



WALLAGA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
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**BIOADSORBENT FROM ORANGE PEEL FOR THE REMOVAL OF
MANGANESE (II) ION FROM AQUEOUS SOLUTION**

M.Sc. Thesis

By

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June 2024

Nekemte, Ethiopia



WALLAGA UNIVERSITY
SCHOOL OF GRADUATE STUDIES

**BIOADSORBENT FROM ORANGE PEEL FOR THE REMOVAL OF
MANGANESE (II) ION FROM AQUEOUS SOLUTION**

**A Thesis submitted to the School of Graduate Studies, Wallaga University
in Partial Fulfillment of the requirement for the Degree of Master of
Science in Chemistry, Analytical Stream.**

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STATEMENT OF THE AUTHOR

I Mr. Debela Tesema hereby declare and affirm that the thesis entitled “Bio adsorbent from Orange Peel for the Removal of Manganese (II) Ion from Aqueous Solution” is my own work conducted under the supervision of Shibiru Yadeta (PhD). I have followed all the ethical principles of scholarship in the preparation, data analysis and completion of this thesis. All scholarly matter that is included in the thesis has been given recognition through citation. I have adequately cited and referenced all the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and I have not misrepresented, fabricated, or falsified any idea /data/fact/source in my submission. This thesis is submitted in partial fulfillment of the requirement for a degree from the Post Graduate Studies at Wallaga University. I further declare that this thesis has not been submitted to any other institution anywhere for the award of any academic degree, diploma or certificate.

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ABBREVIATIONS AND ACRONYMS

ECAE	:	Ethiopian Conformity Assessment Enterprise
FTIR	:	Fourier Transform Infrared Spectroscopy
OP	:	Orange Peel
pH	:	Potential of Hydrogen
PFO	:	Pseudo-First-Order
PSO	:	Pseudo-Second-Order
UV	:	Ultraviolet
WHO	:	World Health Organization

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ABSTRACT

Manganese ions occur most commonly in the water and an excess amount of this ion may be dangerous due to its high toxicity and bioaccumulation within the food chain. In this study, orange peel was used as a bio-sorbent to extract manganese ions from aqueous solutions. To quantify the manganese ion, the ion was complexed with dithizone, whose absorbance of metal ion increases with an increase in concentration of the ion. The initial concentration of manganese ions, duration of contact, pH, and amount of adsorbent used all had a significant effect on the tendency of Mn^{2+} ions to bio-sorb onto orange peel. Since pH was a major factor in bio-sorption, it was determined that pH 6 was the optimal pH for the metals under study. Utilizing Fourier transform infrared (FTIR) spectroscopy, the functional groups of orange peel adsorbent that participated in Mn^{2+} adsorption were identified. The adsorption equilibrium was achieved with in 40ppm initial concentration, 120 min time, and 1.2g adsorbent dose. At these optimum conditions a maximum removal efficiency of (91.73%, 92.63% and 94.04% respectively) was achieved. The adsorption isotherm of Manganese more fitted with Freundlich model because ($R^2 = 0.9614$). Pseudo first order and pseudo second order kinetic models were described for manganese, with pseudo second order (PSO) showing the best fit. The current study's findings suggest that orange peel can effectively remove manganese from aqueous solutions as an adsorbent.

Key words: Manganese ion, orange peel, bio-adsorbent, adsorption isotherms, adsorption kinetics

1. INTRODUCTION

1.1. Background of the Study

Nowadays, water has been critically polluted by domestic, industrial, commercial, or agricultural activities and it affects the water bodies through runoff. Since the emergence of the industrial revolution, it has become one of the crucial sources of water pollution (Abhijeet Thakur *et al.*, 2021). Similarly, water may be affected by different chemicals such as oil spills, biological waste, carcinogenic elements, heavy metals, and various dyes from textiles and other sources (Memon *et al.*, 2008).

Heavy metals are among the significant pollutants that have adversely affected the purity of surface water. They may enter the aquatic environment through the discharge of industrial wastes, storm water runoff, mining activities, smoke stack discharge, and automobile emissions (Sbaffoni *et al.*, 2018). . Some metals are necessary for humans, animals, and plants in trace amounts. However, consuming of large amounts of heavy metal may leads to acute and/or chronic toxicity, which is linked to learning disabilities, cancers and even death (Maryam *et al.*, 2018). Manganese is necessary for the diet of most organisms and is crucial in numerous biological processes. It is commonly found in drinking water and sewage from urban areas, especially in places with manganese production.

However, manganese concentrations above the limit need to be controlled. Manganese concentrations in drinking water that are around 2 mg/L or lower are not considered a risk to health, so manganese levels between 1 to 3 mg/L could be considered safe for drinking water. It has been reported that the excessive accumulation of manganese in the human body causes the disorder disease of hemochromatosis, cirrhosis and diabetes mellitus (Adhikari, 2013). Therefore, the removal of manganese above the recommended level in water is important for water quality. Various techniques have been documented for processes such as reduction, precipitation, filtration, ion exchange, adsorption, and the like. However, most of these methods are comparatively expensive and inefficient to removing high percentage of the contaminating metals from an aqueous system (Leung *et al.*, 2017).

Adsorption is the most common method to remove different metal contaminate from water (Aziz *et al.*, 2016 & Singh *et al.*, 2018). The adsorption process is efficient, cost-effective, and simple to operate compared to all other methods (Moutou *et al.*, 2018). Moreover, low-cost adsorbents that are inexpensive, require easy processing, and are abundant in nature can be employed for this purpose (Bhatnagar *et al.*, 2015). It has been reported that orange peel is a good bio-adsorbent because it consist of different functional groups available for adsorption when activated.

Orange peel is normally treated as wastes, although it has a lot of functional groups, as hydroxyl and carboxyl make it a potential sorbent material in the removal of manganese. Some researchers suggested in the literature the ability to utilize the modified waste of orange peel in rapport with adsorption of heavy metal from water (Ahmed *et al.*, 2019). The purpose of this work was to prepare an orange peel adsorbent and evaluate its capacity to remove manganese ions. Biomass adsorption techniques have been used more often in recent years to remove pollutants that are toxic to the environment. When compared to adsorption, the use of Mn (II) removal technologies such as oxidation and filtering increased from 95% in chemical precipitation to 99.5% in adsorption (Zaki & Haraha, 2018).

1.2. Statement of the Problem

The release of heavy metals into the environment from wastewater is harmful because they are considered as toxic. Contaminated wastewater with heavy metals may penetrate groundwater sources and pollute stream flow. As stream flow is the main source of water supply in Nekemt Town, it will impact the health of individuals when they consume water, particularly for drinking purposes (Tatah *et al.*, 2017). Thus, Researchers are currently searching for a cost-effective method to remove heavy metals from water due to the current wastewater treatment methods being ineffective or expensive. The new approach should prioritize utilizing affordable by-products in developing countries. This study selected an alternative adsorbent for the adsorption technique to eliminate heavy metals. Because waste water has a relatively high Mn ion concentration in Nekemt Town, the study was used orange peels as an adsorbent and Mn (II) as a heavy metal. Thus, one promising field of this research is creating an appropriate method for manganese (II) ion elimination through the preparation of sustainable adsorbent from biomass.

1.3. Objective of the Study

1.3.1. General objective of the study

The main objective of this study was to develop environmentally friendly and cost effective agro waste adsorbent from orange peel for the removal of Mn (II) ions from aqueous solution.

1.3.2 Specific objective of the study

- ✓ To synthesize agro waste adsorbent from orange peel
- ✓ To characterize the bio adsorbents and apply for Mn (II) ion removal.
- ✓ To investigate the operational parameters like pH, Mn (II) ion starting concentration, contact time, and adsorbent dosages on Mn (II) ion adsorption on orange peel.
- ✓ To identify several adsorption isotherms and adsorption kinetics for the Mn (II) ion adsorption on orange peel adsorbent.

1.4. Significant of the Study

Currently, the removal of heavy metal contaminants from aqueous solutions is one of the most important environmental issues being researched. Once metal ions enter the environment, their chemical form largely determines their potential toxicity (Zhang *et al.*, 2014). Neurological problems arise from the harm caused to the nervous system's tissues by the excessive amounts of Mn (II) ion (Niksirat *et al.*, 2019). Thus, the study ensures a method to apply the dual advantages of the orange peels bio-adsorbent. The study may also inform the environmental management authorities about the level of heavy metal pollution in study areas, providing baseline data for environmental analyst intending to conduct further investigations. The results from the study will be used to determine remedial action including water treatment and removal of high levels of Mn (II) ions.

2. LITERATURE REVIEW

2.1 Water Pollution

2.1.1 Water Pollution by Heavy Metal

Heavy metals exhibit toxic effect and persistent characteristics by entering into the food chains and the ecosystem where they cause have adverse impact on the biotic and abiotic components of the ecosystem. Due to this fact water functions as a medium of transport pollutants, heavy metals damaging effects on both living organisms and the environment. Once they enter the biological system through an aqueous medium, the pollutants can bio accumulated and bio magnified over time, and they will reach high concentration and toxifying. When toxicity by heavy metals becomes significant, it reaches human as the final consumer in the food web. Wastewater contaminated with heavy metals is largely generated from electroplating, mining and metal treatment or fabrication industries (Koivula *et al.*, 2011).

2.1.2 Water Pollution with Manganese (II) Ion

Mn is a naturally occurring element that can erode from soils, groundwater, and other surfaces into drinking water. The incorrect disposal of dry cell batteries or other hazardous industrial wastes can lead to higher manganese concentrations than those normally present in environmental water (WHO, 2011). This can have a major detrimental effect on human health (Mthombeni *et al.*, 2022). Water contains the divalent ion manganese (Mn^{2+}), which is considered a pollutant due to its organoleptic properties. Concentrations of Mn^{2+} in water > 0.1 mg /L negatively affect its organoleptic properties, especially taste, odor, and color (Alias *et al.*, 2019). The Environmental Protection Agency recommends a maximum Mn concentration in drinking water of 0.05 mg/L (U.S.Env't Pro, 2018), which is the stricter limit that many countries follow. The WHO determined the maximum acceptable limit of Mn concentration in drinking water of 0.1 mg/L (WHO, 2011).

Mn at the lowest dose (> 0.02 mg/ L) can form a black layer (on pipes), making the water unattractive. Small quantities (0.1 mg /L) can stain enamel and linen, which is a problem from a domestic stand point. As a result, it stimulates the growth of siderobacteria (Gallionella) in water

treatment plants, disrupting the operation of sand filters and resulting in pipe deposits (Rodier *et al.*, 2016)

2.2 Health Effect of Manganese (II) Ion

Manganese at lower doses is an essential nutrient for humans and animals. Mn (II) ion at elevated concentrations is a powerful neurotoxin which affects the nervous system and causes learning disabilities and intellectual impairment in children, due to the fact that they can be easily stored in the body of living organisms without breaking down (Bouchard *et al.*, 2011). When inhaled at a dose of approximately 10 mg/day, the Mn^{2+} ion causes neurological disorders because it is hostile towards calcium (Man good *et al.*, 2021). Chronic manganese exposure causes tremors, respiratory infections, psychological problems, and tiredness (Abdeen *et al.*, 2015).

2.3 Removal Methods for Mn^{2+} Ion from Water

The process of cleaning wastewater is called wastewater treatment. Some toxins or pollutants are difficult to manage after they are released from point sources of pollution into habitats, which makes this operation extremely critical. Accessibility of land for construction of treatment is main factors in the process (Tesfaye D., 2016). Manganese can be removed from contaminated waters using a number of standard techniques, including reverse osmosis, ultra-filtration, electrochemical, ion exchange, chemical precipitation, activated carbon, and adsorption (Ofudje *et al.*, 2020).

2.3.1 Reverse osmosis

Reverse osmosis is a technique used in desalination to extract pure water from water that contains salt. This water filtration method eliminates ions, molecules, and bigger particles from drinking water by using a semi-permeable membrane. An applied pressure is utilized in reverse osmosis to overcome the osmotic pressure (Warsinger *et al.*, 2016). Since it can remove a wide range of dissolved and suspended species, including bacteria from water, it is used in both industrial processes and the production of drinkable water. As a result, the solute is trapped on the pressurized side of the membrane while the pure solvent can pass through to the other side.

It is anticipated that the membrane will exhibit selectivity in preventing the passage of big molecules or ions through its pores, while permitting the passage of smaller components of the solution, like solvent molecules without restriction (Warsinger *et al.*, 2016). Reverse osmosis has the advantages of being easy to construct and run, requiring little maintenance, and being modular, which makes system extension straightforward. One of its drawbacks stems from its intricate membrane structure, which not only eliminates dangerous impurities from the water but also has the potential to eliminate numerous beneficial minerals.

2.3.2 Ultra-filtration

Ultra-filtration is the process of separating compounds from aqueous solution under pressure. Ions and tiny molecules in solution are not removed by the technology; instead, it is employed to eliminate microbiological and particle pollutants. For ultra-filtration, the pressure range is 1 to 10 bar. Ultra-filtration requires less work during operation and is automated. On the other hand, these systems may need to be cleaned frequently. Similar to reverse osmosis membranes, its membranes have a service life of at least three to five years (Jerroumi *et al.*, 2023). Ultra-filtration membranes reject solutes with sizes up to 0.03 microns, which means that the separations are based on size. The pore size and molecular weight are often used to characterize a membrane.

2.3.3 Electrochemical method

Because of its benefits, including its compliance with the environment, adaptability, high energy efficiency, automation amenability, and safety, the electrochemical approach is one of the technologies utilized as an alternative choice for the remediation of water and wastewaters (Pulkka *et al.*, 2014). This method involves passing a current through an aqueous metal-bearing solution that contains a cathode plate and an insoluble anode, and employing an electric field as the driving mechanism for the ion separation process using ion exchange membranes or plates. Negatively charged cathodes attract positively charged metallic ions, which makes it possible to extract and recover the metal deposit. Because they require a substantial initial investment and a costly electrical supply, electrochemical water or wastewater systems have not been generally used (Pulkka *et al.*, 2014).

2.3.4 Ion exchange

Manganese and other heavy metals can be extracted from wastewater using ion-exchange techniques, which are frequently employed. Ions from the substrate and the surrounding medium exchange during this process. Ion exchange resins are insoluble in the majority of organic and aqueous solutions, and they can be used at high temperatures and a wide range of pH values. Regeneration operations make it easy to recover and reuse after removing a variety of heavy metals, however the process is expensive and produces fewer metal ions than desired (Goher *et al.*, 2015).

2.3.5 Chemical precipitation

Chemical precipitation is one of the most widely used for heavy metal removal from inorganic effluent in industry due to its simple operation. Insoluble precipitates of heavy metals, such as hydroxide, sulfide, carbonate, and phosphate, are produced via chemical precipitation procedures. This process's mechanism is based on the reaction of dissolved metals in the solution with the precipitant to generate insoluble metal precipitation. To remove the extremely tiny particles as sludge, chemical precipitants, coagulants, and flocculation procedures are utilized to increase the size of the particles (Faisal *et al.*, 2020). Once the metals precipitate and form solids, they can easily be removed, and low metal concentrations can be discharged. Chemical precipitation has the advantages of being easy to use, affordable, and capable of removing most metals; but, it also has drawbacks, including the generation of a lot of sludge and additional costs associated with disposing of it.

2.3.6 Activated Carbon as an adsorbent

It has been discovered that activated carbon is a useful adsorbent because of its high adsorption capacity, which is caused by its active free valences and tiny particle sizes. Goher *et al* (2015) studied the use of granular activated carbon to remove metal ions, including manganese, from industrial wastes; the results showed an adsorption capacity of 2 mg/g for the removal of manganese ions. Chemical bonding and cation exchange occurred during the adsorption process on the surface of activated carbon, which has aromatic compounds and functional groups of

oxygen (Mohammed *et al.*, 2021). Its disadvantage is costly and no generation performance based on adsorbent.

2.3.7 Adsorption

Adsorption is a crucial procedure used by enterprises to lessen dangerous organic and inorganic pollutants in effluents during the physico-chemical treatment of wastewaters (Yirga *et al.*, 2022). It has been shown to be a cost-effective, environmentally responsible, and efficient treatment method. This technique is strong enough to meet industry-imposed high effluent limits and water reuse obligations. Adsorption is simply a technique of mass transfer that moves a substance from the liquid phase to the solid surface, where physical or chemical interactions bind it. During this partitioning process, a tiny amount of liquid phase contents are moved to the surface of the solid adsorbents. For all adsorption methods, mass transfer rates and solid-liquid equilibrium are required. Adsorption occurs mostly at the molecular level as a result of favorable interfaces between a surface and the group being absorbed (Tripathi & Ranjan, 2015).

The components that contribute to the adsorption process between adsorbate and adsorbents of agricultural waste are the presence of active functional groups (Zaini, & Abubakar, 2018). The adsorption of Mn (II) ions generally occurs based on the interaction between the manganese and functional groups present on the surface of the adsorbent through ion exchange interaction or complex formation, usually occurs on solid surfaces containing functional groups such as -OH, and -COOH (Islam *et al.*, 2015). Chemical plants are often less expensive to install and require less space, and they can be adjusted as needed (Selvam *et al.*, 2017). Economical desorption operations can be achieved through the renewal of the adsorbent, and adsorption processes are often reversible.

All mentioned conventional techniques are not widely used because they are less feasible for small scale industries, having high cost, produce a harmful sludge and have been found to be not ecologically friendly due to high energy operation (Adeyi *et al.*, 2019). It was also mentioned that controlling these technologies was complicated. As a result, it is discovered that the adsorption process is straightforward, easy to use, and successful in removing manganese (II) ions from aqueous solutions.

2.4 Bio-adsorbents used to remove Mn^{2+} Ion from Aqueous Solution.

Adsorbent materials with low costs can be found in nature and are classified as waste products from industry, homes, and agriculture. These materials are more reasonably priced, ecologically friendly, and less costly (Tripathi & Ranjan, 2015). For the removal of hazardous substances like heavy metals, they are quite effective. The process of obtaining and preparing the components is simple and doesn't involve the use of additional resources, chemicals, or procedures. Low-cost material that only requires thorough washing and drying to remove moisture before being sieved is the latest research material being employed for successful adsorption manganese (Ali *et al.*, 2017).

Research on the intrinsic adsorption capacities of various agricultural wastes, including pineapple (Luu *et al.*, 2020), sugarcane bagasse (Quoc *et al.*, 2020), pineapple leaf and cotton waste (Nga *et al.*, 2021), coconut coir dust (Etim *et al.*, 2016), and cotton (Yixi *et al.*, 2018), has been conducted in a large manner. Evaluation of tree leaves, coffee husk, barks, agricultural waste, maize corn, saw dust has also been used for adsorption capability on different metals at different conditions (Tesfaye, 2016). Adsorbents made from agricultural waste, such as cellulose aerogel (Yixi *et al.*, 2018) and pre-treated fruit peel waste (Nguyen *et al.*, 2019), have drawn a lot of interest recently for their ability to filter water contaminated with manganese. A thermally broken-down leaf was employed to investigate Mn (II) adsorption from water. At a concentration of 100 mg/L, the adsorbent dose utilized was 10 g/L. They found that for pH levels between 1.8 and 3.84, the removal percentage of Mn (II) climbed to 99% and that the adsorption capacity was 61–66 mg/g (Lo *et al.*, 2012).

2.5 Orange Peel as Bio adsorbent

Due to its availability, simplicity, low production costs, and lack of secondary pollution when compared to more traditional methods, the use of orange peel agricultural by-products in environmental pollution removal has gained significant traction in recent years (Wang *et al.*, 2020). Orange peels, which have little to no commercial value, are frequently thrown into the environment and cause environmental nuisances even when the oranges are used for their fruit juice. It is concerning that there is more waste made from orange peel due to the population growth and rising demand for oranges.

As a result, the advantages of employing orange peel as an adsorbent in the removal of manganese ions from aqueous solution would not only act as a way to decontaminate pollution but also give value to what was previously thought to be agricultural waste (Lei *et al.*, 2019). In order to do this, the current study describes the sorption of manganese ions from aqueous solution using a less expensive and renewable precursor made from agricultural byproducts derived from orange peel. The adsorbent was identified through the application of Fourier transform infrared spectroscopy (Min *et al.*, 2020). The effects of adsorbent dosage, pH, contact time, and starting adsorbate concentration were examined.

2.6 Study of Adsorption Isotherms

The amount of adsorbate adsorbed by unit mass of adsorbent from the liquid phase at a constant temperature is displayed by the adsorption isotherm. The examination of adsorption equilibrium data is crucial for optimizing the design of an adsorption system. The relationship between the concentration of metal ions in the solution and those adsorbed onto the adsorbents is represented by the adsorption isotherm. The adsorption data have been analyzed using a variety of isotherm models. The interaction between adsorbate and adsorbent was investigated using Freundlich and Langmuir adsorption models.

2.6.1 Freundlich adsorption isotherm

The Freundlich isotherm assumes that multilayer adsorption occurs on heterogeneous surfaces during metal ion adsorption, and that adsorption increases and subsequently decreases with concentration. Given is the Freundlich adsorption isotherm's linear form: (Freundlich, 1907), $X/m = K_f C_e^{1/n}$ changed to $\text{Log } (x/m) = 1/n \log C_e + \log K_f$ when $x/m = q_e$, $\text{Log } q_e = 1/n \log C_e + \log K_f$ where, X/m or q_e = mass of adsorbate adsorbed per unit mass of adsorbent (mg adsorbate/ g OP), K_f = Constant of Freundlich adsorption capacity factor (mg adsorbate/ g OP) (L water/mg adsorbate)^{1/n}, C_e = equilibrium concentration of adsorbate in solution after adsorption (mg/L) and $1/n$ = Constant of Freundlich adsorption intensity parameter. The surface is more heterogeneous if $1/n$ is larger and the affinity between the adsorbate and the adsorbent will be higher. Depending on the type of adsorption process, the value of $1/n$ indicates the relative distribution of energy sites (Ali, 2017).

2.6.2 Langmuir adsorption isotherm

The foundation of the Langmuir isotherm model is the monolayer adsorption of Mn (II) ions onto orange peel surface. The Langmuir adsorption isotherm assumes that the adsorption can only occur at a fixed number of definite localized sites, each site can hold only one adsorbate molecule (monolayer), and the sites are homogeneous. Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. Thus, the adsorbed layer was one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site was not affect the adsorption of molecules at an adjacent site. The linear form of Langmuir adsorption isotherm is given as , $C_e/q_e = C_e/q_m + 1/bq_m$ Where C_e is the equilibrium concentration of Mn (II) in mg/L, q_e is the quantity of metal adsorbed per unit weight of adsorbent (mg/g), and b and q_m are the Langmuir constants of adsorption energy and capacity, respectively. When C_e/q_e is plotted against C_e , a straight line with slope $1/q_m$ is obtained which shows that the adsorption follows the Langmuir isotherm. The Langmuir constants ' q_m ' and ' b ' are calculated from the slope and intercept with Y-axis respectively.

2.7 Kinetics of Adsorption

Adsorption kinetics, which characterizes the rate of solute uptake at the solid-solution interface, provides crucial information about the mechanisms and reaction pathways. To investigate the kinetics of Mn (II) adsorption on orange peel, the pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models are simulated. The acquired data was subjected to Ho's second order kinetics and Lagergren first order kinetics (Lahieb *et al.*, 2017). This was employed to ascertain the adsorption's molecularity and the processes that controlled the rate. The PFO model is solely dependent on the many adsorbate molecules that are present in an aqueous solution at a given moment. But the PSO model explains both the presence of manganese ions in aqueous solution and the abundance of free active sites on the adsorbent's surface.

2.7.1. Pseudo-First-Order (PFO)

The PFO regression model for adsorption was expressed using the following equation: $\log (q_e - q_t) = \log (q_e) - (k_1 / 2.303) t$, where t is the time taken to reach equilibrium, q_t (mg/g) is the amount

of manganese adsorbed on the OP at equilibrium state, and k_1 (min^{-1}) is the rate constant for the PFO reaction equation. The PFO regression model assumes that the unoccupied manganese sites and the rate of adsorption are proportionate to one other. The PFO rate constant, k_1 , and the capacity for equilibrium adsorption were determined using the intercept and slopes of the plot of the graph between the values of $\log(q_e - q_t)$ and time (t).

2.7.2. Pseudo-Second Order (PSO)

The data on adsorption kinetics were once more examined using a PSO kinetic model, which operates under the assumption that the square of the empty sites is proportional to the sorption rate and that the sorption rate is dependent on the adsorption capacity. The formula is as follows: $t/q = 1/k_2 q_e^2 + t/q_e$, where k_2 is the equilibrium rate constant (in grams per minute). Calculating the PSO rate constants k_2 and q_e involved examining the slopes and intercepts of plots of t/q vs. t . The PFO and PSO regression models were compared with respect to the kinetic parameter

3. MATERIAL AND METHODS

3.1. Experimental Sites

From preparations of the adsorbent to Uv-visible measurements as well as adsorption experiment were conducted at Ethiopian Conformity Assessment Enterprise (ECAE), Addis Ababa. The synthesized adsorbent's FTIR analysis was measured at Addis Ababa University's Chemistry Department.

3.2. Chemicals and Reagents

Standard solution of the metal ion was prepared from salts of Manganese (II) chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) (LOBA chemie pvt.ltd, 97%) aqueous solution. Using 0.1M solutions of sodium hydroxide (NaOH) or hydrochloric acid (HCl), the pH was manually adjusted. The reagent used for complexation reaction and quantification was Dithizone ($\text{C}_{13}\text{H}_{12}\text{N}_4\text{S}$) (LOBA chemie pvt.ltd, 98%)

3.3. Instruments and Apparatus

Fourier transform infrared spectroscopy (FTIR) (Spectrum 65FT-IR PerkinElmer), pH meter (MP 220), Refrigerator, Digital shaker (Model HY-5A China), Electronic balance (FA224), Hot air oven (HLW030), and UV-visible spectrometer (EC-70000, OEM/ODM, China) were the instruments utilized in this investigation.

3.4. Preparation of Adsorbent

Oranges were purchased from Nekemte Town, East Wallaga, Oromia Region and peeled after washed. Following transportation to the lab, op was stored in a sterile plastic bag. It was then cleaned to get rid of the filth using a hot water wash and a double distilled water rinse. These Op were chopped into tiny bits and oven dried for 24 hrs. at 80°C , finally grinded and sieved through a 1.80 mm size before it was used in adsorption experiments (Kumari, 2017).

3.5. Adsorbent Modification

An accurate weighted (30 g) sample of an over dried OP was poured with 150 mL of NaOH (0.1M) solution in to 500 mL conical flask for 6 hrs.at room temperature. After saturation, the

soaked adsorbent was washed with distilled water to remove the NaOH from the sample until the pH adjusted to neutral (pH =7). The resulting material was again dried to hot air oven for 7 hrs. at 80°C and kept in an airtight bottle prior to use for sorption experiments.

3.6. Characterization of Orange Peel

Apparatus called Fourier transform infrared spectroscopy (FT-IR) was used to confirm the various functional groups of the orange peel adsorbent both before and after adsorption. The wavenumber of solid orange peel was measured between 500 and 4000 cm^{-1}

3.7. Preparation of Mn (II) Ion Solution

The Mn (II) ion solution was prepared from an analytical reagent grade 1g of Manganese (II) Chloride tetra hydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) (97%) was dissolved in 1000mL of distilled water. All solutions were prepared using distilled water. Next, a 1000 ppm Mn (II) ion stock solution was made. The stock solution was diluted to provide the beginning metal concentrations of 10, 20, 30, 40, and 50 ppm for the calibration curve.

3.8. Study of Operational Parameters

The adsorption of manganese on adsorbent was studied by batch adsorption method. A known weight of adsorbent (e.g. 0.3 g) was equilibrated with 25 ml of the Mn (II) ion solution of known concentration (20, 40, 60, 80, and 100 ppm) in conical flask in orbital shaker for a period (30–150 min.). After equilibration, 10 ml sample collected from each flask, in time interval of 30, 60, 90, 120 and 150 minutes and centrifuged for 15 minutes, the suspension of the adsorbent was separated from solution by filtration using Whatman filter paper No.1. The concentration of Mn (II) ions remaining in solution was measured by Uv-visible spectrophotometer by complexation with the selected reagent. The effect of several parameters, such as pH, contact time, metal ion concentrations and adsorbent dose on the adsorption were studied. The pH of each solution was adjusted by drop wise addition of 0.1 M NaOH or 0.1 M HCl (Kumari, 2017).

3.8.1. Effect of initial Mn (II) ion concentration

To determine the influence of initial Mn (II) ions concentration on (Mn^{2+}) ions removal, 20, 40, 60, 80 and 100 mg/L of metal ion solution was taken and 0.3g adsorbent was added to each solution at constant of 60 minutes and pH of 6. The mixture was stirred, centrifuged for 15 minutes, and then filtered through filter paper to determine the amount of metal ions remaining in solution.

3.8.2. Effect of contact time

To ascertain the impact of contact duration of metal ions adsorption, time intervals of 30, 60, 90, 120, and 150 minutes were employed at an optimum concentration of 40 ppm, constant dose of 0.3 g, and pH of 6. Then, the solution was filtered and concentration of metals after adsorption was measured.

3.8.3. Effect of pH

The solution pH was varied to 2, 4, 6, 8, and 10 using 0.1M HCl or 0.1M NaOH solutions at the ideal conditions of metal ion concentration 40 ppm, contact period 120 min, and 0.3g adsorbent dosage in order to ascertain the impact of pH on the Mn^{2+} adsorption. Following adsorption, the metal ion concentration was determined.

3.8.4. Effect of adsorbent dosage

By varying the dosage at 0.3, 0.6, 0.9, 1.2, and 1.5 g and maintaining an ideal metal ion concentration of 40 ppm, contact time of 120 min, and pH value of 6, the amounts of metal ions adsorbed were computed. Then, the concentration of Mn (II) ion in solution after adsorption was measured.

3.9. Adsorption Capacity and Removal Efficiency

Amount of metal ion adsorbed per unit mass of adsorbent calculated as,

$$q_e = \frac{(C_0 - C_e)}{m} * V \text{----- (1)}$$

The percentage of metal ion elimination was calculated as,

$$\% \text{ Removal} = \frac{(C_o - C_e)}{C_o} * 100 \text{----- (2)}$$

Where V (L) is the volume of Mn (II) ions solution, m (g) is the mass of the adsorbent or mass of orange peel, q_e (mg/ g) is the amount of Mn (II) ions adsorbed, C_o (mg/ L) is the initial concentration of Mn (II) ions, and C_e (mg/ L) is the concentration of Mn (II) ions in solution at equilibrium (Kumari, 2017).

3.10. Data Analysis

To ensure the data precise, almost all adsorption tests were performed in triplicate. To guarantee that errors related to the experimental circumstances were eliminated, blanks were used for every experimental set. In order to create blanks, de-ionized water for every experimental analysis technique, and the blank samples underwent the identical treatment procedure at the same experimental level time.

4. RESULTS AND DISCUSSION

4.1. Manganese (II) adsorbate Preparation

Wavelength determination of Mn (II) was performed by addition of known concentration of Mn (II) ions with dithizone reagent. Based on ultraviolet-visible spectrophotometric measurement, the absorption spectra of Mn (II) were given in Fig 4.1(a), which shows no absorption band at 530 nm. After Mn-dithizone complexation, absorption band appeared at 530 nm which shows increase in intensity with concentration of Mn (II) and used for determination of wavelength of Mn (II) in solution by drawing calibration curve with standard solution of Mn (II) ion. Therefore, in this experiment the wavelength of Mn (II) with complexing agent were made at 530 nm Fig 4.1(b).

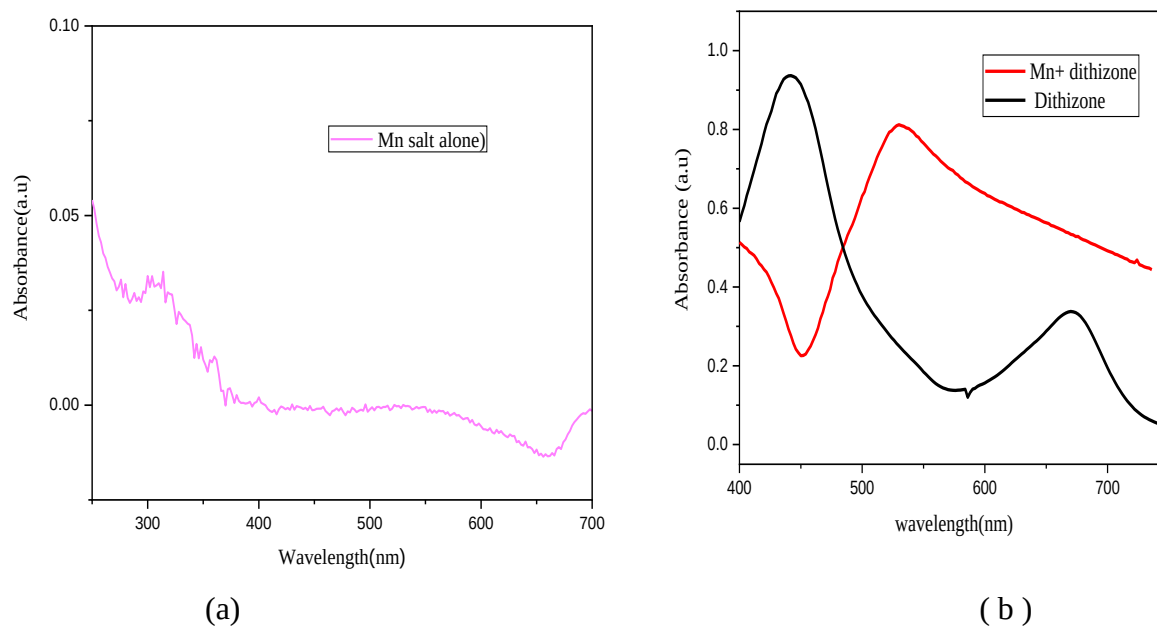
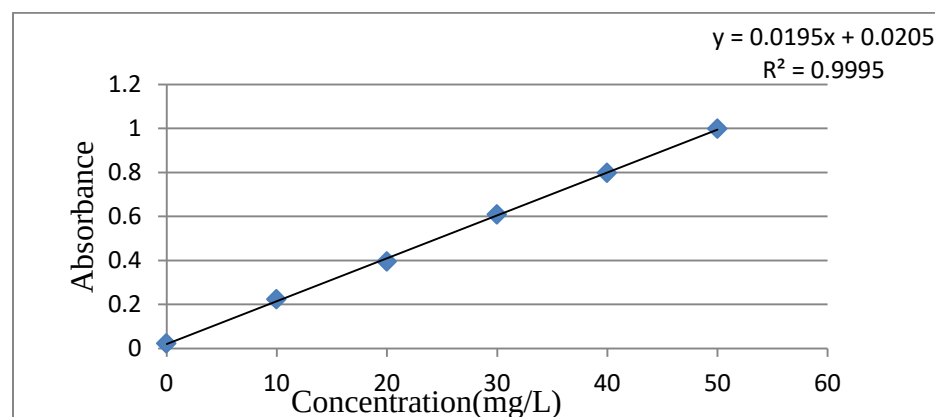


Figure 4.1. UV-Vis Spectrum of Mn-salt alone (a) Dithizone and Mn-dithizone complex (b).

To create the calibration graph, a standard solution of Mn (II) ions at five distinct concentrations was made in a 100 mL volumetric flask. The UV-visible spectrophotometer was used to quantify the concentrations against their corresponding absorbance values at 530 nm using quartz cells measuring 1.0 cm. The linear regression equation for manganese was $Y = 0.0195C_e + 0.0205$ and $R^2 = 0.9995$, is shown in Table 4.1 and Figure 4.2 below.

Table 4.1. Data of Calibration curve for different Mn (II) ion concentration.

Heavy metal	Concentration (mg/L)	Absorbance	Correlation coefficient (R^2)	Regression equation.
Mn	0	0.022	0.9995	$Y=0.0195x + 0.0205$
	10	0.223		
	20	0.395		
	30	0.609		
	40	0.797		
	50	0.998		

**Figure 4. 2.** Graph of calibration curve with different concentration.

4.2. Analysis of Functional Group

This analysis was used to examine the surface chemistry of the orange peel both before and after metal uptake. The orange peel's pre-adsorption FTIR spectrum is shown in Figure 4.3, and all of the peaks that corresponded to the peels before and after metal uptake were rather identical. From FTIR spectra of orange peel before adsorption (Fig 4.3), the strong and broad peaks at 3426 cm^{-1} can be assigned to the stretching of -O-H groups. Therefore, alcohols, phenols, and carboxylic acids present in cellulose and lignin (Gill *et al.*, 2014). The other weak peaks, located at 2922 and 2851 cm^{-1} , suggest that the (CH^- or CH_2^-) aliphatic molecule is stretched symmetrically and asymmetrically. The subsequent sharp peaks, measured at 1739 and 1646 cm^{-1} , were attributed to the C=O stretch of the aldehyde group and the C=C stretch of the phenol group in lignin and

cellulose, respectively. The other broad band around 1150 cm^{-1} assigned for C-O (single bond) of carboxylic acid and around 680 cm^{-1} assigned weak band C-H bending of phenol. The removal of band at 2250 cm^{-1} after metal ion adsorption indicates the complete dissolution (removal) of hemicelluloses from OP. In most cases the spectra of OP after metal ion adsorption shows slight shift due to the adsorption of Mn (II) on OP. Therefore, the FTIR spectra were used for identification of different function groups responsible for adsorption of the metal ions.

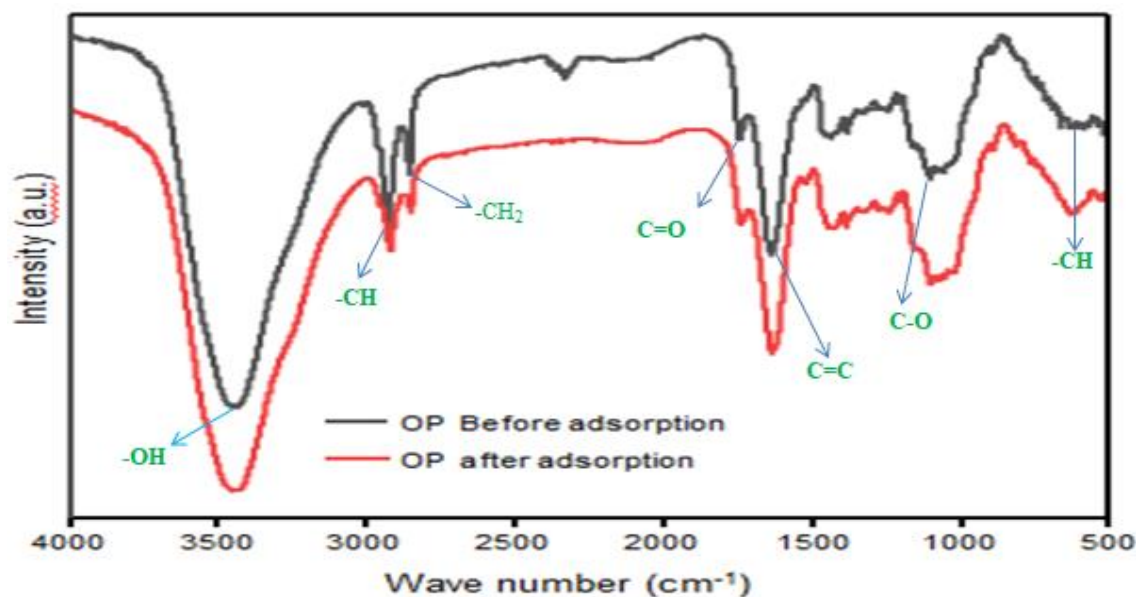


Figure 4.3. Orange peel FTIR spectra both before and after manganese absorption

4.3. Optimization of Experimental Parameters for Adsorption Experiment

4.3.1 Effect of initial concentration of Mn (II) ion

By varying the initial concentration of Mn^{2+} ions (20, 40, 60, 80, and 100 ppm) and holding the other parameters constant (0.3g dose, pH =6, contact time of 60 min, agitation speed of 200 rpm, and temperature of 25°C), the impact of the initial Mn (II) ion concentration on the rate of adsorption was examined. Mn (II) adsorption rises initially when Mn (II) concentration rises from 20 to 40 ppm; it reaches its maximum at 40 ppm (Fig 4.4). This is due to the availability of binding sites and active functional sites on the adsorbent surface which may increase driving force and leads to quick transfer of manganese cation on to OP surface. On the other hand, due to the saturation of vacant sites and equilibrium was attained, adding more manganese concentration cannot increase the rate of adsorption rather resist the free manganese molecules existing in the

solution to their charge repulsion (Asma *et al.*, 2019). The equilibrium was reached at 40 ppm. Due to insufficient surface area to hold much more metal ions accessible in the solution, the percentage removal efficiency of manganese ion on the orange peel after equilibrium dropped from 89.36% to 85.05%, as shown in table 2.2 and figure 4.4. Higher concentrations cause a decrease in adsorption sites because there are more metal ions relative to available adsorption sites. As a result, the amount of the ions adsorbed per unit mass of the adsorbent decreases after equilibrium point. In order to understand the impact of starting concentration on metal uptake by various adsorbents, researchers have conducted a number of investigations (Kumar *et al.*, 2012).

Table 4. 2. Data of Mn (II) initial concentration

Vol. of soln.(L), V	pH	Weigh. Ads.(g)	Cont. time (min)	Init.con (ppm), C_o	Resid.con. (mg/L), C_e	% Mn Removal, (%R)	Adsorption capacity (mg/g), Q_e
0.025	6	0.3	60	20	1.87	90.64	1.51
0.025	6	0.3	60	40	3.31	91.73	3.06
0.025	6	0.3	60	60	6.38	89.36	4.47
0.025	6	0.3	60	80	10.79	86.51	5.77
0.025	6	0.3	60	100	14.95	85.05	7.09

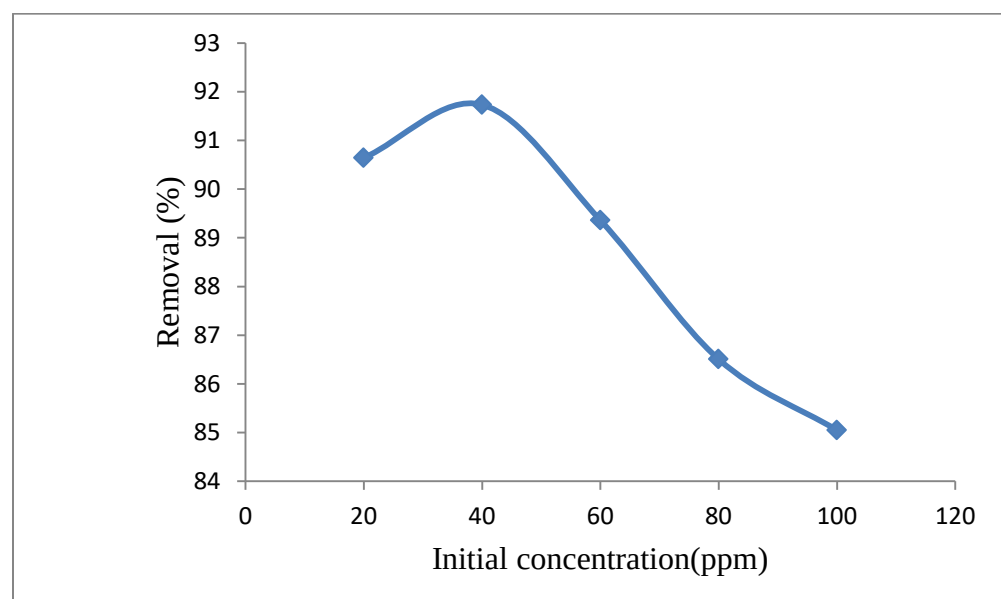


Figure 4.4. Effect of initial concentration on adsorption of Mn^{2+} by orange peel

4.3.2 Effect of contact time on Mn^{2+} removal

Adsorption was performed for multiple time intervals using an optimal concentration of 40 mg/L Mn (II) solution at a constant pH of 6, 0.3 g of adsorbent, and 220 rpm of agitation at 25 °C. Figure 4.5 and Table 4.3 illustrates that the removal of Mn (II) ions increased as the adsorption duration increased. This could be attributed to a greater contact between the Mn (II) ions and the adsorbent surface. Nevertheless, an additional 150 minutes of contact time results in a minor decrease rather than a major shift in Mn (II) elimination. As a result, 120 minutes was determined to be the ideal amount of time for metal ion elimination.

Table 4.3. Data of contact time

Vol.of sol (L),V	pH	Weig.of ads.(g),m	Con.time (min)	Ini.con. (ppm),Co	Resid.con (mg/L),Ce	% Mn re mov.(%R)	Ads.cap. (mg/g),qe
0.025	6	0.3	30	40	5.67	85.83	1.50
0.025	6	0.3	60	40	4.95	87.63	2.92
0.025	6	0.3	90	40	4.13	89.68	2.99
0.025	6	0.3	120	40	2.95	92.63	3.09
0.025	6	0.3	150	40	3.15	92.12	3.07

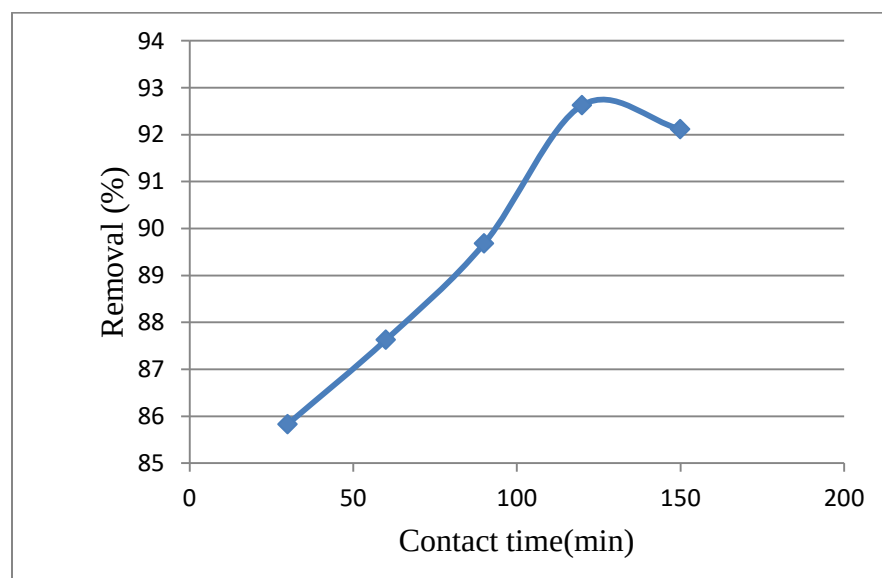


Figure 4.5. Effect of contact time on adsorption of Mn^{2+} by orange peel

4.3.3 Effect of pH on Mn^{2+} adsorption

The protonation and deprotonation of the functional groups of the adsorbent are influenced by the pH of the solution, making it a crucial variable for the adsorption of metal ions. A negatively charged adsorbent interacts with manganese ions, which are present in aqueous solution as $Mn^{2+}(H_2O)_6$. The adsorbent's active sites developed a positive charge, which resulted in reduced Mn (II) adsorption at lower pH values. This is because there may be competition between H^+ ions and $Mn^{2+}(H_2O)_6$ ions in the bulk of solution to bind with the negatively charged surface of the adsorbent at low pH levels due to the large concentration of H^+ ions (Phatai *et al.*, 2014; Taffarel *et al.*, 2010).

When the pH of the solution was raised to six, the adsorption of Mn (II) increased, since only the metal ion computes for adsorption sites as H^+ is decreasing. But after pH 6, there is a decrease in adsorption because hydroxyl low-soluble species like $Mn(OH)_2$ might develop. Table 4.4 and Figure 4.6 data show that the maximal Mn^{2+} ion adsorption value of OP at pH 6 is 93.40%. On the other hand, at higher pH levels, Mn (II) ions may mix with OH^- ions instead of adsorbing on the adsorbents, which would result in a decrease in the rate at which Mn (II) ions adsorb. Additionally, Mn (II) ions begin to precipitate as $Mn(OH)_2$. When pH exceeds 8, Mn (II) hydroxide ions precipitate and produce manganese hydroxide precipitate, which reduces Mn (II) adsorption. Similar research has demonstrated that the ionization state of bio-sorbent functional groups and the solubility of metal ions are both influenced by the pH of aqueous solutions (Fernandez *et al.*, 2015). Thus, it was found that the optimal pH value for the removal of Mn^{2+} from aqueous solution was 6.

Table 4.4. Data of pH of the solution

Vol. of soln.(L), V	pH	Weigh. of ads.(g),m	Cont. time (min)	Init.con (ppm), C_o	Resid.con. (mg/L), C_e	% Mn Removal, (%R)	Adsorption capacity (mg/g), Q_e
0.025	2	0.3	120	40	5.51	86.22	2.87
0.025	4	0.3	120	40	4.23	89.42	2.98
0.025	6	0.3	120	40	2.64	93.40	3.11
0.025	8	0.3	120	40	2.85	92.88	3.10
0.025	10	0.3	120	40	3.21	91.99	3.07

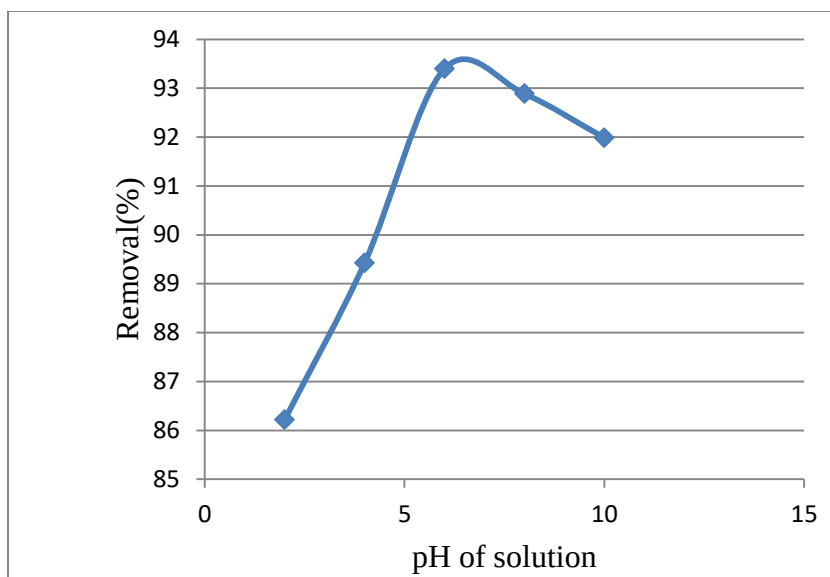


Figure 4.6. Effect of pH on adsorption of Mn^{2+} by orange peel

4.3.4 Effect of adsorbent dose on Mn^{2+} removal

In order to minimize the cost and to enhance efficiency of the overall process, optimizing the amount of the adsorbent is essential. Therefore, dosage of (0.3, 0.6, 0.9, 1.2 and 1.5 g) of OP was used and other factors are optimum. Initially, with increasing adsorbent amount from 0.3 to 1.2g, the adsorption rate of metal ion increases from 88.01 to 94.04, which can be attributed to the availability of more active sites (binding sites) on the adsorbent for interaction per adsorbate ion. The sorption yield drops to 93.53% with additional dosage increases of 1.5 g. This may be because Mn^{2+} ions occupy nearly all binding sites and equilibrium is established between them and the adsorbent in the solution. Therefore, 1.2g/L was the ideal adsorbent dosage for Mn (II) ions under the previously mentioned circumstances.

Table 4.5. Data of adsorbent dose

Vol. of soln.(L), V	pH	Weigh. of ads.(g),m	Cont. time (min)	Init.con (ppm), C_o	Resid.con. (mg/L), C_e	% Mn Removal, (%R)	Adsorption capacity (mg/g), Q_e
0.025	6	0.3	120	40	4.79	88.01	2.93
0.025	6	0.6	120	40	4.03	89.94	3.00
0.025	6	0.9	120	40	2.90	92.76	3.09
0.025	6	1.2	120	40	2.38	94.04	3.13
0.025	6	1.5	120	40	2.59	93.53	3.12

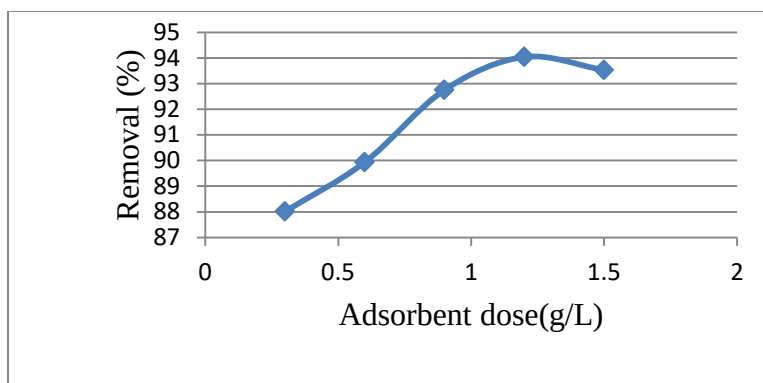


Figure 4.7. Effect of adsorbent dose on adsorption of Mn^{2+} by orange peel

4.4. Adsorption Isotherms

Different adsorption isotherms fitting were done for the metal ion adsorption process study.

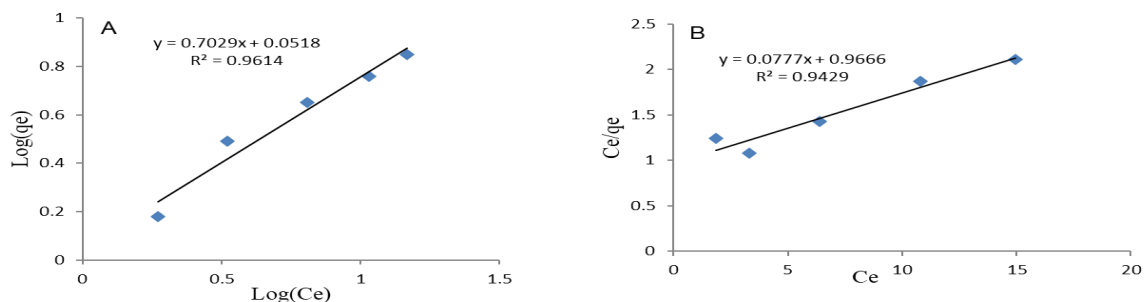


Figure 4.8. Freundlich Adsorption Isotherm (A) and Langmuir Adsorption Isotherm (B)

From the observed data the equation best fits with Freundlich model, Fig 4.8A than Langmuir model, Fig 4.8B (R^2 values of 0.9614). This is because alkali treated OP surface contains a lot of hydroxyl and carbonyl groups present in cellulose and hemicellulose, which has been proven from earlier FTIR study (Xie *et al.*, 2014). A better fit with Freundlich model supports the heterogeneous nature of OP adsorbent. Thus, the OP adsorbent is better for Mn (II) removal.

Table 4.6. Adsorption isotherm of manganese on to orange peel

Adsorbate	Adsorbent	Freundlich			Langmuir		
		N	K_f (mg/g)	R^2	q_{max} (mg/g)	b (mL/g)	R^2
Mn(II)	OP	1.4227	1.1267	0.9614	12.87	0.08039	0.9429

4.5. Kinetics of Adsorption

The data from various Mn (II) ion sorption studies on OP have been fitted using PFO and PSO kinetics models. Based on the generally applicable equation, PFO model assumes that the rate of solute uptake is directly proportional to the difference in saturation concentration and the quantity of solid uptake with time, while PSO kinetics is based on the assumption that the rate of adsorption is directly proportional to the square of the concentration of the adsorbate on the surface of the adsorbent. This assumption is commonly expressed through the Lagergren PSO kinetic model.

The adsorption of Mn (II) on OP adsorbent best fits the second order, as indicated by the finding that the value of R^2 for the PFO model was comparatively lower (0.8837) than that of the PSO kinetics (0.9483) (Fig. 4.9A-B, and Table 4.7). Therefore, the chemisorption, or surface reaction, between the adsorbate and the adsorbent, is the rate-limiting stage of the adsorption process in the Mn (II). This suggests that, as opposed to diffusion, the adsorption process of the metal ion is regulated by the presence of active sites on the adsorbent surface.

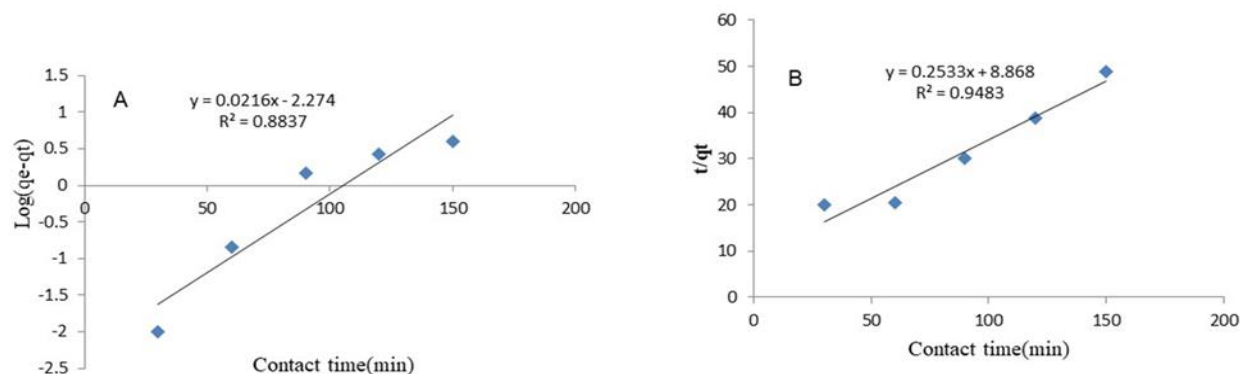


Figure 4.9. Pseudo-first- order (A) and Pseudo -second-order Adsorption Kinetics (B).

Table 4.7. Comparison of pseudo-first-order and Pseudo-second-order models

Adsor bate	Adsor bent	PFO kinetic model			PSO kinetic model		
		Qe(mg/g)	K_1 (min^{-1})	R^2	Qe(mg/g)	K_2 (mg/gmin)	R^2
Mn(II)	OP	0.00532	-0.0497	0.8837	3.948	0.00723	0.9483

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The findings of this research clearly demonstrate the strong adsorption capabilities of orange peels in effectively removing manganese ions from solution. This bio-adsorbent offers several advantages, including its low cost and easy to use, making it a sustainable alternative to conventional adsorbents. Furthermore, the study provides essential insights into the significant impact of various parameters, such as pH, contact time, initial concentration, and adsorbent dosage, on the adsorption process, thus enhancing the efficiency of manganese ion removal using orange peels.

The analysis of different adsorption models for the orange peel adsorbent shows a close fit of the experimental data with the Freundlich isotherm, indicating that the adsorption is a multilayer process, allowing for the formation of several layers of adsorbate molecules on the surface of the adsorbent. Additionally, the investigation into adsorption kinetics reveals that the process aligns well with PSO, suggesting chemisorption involving the exchange of electrons between the adsorbent and adsorbate.

Overall, these results emphasize the feasibility and effectiveness of utilizing orange peels as a bio-adsorbent for water treatment, particularly in the removal of manganese ions. This research significantly contributes to the advancement of sustainable and environmentally friendly approaches to combating water pollution. Future investigations could focus on scaling up the process for practical implementation and exploring real-world applications in water treatment systems.

5.2 Recommendations

Based on the findings of the present study, the following recommendations are suggested: First, considering the demonstrated efficacy of orange peels as a bio-adsorbent for Mn (II) ion removal, future studies should explore the practical application of this method in real-world water treatment systems. This could involve pilot-scale testing to assess its performance under varying conditions and its compatibility with existing water treatment processes. Second, deeper insights into the adsorption mechanisms of Mn (II) onto orange peels bio-adsorbent could be gained through additional studies. Understanding the fundamental processes, including surface interactions and chemical reactions, would facilitate the development of more accurate predictive models and further improve the design and performance of the adsorption system. Finally, while this research primarily focused on manganese ion removal, future investigations could explore the potential of orange peels bio-adsorbent for removing other contaminants from water sources. This could include the adsorption of heavy metals, organic pollutants, or other ions, broadening the scope of its application in water remediation efforts. By addressing the outlined recommendations, future research endeavors can further advance the development and practical implementation of this eco-friendly approach to water treatment, contributing to the ongoing efforts to combat water pollution and promote environmental sustainability.

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APPENDIX I

Optimization Parameters of Raw Data

1: Raw Data of Calibration.

Cell name

Time	Blank	10 ppm	20 ppm	30 ppm	40 ppm	50 ppm
h:m:s	A	A	A	A	A	A
0:00:20	0.021	0.223	0.394	0.608	0.797	0.999
0:00:30	0.022	0.223	0.395	0.609	0.797	0.998
0:00:30	0.023	0.222	0.396	0.609	0.798	0.998

530nm, .Measurement finished Cell Program

2: Optimization of Initial Concentration Raw Data.

Cell name

Time	Blank	20ppm	40 ppm	60 ppm	80 ppm	100 ppm
h:m:s	A	A	A	A	A	A
0:00:00	0.031	0.057	0.084	0.144	0.230	0.313
0:00:30	0.031	0.057	0.085	0.145	0.231	0.312
0:00:30	0.031	0.056	0.085	0.145	0.232	0.312

530nm, .Measurement finished Cell Program

3: Optimization of Contact Time Raw Data.

Cell name

Time	0min	30min	60 min	90 min	120 min	150 min
h:m:s	A	A	A	A	A	A
0:00:00	0.031	0.132	0.118	0.102	0.079	0.083
0:00:30	0.031	0.131	0.117	0.101	0.078	0.082
0:00:30	0.031	0.130	0.116	0.100	0.077	0.081

530nm, .Measurement finished Cell Program

4: Optimization of Solution pH Raw Data

Cell name

Time	BLANK	2pH	4pH	6pH	8pH	10pH
h:m:s	A	A	A	A	A	A
0:00:00	0.030	0.127	0.102	0.071	0.076	0.082
0:00:30	0.031	0.128	0.103	0.072	0.076	0.083
0:00:30	0.031	0.129	0.103	0.071	0.076	0.084

530nm, .Measurement finished Cell Program

5: Optimization of Adsorbent dosage Raw Data

Cell name

Time	Blank	0.3g	0.6g	0.9g	1.2g	1.5g
h:m:s	A	A	A	A	A	A
0:00:00	0.021	0.114	0.098	0.077	0.067	0.071
0:00:30	0.021	0.114	0.099	0.077	0.067	0.071
0:00:30	0.021	0.113	0.100	0.077	0.068	0.072

530nm, .Measurement finished Cell Program

APPENDIXE II.

Data of Adsorption Isotherm, Kinetics Model and Sample Preparation.

A: Data of Isotherm.

V (L)	W (g)	Co (ppm)	Ce (mg/L)	% R	q _e (mg/g)	Ce/q _e (g/L)	Log Ce	Log q _e
0.025	0.3	20	1.872	90.64	1.511	1.239	0.27	0.18
0.025	0.3	40	3.308	91.73	3.058	1.082	0.52	0.49
0.025	0.3	60	6.385	89.36	4.468	1.429	0.81	0.65
0.025	0.3	80	10.795	86.51	5.767	1.872	1.03	0.76
0.025	0.3	100	14.949	85.05	7.088	2.109	1.17	0.85

B: Data of Kinetics

V (L)	W (g)	Tim(min)	qe(mg/g)	qt(mg/g)	(qe-qt)	log(qe-qt)	t/qt
0.025	0.3	30	1.51	1.5	0.01	-2	20
0.025	0.3	60	3.06	2.92	0.14	-0.85	20.55
0.025	0.3	90	4.47	2.99	1.48	0.17	30.1
0.025	0.3	120	5.77	3.09	2.68	0.43	38.83
0.025	0.3	150	7.09	3.07	4.02	0.604	48.86



C: Figures of Sample Preparation

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