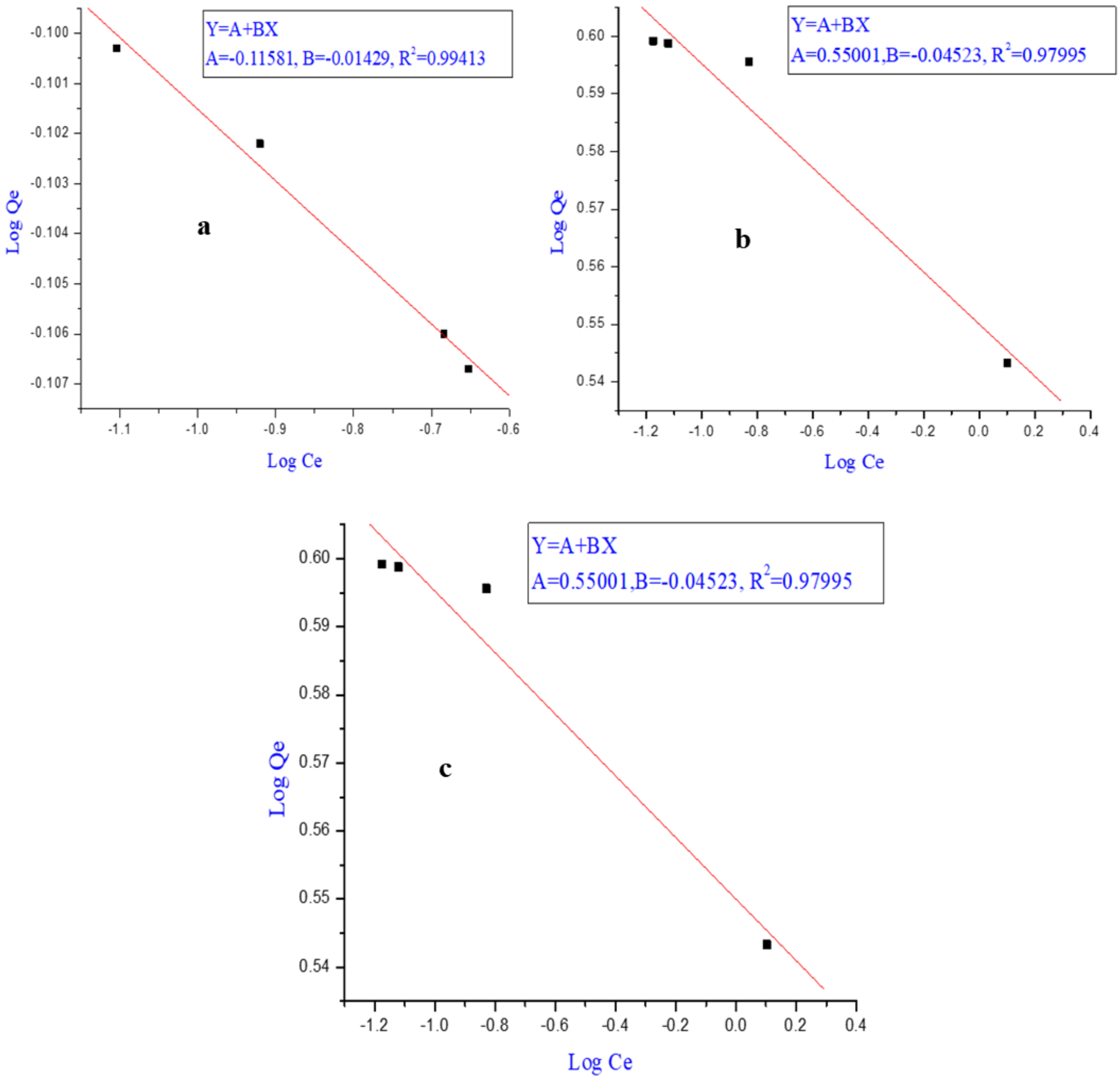

Figure 10: Freundlich adsorption isotherm of a) *Solanum tuberosum* (Potato), b) *Sativum* (garlic) and c) onto *Allium cepa* (onion) peels activated biochars.

Table 2 display the experimental results obtained for Freundlich and Langmuir adsorption isotherms of the adsorbent.

Table2. Freundlich and Langmuir adsorption isotherm model Parameters for adsorbents.

Isotherm model	Parameters		Adsorbents
Freundlich	KF(mg/g)	0.76593	Potato peel activated biochar
	N	-70	
	R^2	0.99413	
	KF(mg/g)	3.5482	Garlic peel activated biochar
	N	-22	
	R^2	0.97995	
	KF(mg/g)	0.9909	Onion peel activated biochar
	N	-758	
	R^2	0.89994	
Langmuir	Qm exp(mg/g)	0.7947	Potato peel activated biochar
	Qm cal(mg/g)	0.7759	
	KL(L/mg)	520	
	RL	0.0002	
	R^2	1	
	Qm exp(mg/g)	3.9698	Garlic peel activated biochar
	Qm cal(mg/g)	3.4622	
	KL(L/mg)	84	
	RL	0.0012	
	R^2	0.99997	
	Qm exp(mg/g)	0.9999	Onion peel activated biochar
	Qm cal(mg/g)	0.9928	
	KL(L/mg)	46408	
	RL	0.000002	
	R^2	1	

KF: Freundlich constant; N: Freundlich exponent; Qm: Adsorption capacity; KL: Langmuir constant

The isotherm model that better describes the MB adsorption process was identified by comparing the obtained correlation coefficients (R^2). According to results represented in Table 2, the bio sorption obeys Langmuir model since correlation coefficients (R^2) of adsorbents are very close to unity which assumes monolayer coverage of MB dye over the homogeneous surface of the adsorbents and the adsorption of each molecule onto the surface has the same adsorption activation energy. The value of RL indicates the shape of the isotherm to be either unfavorable ($RL > 1$), linear ($RL = 1$), favorable ($0 < RL < 1$), or irreversible ($RL = 0$). In this study RL was between 0 and 1 which is favorable adsorption.

4.9. Adsorption Kinetics Modeling

The experimental data of MB adsorption on potato peel, garlic peel and onion peel activated biochar were investigated using Lagergren pseudo first order and pseudo second-order models.

Lagergren pseudo-first-order

The experimental measurements were analyzed using linear form of Lagergren pseudo-first order: which is $\log(Qe - Qt) = \log(Qe) - (K_1/2.303)t$.

Qe is the equilibrium amount of adsorption (mg/g), Q_t is the amount of adsorption of adsorbents at time t (mg/g) and K_1 is the rate constant (min^{-1}).The pseudo-first-order model corresponding to the adsorption of MB on potato, garlic and onion peels activated biochar are shown in Figure11-12, respectively.

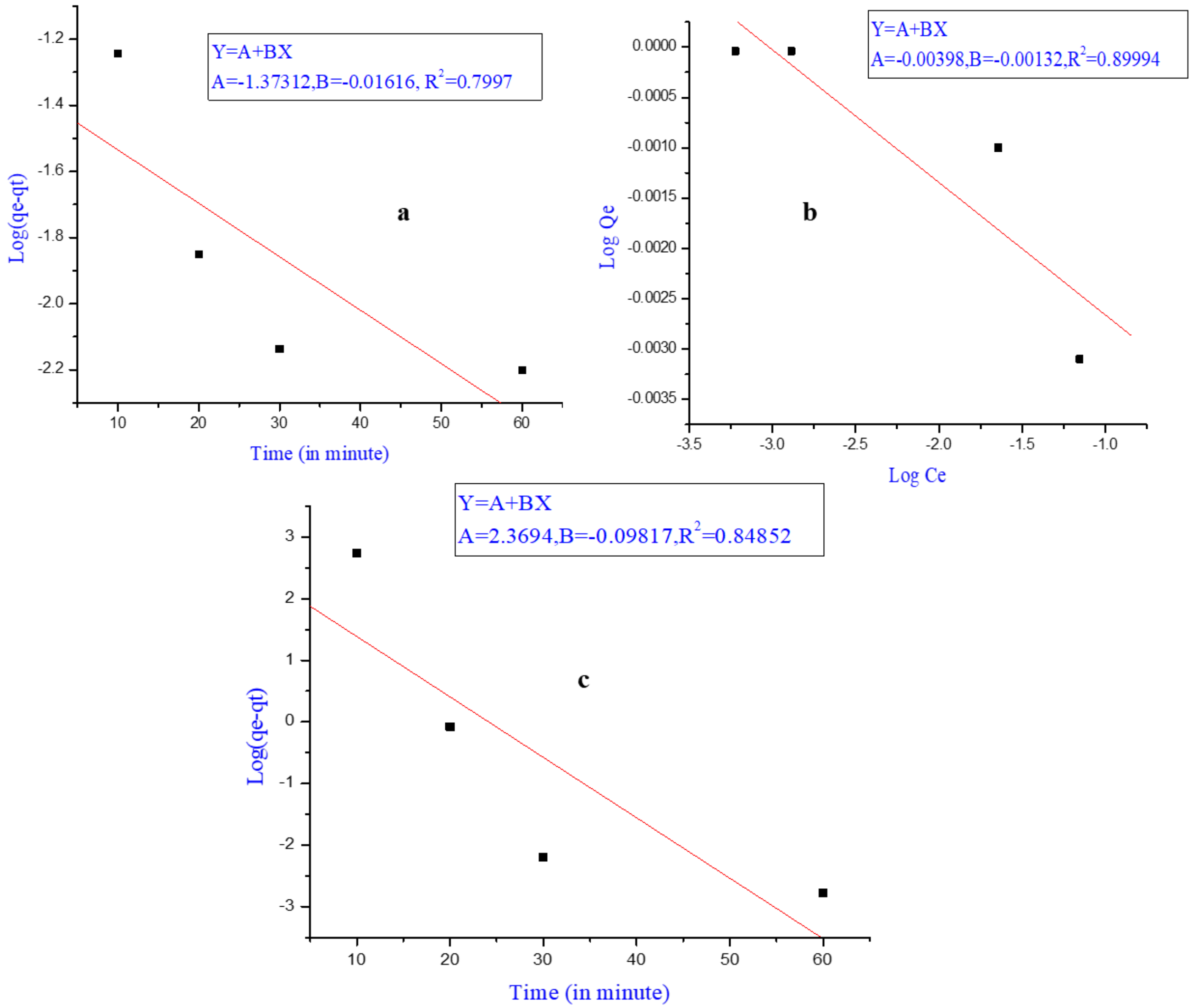

Figure 11:Pseudo first order model for a) *Solanum tuberosum* (Potato), b) *Sativum* (garlic) and c) onto *Allium cepa* (onion) peels activated biochars.

Lagergren Pseudo-second order

The pseudo-second-order kinetic model is expressed in the linear form as the: $t/Qt = t/Qe + 1/K_2.(Qe)_2$ where, K_2 is the rate constant ($g.mg^{-1}min^{-1}$).The pseudo-second-order model is shown in Figure 14-15.

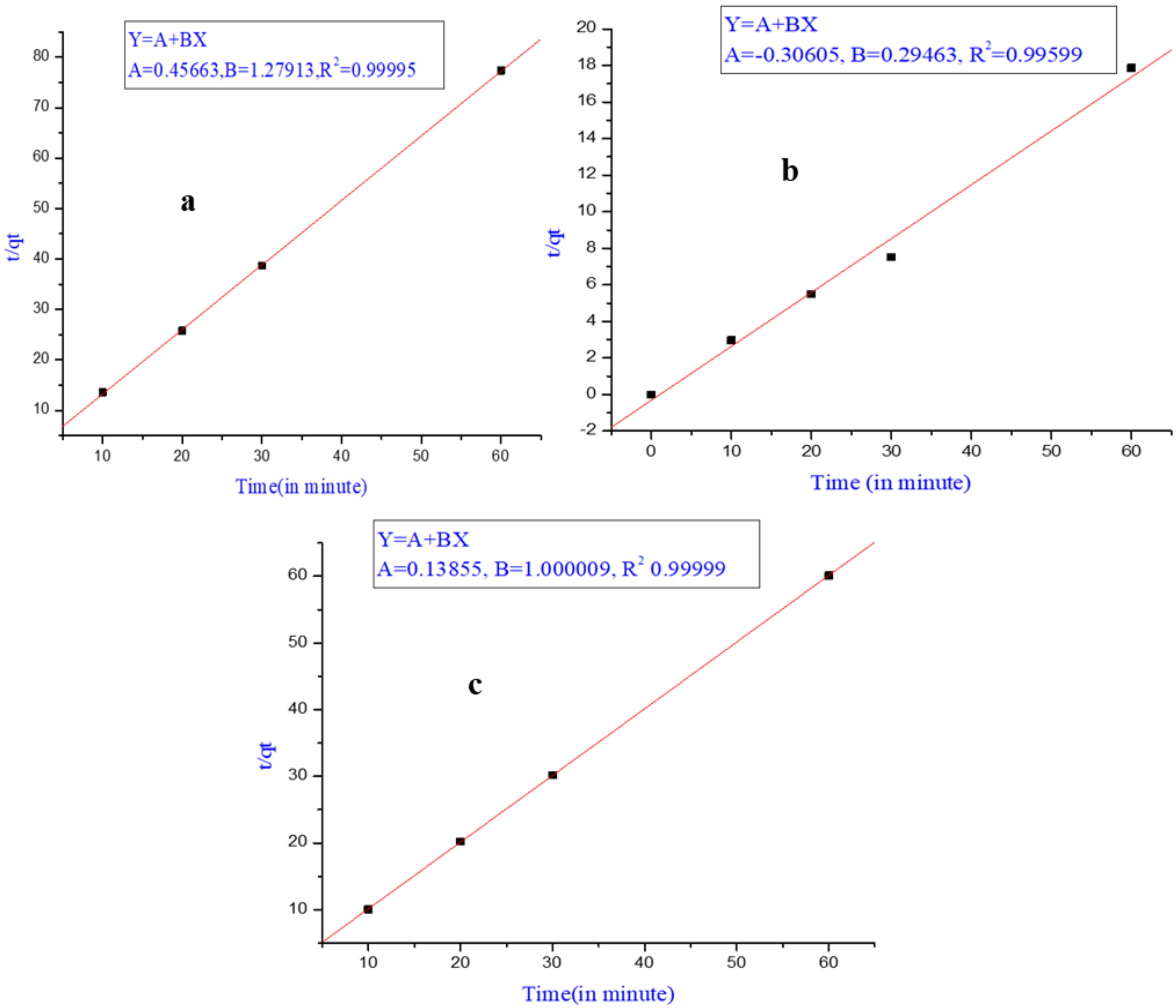

Figure 12: Pseudo second order model for a) *Solanum tuberosum* (Potato), b) *Sativum* (garlic) and c) onto *Allium cepa* (onion) peels activated biochars.

Details of parameters of adsorption kinetic pseudo first and second order modeling are presented in Table 3

Table3. Parameters of adsorption kinetic modeling.

Kinetic modeling	Parameters		Adsorbents
Pseudo first order	K_1(min^{-1})	0.03722	Potato
	R^2	0.7997	
Pseudo second order	K_2(g/mg.min)	0.78178	
	R^2	0.99995	
Pseudo first order	K_1(min^{-1})	0.02213	Garlic
	R^2	0.88744	
Pseudo second order	K_2(g/mg.min)	3.3941	
	R^2	0.99599	
Pseudo first order	K_1(min^{-1})	0.22609	Onion
	R^2	0.84852	
Pseudo second order	K_2(g/mg.min)	0.99999	
	R^2	0.99999	

K_1: rate constant for pseudo first order; K_2: rate constant for pseudo second order; R^2: correlation coefficient.

As shown in Table3, the determination coefficient R^2 values corresponding to pseudo-second-order model of adsorption process for different activated biochar are equal to unity. Results of the kinetic studies suggested that the adsorption process can be explained by using pseudo second order kinetics, suggesting chemisorptions as the main adsorption mechanism. The adsorption kinetics modeling best fit pseudo second order.

4.10. Adsorption Thermodynamic Studies

Thermodynamic study is important for an adsorption process to describe the process type, spontaneity and etc. All corresponding parameters as free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) changes can be estimated using equilibrium constants changing as a function of temperature.$\Delta G^0$is the standard free energy change (J) is calculated by: ΔG^0= -RT ln(KD). KD=Qe/Ce where, R is the universal gas constant (8.314 J/mol K) and T is the room temperature (298 K) and KD is the thermodynamic equilibrium constant (L/g),Qe (mg/g) is the amount of

MB dye adsorbed at equilibrium, Ce (mg/L) is the concentration of MB at the system equilibrium. Van't Hoff curves of the three adsorbents for the adsorption of MB are presented in Figure 13.

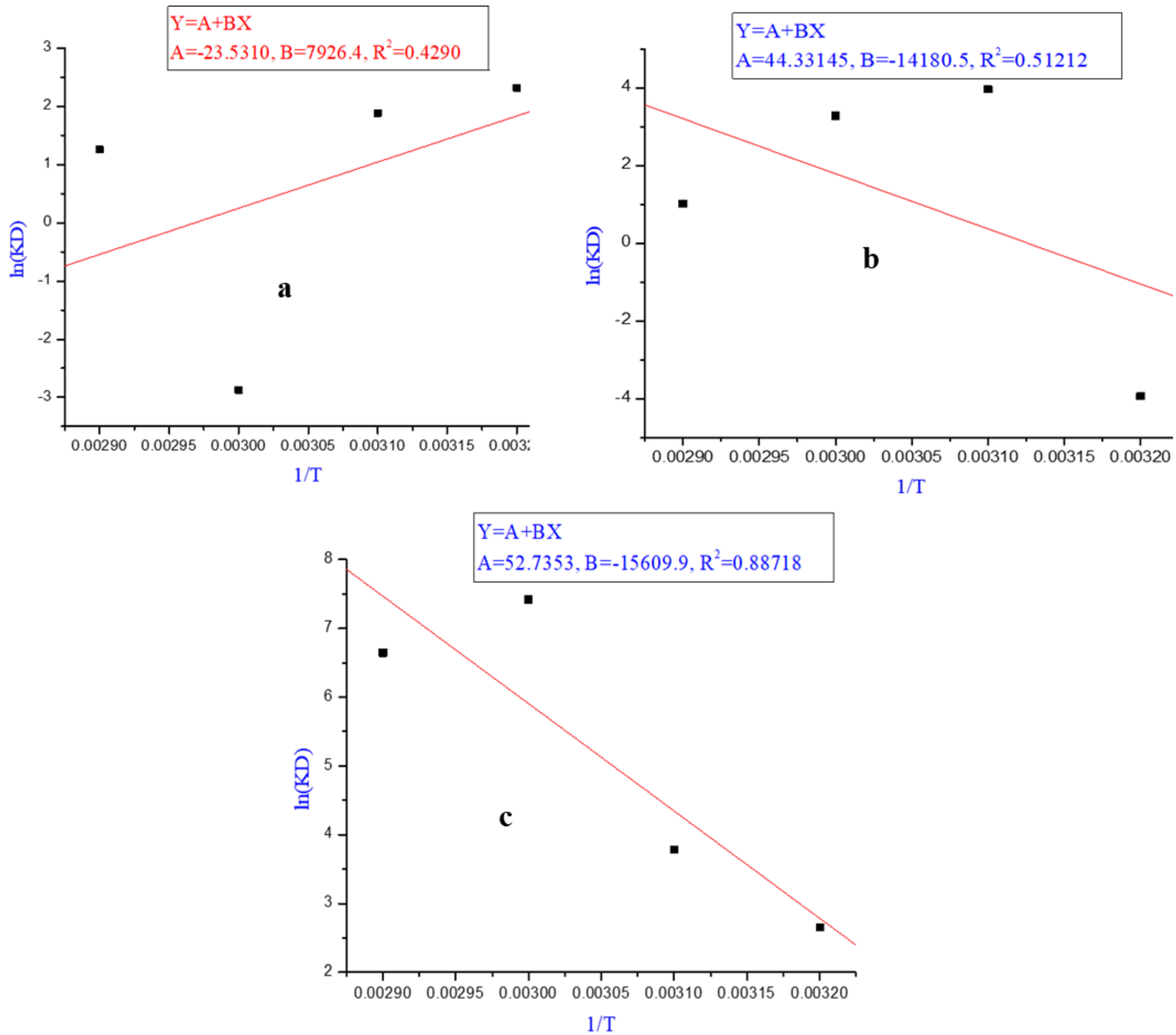

Figure 13: Van't Hoff curves corresponding to the adsorption of MB by a) *Solanum tuberosum* (Potato), b) Allium *Sativum* (garlic) and c) *Allium cepa* (onion) peels activated biochars.

The values of ΔH^0 and ΔS^0 were determined from the slope and the intercept of ln (KD) versus 1/T as shown in the Table 4. Ln (KD) = $-\Delta H^0/RT+\Delta S^0/R$. ΔG^0, ΔH^0, and ΔS^0 are related by: $\Delta G^0 = \Delta H^0 - T\Delta S^0$ [83].

Table 4. Thermodynamic parameters for the adsorption processes.

Adsorbent	Temperature(K)	ΔG°(KJ/mol)	ΔH°(KJ/mol)	ΔS°(KJ/mol)
Potato peel activated biochar	313	-6.017	-65.897	-0.1956
	323	-5.0577		
	333	-7.9555		
	343	-3.5812		
Garlic peel activated biochar	313	-10.2459	117.8967	0.3686
	323	-10.6404		
	333	-9.0881		
	343	-2.8976		
Onion peel activated biochar	313	-6.9057	129.7732	0.4384
	323	-10.1592		
	333	-20.5386		
	343	-18.9501		

ΔG°: standard Gibbs free energy change; ΔH°: standard enthalpy change;
ΔS°: standard entropy change.

4.11. Adsorbents Characterization

The FT-IR and XRD spectra of the results of the samples were listed for each adsorbent XRD analysis was carried to characterize the crystallinity of prepared biochars for all samples.Figure14 displays the XRD pattern of garlic peel activated biochar before and after adsorption and they exhibits diffraction pattern at $2\theta=25^0$ for both garlic peel activated biochars before and after adsorption, onion peel activated biochar before and after adsorption and exhibits diffraction pattern at $2\theta= 27^0$ and 30^0 respectively and potato peel activated biochar before and after adsorption and they exhibits diffraction pattern at $2\theta= 25^0$ for both potato peel activated biochars before and after adsorption.

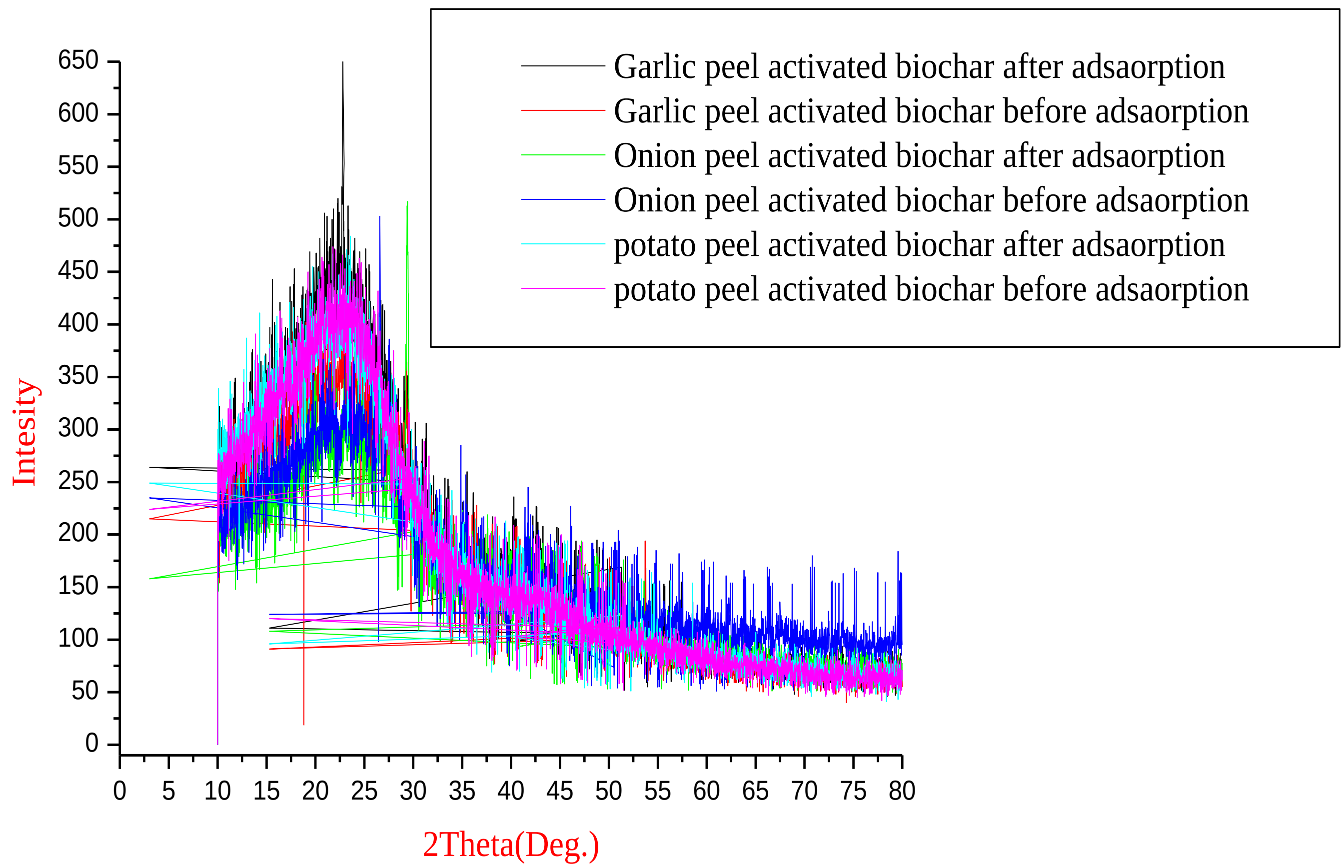

Figure 14: XRD spectra of different adsorbents.

FT-IR spectra were obtained to evaluate qualitatively the chemical structures of potato peel and garlic peel before and after adsorption and are shown in the Figure 15. The spectrum displayed the following bands which indicated various functional groups.

The band near 1571 cm^{-1} shows C=O group and the band around 1150 cm^{-1}indicates C=C, C-H deformation of alkenes. The band around 1404 cm^{-1}may be due to –CH_2 bending and C-O stretching for garlic peel activated biochars before and after adsorption. This compound is an evidence for the Lignocelluloses structure of activated biochar. The band around 1184 cm^{-1} shows C-N stretching and the existence of secondary amine for garlic peel activated biochars before and after adsorption. The band near 754 cm^{-1} indicates C-N and C-H stretching which indicates heterocyclic compounds. The band around 1558 cm^{-1} potato peel activated biochar after adsorption shows C=O group, and around 1104 cm^{-1} there is C=C and C-H deformation mode of alkenes. The bands near 1995 cm^{-1} -2096 cm^{-1} was indicated amino acid hydrochlorides. The band around 1572 cm^{-1} shows C=O group. The band around 1158 cm^{-1} indicate C=C, C-H deformation of alkenes [83].

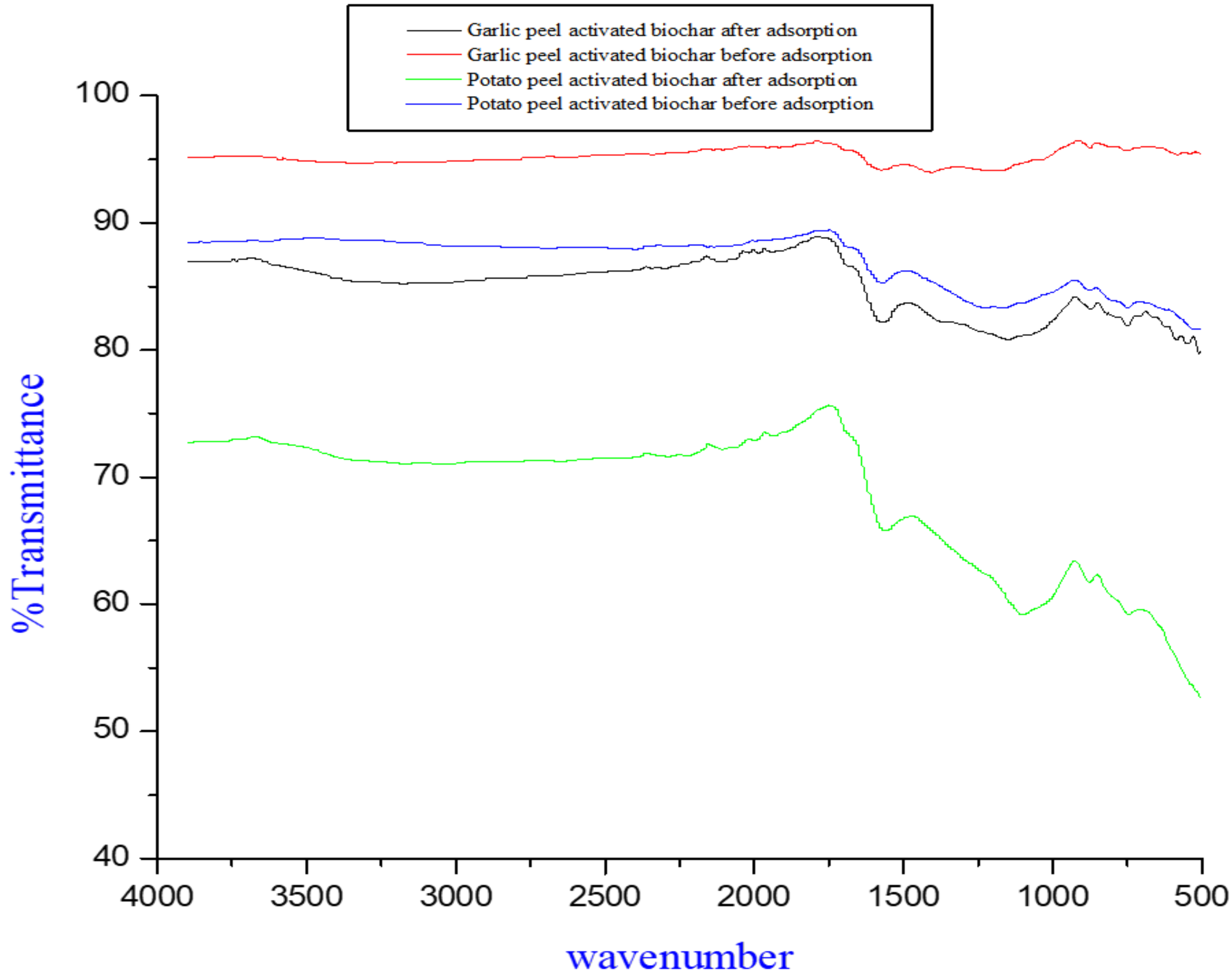

Figure15: FT-IR spectrum of Garlic and potato peels biochars before and after adsorption.

5. Conclusion

In this study several solid food wastes were screened for the MB removal from the waste water which is in line with the concept of waste re use. The obtained results show that the MB dye was adsorbed between pH 4 and 10.Adsorption capacities of adsorbents (potato, garlic and onion peels activated biochars) were 3.95, 14.76, and 4.84 mg/g. The maximum removal efficiencies of potato, garlic and onion peel activated biochar were observed to be 99.22%, 99.33% and 99.99% respectively. The kinetic measurements showed that the mechanism follows the Pseudo-second-order model. The adsorption process was described by the studied kinetic isotherms models (Langmuir and Freundlich).The ΔS°, ΔH° and ΔG° values obtained through the thermodynamic study indicate the exothermic, the stable and spontaneous nature of the adsorption process on the surface of potato, garlic and onion peel activated biochars. The study revealed that these new adsorbents are inexpensive, easily available material and can have an application for the removal of MB dye contained in industrial effluents.

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